# The science of ultrafine aerosols

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Abstract - Ultrafine aerosols are gasdisperse systems containing particles with sizes considerably smaller than the wavelength of light and also smaller than the mean free path of gas molecules under standard conditions. Hence the particle diameters are smaller than 50nm and these particles behave like large molecules. Ultrafine aerosols form mainly by nucleation-condensation processes or, occasionally, by spray-drying. Formation by nucleation from supersaturated vapors yields primary particles in the 1-10nm range at very high concentrations. Brownian motion (and rotation) is large and consequently coagulation dominates, hence the number concentrations come down to about $10^7$ particles per cc within seconds.
Ultrafine Aerosols have a large surface area per unit mass and are therefore chemically active and good absorbers. Their main feature is their large fraction of surface atoms per particle which have relatively high surface energies compared to the bond energies. Considering particles with diameters of 10nm and 1nm respectively: they contain about $10^4$ and 10 molecules per particle and the fraction of surface molecules is 25% and 100%. From 1ng material about $10^9$ and $10^{12}$ particles of that sizes can be formed. The ratio of surface energy to bond energy is 2% and 20%. The fraction charged by unipolar charging is about 50% and 1% or less.
The use of Ultrafine Aerosols for technical processes (production of unusual and/or very pure materials) as well as their importance for atmospheric processes like smog formation and due to air pollution induced intensive research during the past decade. The wide interest in turn led to the development of new instruments and new techniques.

## DEFINITIONS

Ultrafine Aerosols, UA, a new class of systems, a subclass of high dispersed or of submicron aerosols (ref.1), are systems comprised of particles suspended in gases; the particles have sizes, d (diameters), considerable smaller than the wavelength, , of visible light and the mean free path, l, of gas molecules, M, under standard conditions.

$$d << \quad = 500 \text{ nm}$$
$$d << l = \quad 70 \text{ nm}$$

The sizes of UA-particles extend from M to 50 nm, most important is the "core-range" from 1 nm to 10 nm, considered only in this study. For the following the same hypothetical M is assumed for the gas and as the building unit of the particles. M is assumed to be a sphere of d = 0.5 nm ; having a mass of 40 atomic mass units, i.e. m = $7.10^{-26}$ kg ; a density of 1000 kg/m³ ; a volume as of $7.10^{-29}$ m³ ; a cross section of $2.10^{-19}$ m² .

## THE PROPERTIES OF INDIVIDUAL PARTICLES

Compared with other aerosols UA-particles (diameter, d, cross section, cs, mass, m, contain only a relatively small number of M, $N_{MP}$, the fractions, frM, are surface-M (the estimates are made assuming spherical particles and correspondingly circular cross sections of M and complete filling of the surface). Another estimate was given by Jimbo 1990 (ref.2),see TABLE 1.

TABLE 1. Diameter (d),cross section (cs), mass (m), number of M ($N_{MP}$), fraction of surface M (frM), this study (1), and as given by Jimbo 1990 (ref.2)

| d | cs | m | $N_{MP}$ | frM % | |
|---|---|---|---|---|---|
| nm | m² $10^{-18}$ | kg $10^{-24}$ | | (1) | (2) |
| 0.5 | 0.1963 (c.0.2) | 0.0654 (c.0.07) | 1 | / | / |
| 1.0 | 0.7854 | 0.5236 | 8 | 100 | 99 |
| 2.0 | 3.142 | 4.189 | 64 | 90 | 80 |
| 5.0 | 19.64 | 65.45 | 1 000 | 50 | 40 |
| 10.0 | 78.54 | 523.6 | 8 000 | 25 | 20 |

It is important to compare surface energies to binding energies. Usually binding energies are given in kJ/mol and surface energies (tensions) in dyn/cm = $10^{-3}$ J/m² . For UA the most appropriate unit is eV/M; the conversion factor: 1 kJ/mol = $1.04.10^{-2}$ eV/M .

The number of M per unit area was estimated and the surface energies of the particles derived using surface energies of plane bulk materials. Typical values, Handbook 1980 (ref.3): Au...1000 dyn/cm; liquids...10-60 dyn/cm; water...72 dyn/cm; and bond strengths: C-C...607 kJ/mol; H-OH...520 kJ/mol; H-H...436 kJ/mol; Au-Au...221 kJ/mol; H-bridges...15-25 kJ/mol, used value 20, Römpp 1988 (ref.4); Cl-Xe...7 kJ/mol . The used surface energies are: 1 eV/M for Au and 0.07 eV/M for water. The estimated energies are given in TABLE 2.

