AEROSOLS

An Industrial and Environmental Science

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Environmental Research & Technology, Inc.
Westlake Village, California

1984

ACADEMIC PRESS, INC.

(Harcourt Brace Jovanovich, Publishers)

Orlando San Diego San Francisco New York London
Toronto Montreal Sydney Tokyo São Paulo

ACADEMIC PRESS, INC.
Orlando, Florida 32887

United Kingdom Edition published by
ACADEMIC PRESS, INC. (LONDON) LTD.
24/28 Oval Road, London NW1 7DX

Library of Congress Cataloging in Publication Data

Hidy, George M.
Aerosols, industrial and environmental science.

Includes bibliographical references and index.
1. Aerosols. I. Title.
TP244.A3H53 1984 660.2'94515 84-2743
ISBN 0-12-347260-1

PRINTED IN THE UNITED STATES OF AMERICA

84 85 86 87 9 8 7 6 5 4 3 2 1

To Dana, Anne, Adrienne, and John
—To Prin, Ogden, Red, Leon, and Rosebud

PREFACE

When Milton Kerker convinced me to undertake the writing of this book, I viewed the project with enthusiasm. With many years of experience in some elements of aerosol science and technology and a working knowledge of the field, I felt the venture was achievable with reasonable effort. To my surprise, I found the diversity of literature on aerosol science and technology to be far in excess of expectations. Consequently, I seriously underestimated the task of bringing together the wealth of information accumulated in this field, but the project has been completed. The results of several years of effort constitute the whole of this book. Although it is not perfect by any means, it does serve to introduce the interested reader to the aerosol field at a level comparable with H. L. Green and W. R. Lane's famous volume of the 1950s, *Particulate Clouds, Dusts, Smokes and Mists*. Comparison between the contents of their book and this manuscript will provide some perspective on the dramatic increase in knowledge about aerosols through the past three decades. Aerosol science and technology has kept pace with the general expansion of information in the physical sciences and engineering. Its traditional stimulation has come from applications to industrial challenges and to the environmental and health-related sciences.

Consistent with Green and Lane's approach, this book is intended to be at least partially encyclopedic in scope as a survey of knowledge. The book is intended to serve scientists and engineers who are concerned both with the underlying principles of aerodynamic and physical chemical behavior of suspended particles and with the nature of the application of these principles to a wide variety of uses. The applications range from consideration of pest control, combustion, and powder technology to environmental concerns for the potential hazards of suspended particles in ambient air.

Since aerosol science and technology remains basically experimental or observational in character, much of the book is devoted to description of measurement techniques and results in terms of a framework of classical mechanics and macroscopic chemistry.

The book could be used as a text for graduate students in specialized courses on aerosol or colloid chemistry, atmospheric processes, and chemical, mechanical, or environmental engineering. However, an instructor would want to select carefully the material to be presented in a restricted period of time. For a basic course in colloidal science, Chapters 1–5 would be most appropriate. For a course useful to atmospheric scientists, Chapters 1–3, 7, and 8 would be appropriate. An engineering curriculum should consider Chapters 1–5, 6, and 10. Training of environmental scientists or those interested in regulatory considerations would focus on Chapters 5, 7, 9, and 10.

Although I hoped that this work would be comprehensive in its survey of knowledge applicable to aerosol behavior, the book has a certain bias of viewpoint from my own experience and interests. The approach taken in organization, selection, and emphasis of material reflects the influence of many of my friends and colleagues. There is strong emphasis on elements of the fluid dynamic models of aerosol particles and rigid spheres, an area in which I worked for many years with my friends Sheldon Friedlander and James Brock. There is also considerable effort devoted to atmospheric phenomena involving suspended particles, an area of central interest to me for many years. With the current concerns for clean air and environmental conservation, this application follows naturally from atmospheric science. To those workers whose studies may be neglected inadvertently in my selection and treatment, my apologies before you read the book. Given the limitations of my own time and energy, I hope that readers will be sufficiently stimulated by one viewpoint to seek a broader penetration into the aerosol literature than that contained here. In this way, they may discover a diverse expression of viewpoints and judge for themselves a direction appropriate to their individual work that touches or advances this field of science and technology.

