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Nanoaerosol

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Synonyms

Aerosol; Nanoparticle; Electrical properties; Filtration; Nanoaerosol; Nanoaerosol characterization; Nanoaerosol drug delivery; Nanoaerosol dynamics; Occupational exposure; Thermal rebound

Definition

Nanoaerosols are nanoparticles suspended in a gas. These nanoparticles could be liquid droplets but are usually solid particles with at least one dimension being less than 100 nm. Most researchers consider nanoaerosol as another name of ultrafine aerosol or ultrafine particulate matter. There is actually a slight difference between ultrafine aerosol or particulate matter and nanoaerosol. The former is commonly used to describe airborne nanoparticles that are produced incidentally without intension and are suspended in the atmosphere. The latter has a broader coverage including both environmental and engineered nanoparticles in any carrier gas. A nanoaerosol can be either organic or inorganic and generated by nature or engineering processes.

Chemical and Physical Principles

Nanoaerosols are produced from all kinds of sources intentionally or as a by-product. Environmental nanoaerosols are produced in the atmosphere by natural nucleation and condensation or incomplete combustion of hydrocarbons. The latter are mostly soot particles between 10 and 100 nm in diameter. Engineered nanoaerosols are a result of recent rapid advances in nanotechnology, produced when manufactured nanomaterials become suspended in the air or other carrier gases. These particles usually have complex shapes, including sphere, cube, cylinder, flake, crystal, etc. These different shapes affect their aerodynamics.

The small size of nanoparticles leads to a great surface area to mass ratio and consequently other unique properties of nanoparticles. The high surface area leads to a great surface reactivity. At a nanoscale, both classical physics and quantum physics play roles in the interfacial behavior of nanoaerosols. Some researchers believe that nanoparticles in high concentrations in the air agglomerate rapidly to form larger particles by chemical bonding and physical reactions. As a result, the life span of individual nanoaerosol particles is usually short. Nanoparticles with the sizes of 1–10 nm have the life span of a few minutes to hours. Meanwhile, larger

nanoparticles are formed by agglomeration. As a result, the size distribution of the nanoaerosol in a certain environment may change over time. The agglomeration mechanisms of nanoaerosols are not yet well understood.

On the other hand, well-dispersed atmospheric nanoaerosols at low concentration may remain airborne for a long period of time; their setting velocity is extremely low because of their small aerodynamic sizes. At low concentration, the chance for nanoaerosol particles to agglomerate is low because of their great impact velocities.

Noncontinuum Behavior

Nanoaerosol particles interact with the carrier gas molecules and consequently affect their dynamics. Nanoaerosol particles are small enough to approach the mean free path of air, which is about 67 nm under standard conditions. For nanoaerosol the continuum assumption is no longer valid and can attain free molecular flow; there is a noncontinuum interaction between the particles and the carrier gas. The corresponding slipping effect is quantified by the Cunningham coefficient in terms of gas mean free path (λ) and particle diameter:

$$C_C = 1 + K_n\left[1.257 + 0.4\exp\left(-\frac{1.1}{K_n}\right)\right] \quad (1)$$

where the Knudsen number, K_n, is the ratio of gas mean free path (λ) and particle radius ($d_p/2$), $K_n = 2\lambda/d_p$. A greater K_n means a higher probability of noncontinuum nanoaerosol.

Diffusion is the primary transport mechanism of a nanoaerosol. The thermal velocities of nanoaerosol particles follow certain distribution due to the random motion of the surrounding gas molecules. The actual velocity distribution is not well determined, but most researchers assume it to follow the Maxwell–Boltzmann distribution [1]. The diffusion coefficient of aerosol particles in the air with low Reynolds number is determined by the Stokes–Einstein equation

$$D_n = \frac{KTC_c}{3\pi\mu d_p} \quad (2)$$

where K is the Boltzmann constant, T the temperature, μ the kinetic viscosity of the carrier gas, and d_p the particle diameter. For nanoparticles in the range of 0.5–2 nm, which is approaching the gas mole sizes, the diffusivity is given as [2]

$$D_n = \frac{0.815V_m}{12\pi N(2r + d_p)^2}\sqrt{1 + \frac{m}{M}} \quad (3)$$

where V_m is the mean velocity of the carrier gas molecules, r is the gas molecule radius, N is the number concentration of gas molecules, m is the molecular weight of the carrier gas, and M is the molecular weight of nanoaerosol particles.