TABLE 2. Diameter (d), the sum of the binding energies of all M of one particle ($E_B$), the sum of the surface energies of all surface M for one particle ($E_S$), for the solid Au (S), for water (W), the ratio (R), R = $100E_S/E_B$, for this study (1) and as estimated by Jimbo (2).

| d nm | $E_B$ eV | | $E_S$ eV | | R = $100E_B/E_S$ % | | |
|---|---|---|---|---|---|---|---|
| | S | W | S | W | S | W | (2) |
| 0.5 | 2.3 | 0.2 | 1.0 | 0.07 | / | / | / |
| 1.0 | 18.0 | 1.6 | 8 | 0.56 | 44 | 35 | 18.9 |
| 2.0 | 147 | 12.8 | 58 | 4.06 | 39 | 32 | 10.0 |
| 5.0 | 2 290 | 200 | 500 | 35.0 | 22 | 16 | 4.0 |
| 10.0 | 18 300 | 1 600 | 2 000 | 140.0 | 11 | 9 | 2.0 |

## THE PARTICLES IN THE GAS

An essential parameter is the Knudsen number Kn (ref. 5), the ratio of the mean free path of the gas molecules and the particle radius (assuming spherical particles). For Kn >> 1 : the aerosol is in the free molecular regime, the particles act like large molecules, their air resistances are proportional to their cross sections. Selected pertinent parameters are given in TABLE 3 and TABLE 4.

TABLE 3. Diameter (d), Knudsen number (Kn), the particle thermal (root mean square) velocity (v), $v = (3kT/m)^{1/2}$ , with $k = 1.38.10^{-23}$ J/K , T = 298 K , and m, the particle mass; the thermal sweep volume (SV), $SV = v.q^*$ , with $q^*$ the particle collison cross section, $q^* = (d+0.5)^2( /4)$; the number of molecules in the SV (Z), (using $2.69.10^{25}$ M/m³), this is also the number of collisions of M with the particle in one second; the mean time between two consecutive collisions of M with the particle, $t_{MP} = Z^{-1}$ ; the mean free particle path between consecutive collisions with M's ($l_{MP}$) $l_{MP} = v.t_{MP}$ ; the relaxation time of the particle $t_R$ (ref.6) $t_R = mB$ , with B, the mobility.

| d<br>nm | Kn<br>/ | v<br>m/s | q*<br>m²<br>$10^{-18}$ | SV<br>m³/s<br>$10^{-16}$ | Z<br>s⁻¹<br>$10^9$ | $t_{MP}$<br>s<br>$10^{-9}$ | $l_{MP}$<br>nm | $t_R$<br>s<br>$10^{-9}$ |
|---|---|---|---|---|---|---|---|---|
| 0.5 | 280 | 431.4 | 0.7854 | 3.388 | 9.11 | 0.197 | 47.34 | 0.35 |
| 1.0 | 140 | 152 | 1.7671 | 2.686 | 7.22 | 0.138 | 21.04 | 0.71 |
| 2.0 | 70 | 53.8 | 4.909 | 2.641 | 7.10 | 0.141 | 7.57 | 1.41 |
| 5.0 | 28 | 13.6 | 23.76 | 3.231 | 8.69 | 0.115 | 1.56 | 3.52 |
| 10.0 | 14 | 4.81 | 86.59 | 4.185 | 11.26 | 0.089 | 0.43 | 7.07 |

TABLE 4. Diameter (d); the particle mobility $B = 0.350.1/d^2.vi$ , with $vi = 18.2.10^{-6}$ Pa.s, the viscosity of air at 293 K, for large Kn (ref.7); the particle diffusion coefficient $D = kTB$ (ref.8), the Brownian displacement in the time interval t (BD), $BD = (4Dt/ )^{1/2}$ (ref.9); the momentum of inertia $I = (qd^5/60)$ with q the density; the mean angular (thermal) displacement of Brownian Rotation (BR), $BR = (kT/I)^{1/2}$ , the corresponding linear displacement of a point at the particle surface (at the "equator" relative to the momentary axis of rotation) (BRT) $BRT = (BR)d/2$ ;