If nothing else, I believe the book will serve to introduce the reader to the wide variety of physics and chemistry that has been used to characterize and interpret aerosol behavior. With assimilation of the knowledge contained here, the reader should be prepared to contribute actively to the continued evolution of this component of modern science and technology.

ACKNOWLEDGMENTS

I am indebted to the many co-workers whose research made this book possible. Without the benefit of the knowledge, cooperation, and resources of a large number of people, a comprehensive book dealing with aerosol science and technology would not be feasible. I acknowledge especially the continued association, for more than twenty years, with Sheldon Friedlander and N. A. Fuchs. Through Sheldon's closely related research and Dr. Fuchs' pioneering leadership, I have retained the interest in this field to permit the effort needed to undertake this work.

It is appropriate to recognize especially the contributions of my friend Kenneth Whitby. His sudden death in 1983 saddened the aerosol community. However, his legacy of work remains with us and is well referenced in this book.

I want to express my gratitude to Doris (Sharp) Wilson. As my secretary and friend for many years, she assisted crucially in the many tasks involved in the preparation of the manuscript and the correspondence required to confirm information sources. I am also indebted to Marcia Henry and Harry Bowie who have assisted me with the literature research and graphics needed to prepare the manuscript.

I am grateful to Milton Kerker and Richard Countess who read the draft of the manuscript and provided many suggestions for its improvement before publication.

It has been my privilege to be a part of the development of the aerosol field and to work personally with B. Appel, K. Bell, J. R. Brock, C. S. Burton, R. Cadle, S. Calvert, J. Calvert, R. J. Charlson, R. Countess, B. V. Derjaguin, J. Durham, A. Goetz, D. Grosjean, J. Hales, S. L. Heisler, R. C. Henry, B. Herman, P. Hobbs, D. Hochrainer, R. B. Husar, J. L. Katz, M. Kerker, C. and N. Knight, A. Lazrus, M. Lippmann, B. Y. H. Liu, J. P. Lodge, Jr., P. McMurry, T. Mercer, V. Mohnen, P. K. Mueller, L. Newman, B. Ottar, O. Preining, H. Pruppacher, H. Reiss, J. Rosinski, J. Seinfeld, G. Slinn, P. Squires, W. Stöber, G. Sverdrup, O. Vittori, A. Waggoner, J. G. Watson, J. Wesolowski, W. Wilson, G. Wolff, and G. Zebel.

NOMENCLATURE

The following nomenclature is used in the text most frequently.

Symbol	Meaning
A	Stokes–Cunningham correction [Eq. (2.6)]
A_F	Attractive force coefficient [Eq. (4.23)]
A_p	Acoustic amplitude factor [Eq. (3.58)]
A_{ij}	Loading factor for principal components [Eq. (7.3)]
a	Characteristic external radius or diameter of body (cm)
$\mathcal{A}$	Inverse product of the particle mass and the mobility, $(m_p B)^{-1}$ (sec^{-1}).
B	Particle mobility (sec/gm) or luminance (lm/m^2 sr)
B_F	Attractive force retardation coefficient [Eq. (4.23)]
b or b_{ij}	Coagulation coefficient (cm^3/sec)
b_{ext}	Light extinction coefficient (m^{-1})
b_{ag}	Light absorption coefficient for gases (m^{-1})
b_{ap}	Light absorption coefficient for particles (m^{-1})
b_{sg}	Light-scattering coefficient for gases (m^{-1})
b_{sp}	Light-scattering coefficient for particles (m^{-1})
b_i	Regression coefficient [Eq. (7.5)]
$\mathcal{B}$	Condensation–coagulation scale parameter [Eq. (3.65)], or flame theory transport scale [Eq. (6.4)]
C	Contrast
$C_{\mathcal{D}}$	Drag coefficient
C_{at}	Bradley–Hamaker attractive force constant [Eq. (4.22)]
C_M	Modulation contrast
C_p	Heat capacity at constant pressure (cal/g mol °K)
C_v	Heat capacity at constant volume (cal/g mol °K)
c	Speed of sound (m/sec)
c_i	Molar concentration, species i liter (mole/liter)
c_m	Momentum slip coefficient
c_p	Specific heat at constant pressure (cal/g °K)