Under normal conditions, airflow immediately surrounding a nanoaerosol particle is laminar or in the Stokes region, although the bulk airflow may be turbulent. The drag force exerted by the air on the nanoaerosol is calculated by

$$F_D = 3\pi(V_p - D_g)d_p/C_c \quad (4)$$

where V_p the particle velocity and V_g the gas velocity. Under normal conditions, a nanoparticle tends to follow the moving carrier gas and it is very difficult to separate them simply by inertia.

Under carefully engineered condition with low pressure, however, nanoaerosol particles can be separated from the gas phase because of the relatively small amount of molecules surrounding the nanoaerosol. The nanoaerosol can then be focused to a beam after expansion through an orifice, referred to as aerodynamic particle focusing. In this case, as depicted in Fig. 1, the trajectories of the aerosol particles depend on their corresponding *Stokes* number

$$Stk = \frac{\tau v_f}{d_f} \quad (5)$$

where d_f is the diameter of the focusing orifice, v_f the average velocity in the focusing orifice exit plane, and τ the particle relaxation time based on the carrier gas properties at the orifice throat.
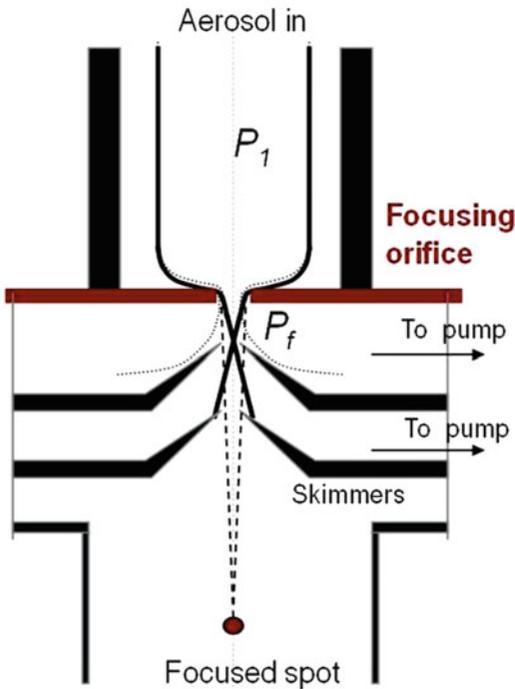
Nanoaerosol, Fig. 1 Schematic of aerodynamic particle focusing

Particles with $Stk = 1-2$ are most effectively focused to a spot downstream to the orifice [3]. For nanoaerosols, this is accomplished by adjusting the mean free path of the carrier gas, which is a function of the gas pressure. Under certain vacuum conditions, particles down to 1–2 nm could be focused to a spot, but it is very challenging in practice. Particles focused to the spot can be ionized by a laser beam for online elemental analysis. However, due to the high diffusivity of nanoaerosol particles, the focusing beam diameter varies with particle size and the distance between the focusing orifice and the spot. Typical particle beam diameter is much less than 1 mm and it decreases with the increase of particle size [3].

Adhesion and Thermal Rebound

When an aerosol particle impacts on a surface, there is an interfacial adhesion force attempting to hold them together. When the adhesion force is strong enough to offset the outgoing momentum at the end of impact, the particle is captured by the solid surface. It has been well accepted that aerosol particles always stick on the surface in contact. However, this may not be true for nanoaerosol particles because the impact between a solid nanoparticle and a solid surface is most likely elastic because of the small contact area and the particle velocity is too low to form plastic deformation. As a result, the nanoparticle may rebound from the solid surface. This phenomenon is referred to as thermal rebound.