| d<br>nm | B<br>s/kg<br>$10^{13}$<br>(1) | <br><br><br>(2) | D<br>m²/s<br>$10^{-8}$ | BD<br>mm<br>in 1s | <br>nm<br>in 1ns | I<br>kgm² | BR<br>radians<br>per ns | BRT<br>m/s |
|---|---|---|---|---|---|---|---|---|
| 0.5 | 538 | | 2160 | 5.23 | 165 | $1.64.10^{-45}$ | 1570 | 393 |
| 1.0 | 135 | 127 | 546 | 2.64 | 83.5 | $5.24.10^{-44}$ | 278 | 139 |
| 2.0 | 33.6 | | 135 | 1.31 | 41.4 | $1.68.10^{-42}$ | 49.0 | 49 |
| 5.0 | 5.38 | | 21.8 | 0.527 | 16.7 | $1.64.10^{-40}$ | 4.96 | 12 |
| 10.0 | 1.35 | 1.30 | 5.5 | 0.264 | 8.3 | $5.24.10^{-39}$ | 0.88 | 5 |
| (1) this study, (2) (ref.11) | | | | | | | | |

## COAGULATION OF ULTRAFINE AEROSOLS

The coagulation equation is very simple, $(dn/dt) = -K n^2$ (ref.12), the essential parameter is K, the coagulation constant. In the free molecular regime, assuming a sticking probability of one, and assuming further that there is no force between the particles, (an assumption wich also excludes charges) and monodispersed particles K becomes (ref.13) $K = d^2v(2)^{1/2} /2$ . In case there is any particle-particle interacting force, a size dependent correction factor has to be added, which may amount even for week van der Waals forces to 5 or more (ref.14, ref.15). The time it takes to reduce the concentration from its initial value of $n_0$ to $n_0/2$ $t_{1/2} = 1/n_0K$ is given for different concentrations and sizes in TABLE 5.

TABLE 5. Diameter (d); Koagulation constant (K); number of particles produced from one gram of material of density 1000 kg/m³ dispersed in one m³, the time it takes to reduce the initial concentration to 1/2 for different initial concentrations and sizes ($t_{1/2}$).

| d<br>nm | K<br>m³/s<br>$10^{-16}$ | $n_{0,1g}$<br>m⁻³ | $t_{1/2}$<br>s | | | |
|---|---|---|---|---|---|---|
| | | | 1g/m³ | 1mg/m³ | 1ug/m³ | 1ng/m³ |
| 0.5 | 2.40 | $1.5\ 10^{22}$ | $3.9\ 10^{-7}$ | $3.9\ 10^{-4}$ | $3.9\ 10^{-1}$ | $3.9\ 10^{2}$ |
| 1.0 | 3.38 | $1.9\ 10^{21}$ | $2.2\ 10^{-6}$ | $2.2\ 10^{-3}$ | $2.2\ 10^{+0}$ | $2.2\ 10^{3}$ |
| 2.0 | 4.78 | $2.4\ 10^{20}$ | $1.2\ 10^{-5}$ | $1.2\ 10^{-2}$ | $1.2\ 10^{+1}$ | $1.2\ 10^{4}$ |
| 5.0 | 7.55 | $1.5\ 10^{19}$ | $1.2\ 10^{-4}$ | $1.2\ 10^{-1}$ | $1.2\ 10^{+2}$ | $1.2\ 10^{5}$ |
| 10.0 | 10.7 | $1.9\ 10^{18}$ | $7.0\ 10^{-4}$ | $7.0\ 10^{-1}$ | $7.0\ 10^{+2}$ | $7.0\ 10^{5}$ |

## PRODUCTION OF ULTRAFINE AEROSOLS

UA cannot be produced by atomisation (neither from liquids nor from powders) because the strong adhesion between particles and the great energy demand for creating new surfaces are prohibitive (ref.16). The atomisation of very dilute solutions, the removal of larger droplets, and the subsequent evaporation of the solvent may create UA. Another possibility is to produce highly supersaturated precursor gases (either by chemical reactions in the gas phase, by rapid cooling, e.g.by adiabatic expansion, or by mixing of gas streams), which then nucleate homogenously.

The number of nuclei created per second and unit volume, the nucleation rate J, is a very steep function of supersaturation.