Symbol	Meaning
c_v	Specific heat at constant volume (cal/g °K)
c_t	Thermal slip coefficient
c_{tm}	Isothermal slip coefficient
CN	Condensation nuclei concentration (no./cm^3)
CCN	Cloud condensation nuclei (no./cm^3)
$\mathcal{C}$	Coagulation or reaction efficiency (probability)
c	Speed of light (m/sec)
D_{AB}	Binary gas diffusion coefficient for A diffusing into B (cm^2/sec)
D_i, D_p	Particle (Stokes–Einstein) diffusivity (cm^2/sec)
D_j	Generalized dispersion factor [Eq. (10.1)]
D_t	Turbulent diffusion coefficient (cm^2/sec)
d	Characteristic diameter (cm)
d_A	Diameter of molecule A (Å)
d_a	Aerodynamic equivalent diameter (μm)
d_e	Stokes equivalent diameter (μm) for nonspherical particle
d_p, d_i	Particle diameter (μm)
d_{ac}	Probable droplet diameter (μm) from acoustic generator [Eq. (4.14)]
$\mathcal{D}$	Drag force (dyn)
$\mathcal{D}^*$	Dimensionless drag force on filter ($\mathcal{D}/q_o\mu_g$)
E, E_o	Electrical field (V)
ΔE	Change in chromaticity
E_j	Emission rate (kg/sec)
EF	Enrichment factor
EOF	Empirical orthogonal function
ERV	Expiratory reserve volume
e	Unit electrical charge (esu; coulomb)
e_k	Embryo unit of kth size
e_{ij}	Relative entrainment [Eq. (3.57)]
$\mathcal{E}$	Total (overall) collection efficiency (%)
$\mathcal{E}_d$	Energy dissipated per unit mass (erg/g) [Eq. (4.5)]
F, $\mathbf{F}$	External force (dyn)
F', $\mathbf{F}'$	Normalized force, F/m_p (cm/sec^2)
F_{at}	Attractive force between particles (dyn)
FR	Fractional reduction for linear rollback
f	Frequency (sec^{-1})
$G(d_p)$	Total light extinction per unit volume (m^{-1}/μm^3 cm^{-3})
G	Velocity ratio, q_G/q_o or E_0QB/U_∞, or group combustion number
Gr	Filtration scale factor, $\tau_p g/q_0$ [Eq. (5.39)]
$\hat{G}_i$	Gibbs free energy (kcal/mol; kcal/molecule or kcal/embryo)
$\Delta\hat{G}^*$	Gibbs free energy to form critical-size embryo (kcal/mol or kcal/molecule)
g	Gravitational acceleration constant (cm/sec^2)
$g(v,n_i,\mathbf{r},t)$	Composition–size probability density function
$\mathcal{G}$	Shearing rate in fluid
H	Velocity ratio, $2Q'QB/U_\infty a$; impactor jet nozzle to plate distance; source stack height; height of control device
ΔH	Enthalpy change (heat of reaction)(kcal/mol)
h_∞	Specific enthalpy (kcal/g)
$\mathcal{H}$	Henry's-law constant (dyn/cm^2)
h	Heat transfer coefficient (cal/cm^2 sec)
$\hbar$	Planck's constant (erg sec)
I	Interception parameter R/a or light intensity [Eq. (5.9)](erg/cm^2 sec)
$\mathbf{I}$	Radiation flux (erg/cm^2 sec)
I_c	Combustion intensity
I, I_i	Particle current (no. cm^3 sec)
i	Electrical current (A)
IH	Filter inhomogeneity factor
IFN	Ice-forming nuclei
$\mathcal{J}$	Particle interaction parameter