The critical particle velocity that enables elastic rebound is a function of adhesion energy (E_{ad}), particle mass (m), and the coefficient of restitution (e):

$$V_{cr} = \sqrt{\frac{2E_{ad}}{m.e^2}} \qquad (6)$$

For nanoaerosol, e $\approx$ 1 because of the great rigidity. Several theoretical models of adhesion energy can be found in the literature. Two of the most well-known ones are JKR model and DMT model. These two models contradict each other because they represent two extremes in the Tabor parameter spectrum. JKR model is applied for soft material, large radius, compliant spheres, and large adhesion energy, and DMT model is for hard material, small radius, and low adhesion energy. Therefore, DMT model should be considered first for nanoaerosol thermal rebound analysis.

Electrical Properties of Nanoaerosol

Aerosol particles are charged when they pass through a cloud of ions. Unipolar ions can be produced by unipolar corona discharge, UV charging, carbon fiber ionizer, and separation of ions produced by bipolar ions. Bipolar ions are usually produced by radioactive sources such as Kr^{85} or Po^{210}, soft X-ray, AC corona discharge, or dual electrode corona discharge. High concentration of ions and sufficient charging time allow particles to reach maximum charging.

The maximum charging by unipolar charging enables the particles to carry ions with same polarity, negative or positive. They are subject to electrical forces in an electrical field. The bipolar charging process eventually leads to Boltzmann charge equilibrium if the particles experience sufficient charging. In such cases, they are considered neutralized. Highly charged particles may be discharged by colliding with ions with different polarity. In bipolar charging, larger and smaller nanoparticles may acquire different polarities. This poses a great challenge to effectively neutralize the nanoaerosol particles, which is necessary to many instrumentation techniques.

Nanoaerosol particles are primarily charged by diffusive charging. The maximum number of ions that can be acquired by a nanoparticle is estimated as [3]

$$n = \frac{d_p KT}{2e_i^2 K_e} ln\left[1 + \left(\frac{d_p . K_e . C_i . \pi e^2 N_i}{2KT} \right) . t \right] \quad (7)$$

where C_i is the mean thermal speed of ions, K_e a Coulomb constant of proportionality, e_i the elementary unit of charge, N_i ion concentrations, and t the charging time.

While micron particles may be charged with hundreds of ions, a nanoaerosol particle smaller than 20 nm will probably acquire only a couple of ions and in some case will not acquire any, resulting in an insignificant electrostatic force. If polydisperse nanoaerosol particles pass through a bipolar charger, two nanoparticles of the same size may obtain different charges. Experimental data [4] show that charged sub-20 nm particles carry a negative charge, while larger particles carry a positive charge.

Nanoaerosol can be sampled on a filter or grid for offline analyses of the morphology and composition of individual particles. The most common offline method is transmission electron microscope (TEM) and energy-dispersive X-ray spectroscopy (EDX). However, the physical and chemical properties may change due to agglomeration and/or chemical reactions during the sampling, transport, and offline characterization processes.

Key Research Findings

Occupational Exposure to Nanoaerosol

While the society is enjoying the benefits and excitement brought by nanotechnology, some scientists and engineers are concerned about its negative impact on human health and the environment. In addition to the nanoaerosol produced in nature and by combustion, recent rapid advances in nanotechnology have outpaced the risk assessment and government regulations in this industry. Nanoaerosol can be more toxic than larger ones of the same material because of their small size, large surface area, and great diffusivity. Long-term exposure to these particles may cause ischemic heart disease, cardiovascular diseases, stroke, chronic bronchitis, asthma, and respiratory tract infections.

The most frequent exposure to nanoaerosol is inhalation in the workplace or in the environment. By number, nanosized particles constitute 90 % or more of ambient aerosols, although they only account for a very small fraction of the total mass [5]. These particles have a considerable high deposition (more than 90 %) in alveolar region or other respiratory tract region which can lead to diffusion into the circulatory system. Since the size of nanoaerosol particles is smaller than cells, they can penetrate through the respiratory or integumentary system and leach into the bloodstream. Contrary to neutral nanoaerosols of the same size, charged nanoaerosol particles have a much greater probability of depositing into the lungs [6].

Employees who are exposed to nanoaerosols should have adequate protection against nanoparticle exposure. The best option is exhaust by hood; conventional dust masks may not be as effective as expected. At this moment, there is no legal standard that sets the occupational exposure threshold. The development of risk assessment of exposure to nanoaerosol has been limited by the lack of standard methods and compact instrumentation for long-term monitoring. Accurate risk assessment requires advanced nanoaerosol sampling and characterization techniques for the analysis of both physical and chemical properties of nanoaerosol.