$J = C_1\exp(-C_2/T^3(\ln S)^2)$ with the supersaturation S, the Temperature T, and the constants $C_1$ and $C_2$ (ref.17). For water the constants become $C_1$ = about $9 \times 10^{32}$ s⁻¹m⁻³ and $C_2$ = $2.15 \times 10^9$ K³ which yield for T = 300 K:     J = 1s⁻¹m⁻³ for S = 2.78,   J = $10^6$s⁻¹m⁻³ for  S = 3.1, and J = $10^{15}$s⁻¹m⁻³ for S = 4.0. The very high concentrations of particles produced by nucleation of supersaturated vapors result in fast coagulation within fractions of a second (ref.18). The observed aerosol is mostly the result of combined nucleation, coagulation, and condensation. In order to produce UA at high rates (e.g. for industrial production ref.19) coagulation must be prevented, investigations on this topic are under way in several laboratories (ref.20).

## INVESTIGATION OF ULTRAFINE AEROSOLS

The simple straight forward method is to sample UA-particles on an appropriate substrate (e.g. by thermal precipitation) and analyze using electron microscopy. The shortcoming of this procedure is the small sample size (only few particles) and the possible artefacts produced by sampling and preparation techniques. However deep insights on particle structures can be gained, modern electron microscopy resolves at its resolution limit individual atoms in metal clusters (ref.21).

UA cannot be observed by light scattering techniques directly. A most used technique is to grow the UA-particles to visible sizes and then use conventional optical single particle counting or light scattering methods.

An example is the SANC-system developed in Vienna, which uses water as the growing agent, an expansion cloud chamber to create the supersaturation, and constant angle Mie scattering for observing the monodispersed growing droplets. It has been used sucessfully to investigate UA-particles of 6 nm diameter (and up) of silver and sodium chloride of the same size. These were found to nucleate at different supersaturations corresponding to different water-Kelvin equivalent diameters. The water-Kelvin diameter is defined as the diameter of a droplet of pure water which is activated to growth at the same supersaturation. Particles of diameters of 6 nm, the

size determined by electrical mobility spectrocopy and by electron microscopy, of pure silver had a Kelvin diameter of 3.3 nm, of sodium chloride a Kelvin diameter of 15 nm (ref.22 and ref.23).

Another example is the instrument originally designed by the late Prof. A. Bricard (ref.24) and now produced comercially by TSI Incorporated (ref25). A modified version, specially adapted for UA, has been developed recently (ref.26). The UA-particles are grown in a condensation chimney, the growing agent is n-butyl alcohol, the detection system is a optical single particle counter. The use for particles as small as 2.5 nm has been demonstrated (ref.27); in this system silver and sodium chloride particles have the same "n-butyl alcohol-Kelvin size".

Another technique for measuring UA is electrical mobility spectroscopy (ref.28) which has been extended to UA sizes. An electrical mobility spectrometer (EMS) is built in essence of three largely independent subunits: a charger, a classifier and a (particle) detector (ref.29).

An instrument developed in Vienna uses a simple bipolar charger which is based on earlier work. Measurements showed: bipolar charging (using a 2 mCi Kr85 beta source and a product $Nt = 0.7 \times 10^9$ s cm$^{-3}$, with N, the ion concentration and t, the time) yields a charging probability of about 0.02 for particles of diameters of 5 nm, independent of the particle material (Silver and sodium chloride tested) (ref.30). In the classifier the charged aerosol is superimposed as a laminar sheet flow over a laminar stream of clean air (gas) in a cylindrical condenser. The charged UA particles migrate under the influence of an electric field to the central electrode, through which, via a sampling slit, a fraction of the flow is extracted. The particles contained in this sample flow belong to a narrow range of electrical mobilities and since all particles carry just one elementary charge, they belong to a narrow size class. The detector is either a Faraday-cup electrometer, which measures the tiny electric current caused by the charged particles collected on a filter, or a continuous flow condensation nuclei counter, which registers the arriving particles individually. Since the charging probability of UA is low and the diffusion losses are considerable the lower detection limit is a concentration of about 2000 cm$^{-3}$ for 2 nm particles.

The parallel use of several EMS, each following the time development of a narrow size class of UA, and of a scanning EMS (ref.31) permitted for the first time to investigate the fast reactions in a smog chamber (ref.32). In the presence of larger seed particles of about 34 nm the concentrations of the 3.4 nm particles oscillated with a periode of about 8 minutes between $0.2 \times 10^5$ cm$^{-3}$ and $1.2 \times 10^5$ cm$^{-3}$ above the detection limit of $1.5 \times 10^3$ cm$^{-3}$ (ref.29).

This just illustrates the complexity of reacting aerosol systems, indicates our lack in understanding, and demonstrates the need for further research.

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