Symbol	Meaning
J	Light source function [Eq. (5.36)](erg/cm^3 sec)
j_ν	Heat or mass flux (e.g., g/cm^2 sec)
JND	Just noticeable difference in contrast C
$\mathbb{K}$	Shape factor (Table 2.2)
K	Burning rate constant [Eq. (6.2)](cm^2/sec)
K_a	Empirical factor in Duetsch equation [Eq. (10.35)]
K_{abs}	Light absorption efficiency
K_c	Burning rate coefficient [Eq. (6.20)](cm/sec)
K_{ext}	Light extinction efficiency
K_H	Hydrodynamic factor for cylindrical fibers [Eq. (5.42)]
K_p	Plate column scale factor
K_{scat}	Light-scattering efficiency
K_v	Constant in prevailing visibility–particle mass relation [Eq. (8.5a)]
K_{Ve}	Venturi throat parameter
k	Boltzmann constant (erg/molecule °K)
k_p, k_i, k_g	Thermal conductivity (cal/sec cm °K)
$\mathscr{k}_p$	Mass transfer coefficient or deposition velocity (cm/sec)
$\mathscr{k}_1$, $\mathscr{k}_2$	Adsorption coefficients for chemisorption and desorption [Eq. (6.11)]
$\mathscr{k}^+$	Dimensionless mass transfer coefficient ($\mathscr{k}_p/u^*$)
L	Length scale; throat length for impactor nozzles (cm)
$\mathscr{L}_c$	Average column packing diameter (cm)
$\mathscr{L}_h$	Sieve hole diameter (cm)
L_p	Prevailing visibility (km)
L_v	Visual range (km)
l	Stopping distance (cm)
M	Particle mass concentration (μg/m^3)
M_A	Molecular weight of species A (g/mol)
$\hat{M}$	Mass of dust per unit filter surface
m_i, m_p, m_A	Particle mass or gas molecule mass (g/molecule)

Symbol	Meaning
m_c	Interfacial tension ratio, $\sigma_{cg}-\sigma_{cl}/\sigma_{lg}$
$\dot{m}_F$	Mass burning rate (g/sec)
MD	Modulation depth
$\mathfrak{M}_\nu$	Moments of size distribution
$\mathfrak{M}_{ij}$	Symmetry factor
m	Index of refraction
N, N_∞	Total particle concentration (no./cm^3)
N_o	Total number of particles per unit volume initially present, or present at ground level (no./cm^3)
N_R	Total number concentration of rain or cloud drops (no./cm^3)
N_t	Number of cyclone turns to remove particles of size R
n_ν	Number density of species, ν (no./cm^3)
$n(v,\mathbf{r},t)$,	Size distribution function based on particle volume (no./cm^3 μm^3)
n_e	Charge accumulation
$n_R(R,\mathbf{r},t)$	Size distribution function based on particle radius (no./cm^3 μm)
NO_x	Nitrogen oxides, nitric oxide (NO); nitrogen dioxide (NO_2)
NMHC	Nonmethane (often photochemically reactive) hydrocarbon vapors
n_i	Moles of species i
P	Total pressure (dyn/cm^2) or scale parameter, Re^2/Stk,
ΔP	Pressure drop (dynes/cm^2)
P_e	Penetration of control device ($1 - \mathscr{E}$)
P_{jk}	Principal component [Eq. (7.4)]
$p_\nu(n_i, P, T)$	Partial pressure of species (ν)(dyn/cm^2)
$p_0(n_i, T)$	Partial pressure in equilibrium with a flat liquid surface (dyn/cm^2)
$p_s(T)$	Vapor pressure in equilibrium with a droplet (dyn/cm^2)