Thermal Rebound in Nanoaerosol Filtration

Separation of nanoaerosol particles from its carrier gas is important to nanoaerosol sampling and characterization as well as air cleaning for the protection of human health. Since nanoaerosol particle charging efficiency is low and charged nanoparticles only carry low charges, it is technically challenging to remove nanoparticles from the air by electrostatic precipitation (ESP) only. Furthermore, extra nanoaerosol particles are likely to be produced in corona chargers [3], which is a critical component of an ESP. Passing nanoaerosol through a water column can effectively remove the unwanted particles from the air. It may work effectively for small quantity of air; however, it becomes costly for large airflow rates.

High-efficiency particulate air (HEPA) filtration seems to be the most cost-effective approach to nanoaerosol removal from the air. Although charging nanoaerosol particles is likely to improve the filtration efficiency by ESP effect, diffusion is the dominating mechanism for nanoaerosol filtration. Conventional filtration theory indicates that nanoaerosol filtration efficiency increases inversely with particle size. Base on this hypothesis, filtration efficiency of nanoaerosol particles can reach 100 % for a properly designed filter. In reality, however, there should be a critical size from which filtration efficiency drops with the decrease of particle diameter (see Fig. 2). Otherwise, gas molecules, which are indeed extremely small particles, should be captured by filters resulting in no separation of aerosol particles from the carrier gas. Knowledge of this critical size is important to the design of effective nanoaerosol filters.

Wang and Kasper [1] first quantified this critical size by considering nanoaerosol thermal rebound effect. This analysis was based on several assumptions, including a Maxwell–Boltzmann distribution of nanoaerosol thermal velocity and perfect elasticity of nanoparticles. Their analysis showed that the critical size was between 1 and 10 nm in diameter depending on mechanical constant and interfacial adhesion energy. Due to the absence of mechanical constants for nanoaerosol particles, the critical size has to be determined experimentally. A handful of experiments have been conducted attempting to determine the critical size by comparing experiments using single-fiber filters with the single-fiber filter theories. Unfortunately, none of them saw any drop in efficiency in the range of 3–20 nm, even at elevated temperatures. Recently, Mouret et al. [7] conducted an alternative analysis based on different adhesion models for nanoaerosol particles. They proposed that thermal rebound may occur only for sub-1 nm particles. Now it becomes even more challenging to experimentally determine the critical size because, at the moment of writing this text, no online instrument can measure nanoaerosol smaller than 1 nm.
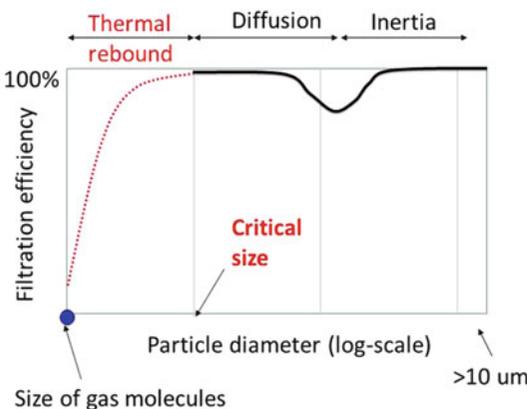
Nanoaerosol, Fig. 2 Filtration efficiency versus aerosol particle diameter (not in scale)

Examples of Applications

Nanoaerosol for Health

Although some scientists suggested spraying nanoaerosol into the upper atmosphere to battle climate change, it seems to make more sense to take advantage of the unique properties of engineered nanoaerosols to improve the quality of life on the planet earth. Thousands of years ago, the Chinese started collecting soot particles from burnt pine to make high-quality ink for fine painting. This may be the earliest engineering application of nanoaerosol. Nowadays, engineered nanoaerosols find more applications to the improvement of our quality of life.

Many different types of nanosized drugs have been developed, and some of them can be aerosolized and delivered by inhalation. Respiratory nanomedicine delivery benefits due to high drug deposition in the central and peripheral regions of the lungs. However, the human respiratory system did not seem to be effective in capturing nanoaerosol particles smaller than 40 nm [8]. Drug delivery systems for nanoaerosol are believed to have potential to significantly reduce extrathoracic depositional drug loss. Dosing effect can be improved by charging the particles. Manufacturing cylindrical or tubular-shaped nanoaerosol drugs may also help since their actual aerodynamic diameters are increased to micron range and tend to travel only one way into human respiratory system. On the other hand, manufacturing sub-10 nm drugs and associated delivery devices is challenging because they agglomerate easily at high concentrations.

Another example is the wide use of nanosilver spray as a disinfectant [9]. During the short life of nanoaerosol after spraying, high-dose exposure could result in acute or chronic health effects. The mechanisms of toxicity of silver ions (Ag^+) are well known, but little is known about toxicity nano-silver induced to living organisms. In addition, limited data available has shown that other potentially hazardous and toxic materials are involved in the product and the disinfectant spray could also have negative impacts on the environment and human health.

Online Nanoaerosol Instrumentation
A number of technologies have been developed to measure airborne nanoparticle size distribution (PSD) online for use in a laboratory setting. Scanning mobility particle sizer (SMPS) is able to measure particle size with precision to a couple of nanometers within a time span of 3 and 5 min for a single measurement. SMPS employs a differential mobility analyzer (DMA) to classify nanoaerosols based on their electrical mobility after passing through a bipolar charger; the performance of a DMA is mostly limited to the low charging efficiency of sub-20 nm nanoaerosol particles. Sub-20 nm classified

nanoparticles are sent into a condensation particle counter (CPC), where they grow to 25 μm by condensation in butanol or water vapor. Then these large particles are counted by light scattering technique.

Fast mobility particle sizer (FMPS) from TSI is based on electrical aerosol spectrometer to classify particle size distribution in the range of 5.6–560 nm. FMPS is suitable for measuring fast-changing particle size distribution. Engine exhaust particle sizer (EEPS) spectrometer could measure the particle size distribution of concentrated engine exhaust continuously in the size range of 5.6–560 nm in real time. EEPS has the fastest resolution time that is suitable for dynamic measurement. Similar to SMPS, it is based on diffusion charging and electrical mobility measurement. It employs multiple electrometers to get the simultaneous measurements; however, its size resolution is low compared to SMPS. Nanometer aerosol size analyzer (nASA) uses the radioactive source bipolar charger (PO^{210}) for charging particles and the nanometer differential analyzer (n-DMA) to classify them. nASA is used to measure high-concentration particle size distribution in the range of 3–100 nm in an exceptionally short time period. nASA is utilized for a wide range of sample pressure and temperature because of its thermodynamic stability.

GRIMM Inc. developed SMPS + E to measure particle number concentrations in the size range of less than 1 nm to a few hundreds of micrometers. It uses a combination of Faraday cup and electrometer to measure the particle number distribution according to their charges. There are also several other technical approaches published in nanoaerosol monitoring. Unfortunately none of the existing technologies can be widely deployed to industry because of their high cost, sensitivity to the environment, or low accuracy.

Compared to size distribution instruments, much less is developed for online analysis of nanoaerosol chemical composition. By coupling aerodynamic focusing techniques (see above) with particle ionization and mass spectrometry,

instruments have been developed for effective online chemical analysis for single micron-sized particles. However, it is challenging to extend the same approach to the application to nanoaerosol chemical composition due to low signal produced. At this point of time, researchers in this area have been able to characterize nanoaerosol in the range of 40–100 nm. No instrumentation has been reported aiming at online single particle chemical analysis for sub-10 nm nanoaerosols, which is crucially needed in order to fully understand the mechanisms of secondary aerosol nanoaerosol formation [10]. Currently, it has to be conducted by a combination of offline and online approaches in a statistically significant manner.

Future Directions for Research

Due to the unique properties of nanoaerosol, much is unknown in this emerging area of research. To take advantage of the unique properties of nanoaerosol, one of the future trends in nanomedicine is targeted drug delivery to the respiratory system by nanoaerosol; it is important to improvement of drug therapies, lung imaging, gene delivery and therapy, tuberculosis diagnosis, and treatment. Meanwhile, many researchers also raised their concern about the potential negative impact of nanoaerosol on human health and the environment. This concern has been growing with the advances of nanotechnology.

Despite the awareness of occupational exposure to nanoaerosol, assessment of the associated risk is still at its early stage. There are very limited reports about the real cases of nanoaerosol exposure. At this point, it is important to clearly understand the toxicological effect of inhaled nanoaerosol to address the increasing concerns over potentially harmful public and occupational exposure. And this type of research should be conducted systematically on a global scale.

Success of the above scientific research relies on the availability of engineering tools that enable effective sampling and characterization of nanoaerosol. There is still a great need to develop stationary or portable instrument to measure particle size distribution that are practical for broad industrial applications. Online chemical characterization of nanoaerosol is another challenge with significant potential for future research. Light scattering and laser-based ionization become inefficient to nanoaerosol particles. This hinders the advances in online chemical analysis of nanoaerosol. Unconventional alternative approaches to online instrumentation for sub-30 nm nanoaerosol are critically needed for accurate and sensitive analysis. These are limited by the unknown fundamentals about nanoaerosol, such as interfacial behavior, thermal rebound effect, and electrical and light properties.

Nanoaerosol filtration is another area of interest to the reduction of occupational exposure. While HEPA filters have been believed to be effective for separation of nanoaerosol from the carrier gas, this is actually an assumption that cannot be proved experimentally. In addition, HEPA filters are still energy intensive, and alternative approaches to nanoaerosol filtration are needed. And they should be experimentally evaluated using a variety of nanoaerosols.

Cross-References

▶ Amperometric Techniques
▶ Brownian Motion in Microfluidics and Nanofluidics
▶ Bubble Dynamics in Microchannels
▶ Electrical Current Monitoring Methods
▶ Flow-Based Particle Trapping and Manipulation
▶ Induced-Charge Electrokinetic Motion of Particle in a Microchannel
▶ Mechanical Nanosensors
▶ Microfilters
▶ Noncontinuous Approaches
▶ Nanoparticle Synthesis in Microreactors
▶ Plasma Treatment of Nanoparticles and Carbon Nanotubes for Nanofluids
▶ Powder Blasting

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Nanochannel Fabrication

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Synonyms

Nanofluidic channels; Nanopores; Nanopore fabrication

Definition

A nanochannel is a hollow channel with at least one dimension of its cross section in the 1–100 nm range. Depending on the cross-sectional configuration, a nanochannel can be classified as a "two-dimensional (2D)" nanochannel or a nanoslit with one side of its cross section in the nanometer regime or a "one-dimensional (1D)" nanochannel or a nanotube with its diameter (or both width and depth) in the nanometer regime. Short nanochannels are usually denoted as nanopores.

It is worth noting that some confusion exists at present in classifying nanochannels as 1D or 2D. Nanoslits are also referred to by some researchers as 1D confined nanochannels, and sometimes simplified as 1D nanochannels, while nanotubes are called 2D confined nanochannels. This is exactly opposite to the above classification, so caution must be used to find out what a researcher means by 1D and 2D nanochannels in his writing. Here the definition follows the common practice in naming low-dimensional structures; for example, thin films are usually denoted as two dimensional, and nanowires are usually denoted as one dimensional.

Overview

Nanochannels or nanopores are interesting nanostructures due to the fact that their sizes are comparable to either the size of DNAs or proteins or the Debye screening length of electric double layers. Current interest in nanochannels or nanopores in nanofluidic research was largely inspired by the pioneering work of single molecule sensing with a naturally occurring protein nanopore, α-hemolysin, which is a nanopore of about 10 nm long and has an smallest inner diameter of about 1.4 nm. The nanopore was embedded in a lipid bilayer membrane separating two fluid cells, and a baseline ion current was set up under an electric bias across the nanopore. When single-stranded DNA or RNA molecules were translocated through the nanopore, the ion current was partially blocked, making an extremely sensitive single molecule detector. These promising results motivated the development of robust and size-tunable inorganic nanopores as single molecule sensors with solid-state