Symbol	Meaning
$\mathcal{P}$	Precipitation rate (cm/hr), or sheering scale parameter
p	Phase function [Eq. (5.32)]
Q, Q'	Electrical charge (esu; coulomb)
Q_l, Q_g	Liquid or gas volume flow rate (liter/min)
Q_s	Saturation charge (esu; coulomb)
q, $\mathbf{q}$	Aerosol component velocity (cm/sec)
q_E	Electrical migration velocity (cm/sec)
q_g	Gas velocity (cm/sec)
q_G	Gravitational sedimentation velocity (cm/sec)
q_o	Face velocity for filters (cm/sec)
q_m	Mainstream velocity (cm/sec)
q_s	Sampler velocity (cm/sec)
$\bar{q}_i$, $\bar{q}_p$, $\bar{q}_g$	Average thermal velocity (cm/sec)
R, R_p	Particle radius (μm)
R_a	Aerodynamic particle radius (μm)
R_c	Flame radius (cm)
R_{CL}	Combustible-droplet cloud radius (cm)
R_e	Stokes equivalent radius (μm)
R_s	Sphericity
$\bar{R}$	Mean number; surface or volume radius (μm)
R^*	Radius of critical sized embryo (μm)
R_{ij}	Sum of radii, $R_i + R_j$ (μm)
R_{min}	Minimun radius for cyclone removal [Eq. (5.51)](cm)
r, $\mathbf{r}$	Radial coordinate
r_o	Pore radius (μm)
$\mathcal{R}$	Universal gas constant (1.987 cal/g mol °K; 8.314 $\times 10^7$ g cm^2/sec^2 g mol °K)
r	Reaction rate
S	Total surface area per unit volume ($4\pi\mathfrak{M}_2$)(μm^2/cm^3), or distance from the impactor nozzle to plate (cm)
S_E	Surface area of electrostatic precipitator (cm^2) [Eq. (10.36)]
S_f	Effective filter fiber mat surface (cm^2) [Eq. (10.33)]
S_j	Source contribution [Eq. (10.1)]
s_i	Surface area of particle i
SO_x	Sulfur oxides, as SO_2 and SO_4^{2-}
SC	Solubility coefficient [Eq. (7.8)]
SU	Suction coefficient [Eq. (5.2)]
SBE	Scenic beauty estimate
$\mathbb{S}$	Supersaturation ratio, p_s/p_o
T	Temperature (°C, °K)
T_s	Surface temperature (°K)
t	Time (sec)
t_e	Saturation time, $\pi e B_i N_0$ [Eq. (5.6)]
t_g	Penetration time (sec) [Eq. (10.29)]
t_H	Characteristic time of spray droplet motion (sec)
t_s	Characteristic time of spray droplet disintegration (sec)
TP	Thoracic particle concentration (μg/m^3)
TSP	Total suspended particulate concentration (μg/m^3)
$\mathcal{T}$	Coagulation time, $3\pi\mu_g/8kTN_o$ [Eq. (3.61)]
U_∞	Free-stream fluid velocity (cm/sec)
$\bar{u}$	Mean wind or gas speed (cm/sec)
u^*	Friction velocity $(F/\rho_g)^{1/2}$
V	Volume fraction of particles ($\frac{4}{3}\pi\mathfrak{M}_3$)(μm^3/m^3)
VM	Volatile matter in coal
VMD	Volume median diameter (μm)
VAQI	Visual air quality index
v_p, v_i	Particle volume (μm^3)
$\bar{v}$	Average particle volume (V/N)(μm^3)
v_m	Molecular volume of condensed species (cm^3)
$\bar{v}_\nu$	Molar volume of solution

Symbol	Meaning
W	Width of impactor jet nozzle, or optical shape factor (cm)
W_{res}	Limiting resolution of microscope
W_o, W_1	Diffusion or chemical resistance in particle combustion
X	Color tristimulus coordinate [Eq. (8.9)]
X_{ik}	Value of i variable [Eq. (7.3)]
x	Mole fraction or Cartesian coordinate (1), or dimensionless wave number, 2
$\bar{x}$	Normalized color tristimulus [Eq. (8.10)]
Y	Color tristimulus coordinate [Eq. (8.9)]
y	Cartesian coordinate (2)
y_ν	Mass fraction of species ν (g/gm)
$\bar{y}$	Normalized color tristimulus [Eq. (8.10)]
Z	Color tristimulus coordinate [Eq. (8.9)]
Z_c	Collision factor [Eq. (3.38)]
Z_{ik}	Generalized variable for statistical analysis [Eq. (7.3)]
z	Cartesian coordinate (3)
z_i	Number of charges on a particle
z_o	Roughness length (cm)
$z_\pm$	Number of ions per molecule
$\bar{z}$	Normalized tristimulus component [Eq. (8.10)]
α_c, α_m, α_t	Accommodation coefficients for condensation (evaporation), momentum, and thermal energy
$\bar{\bar{\alpha}}(a)$	Polarizability tensor (scalar)
β	Vapor flux parameter [Eq. (3.14)]
β'_k	Vapor flux parameter [Eq. (3.15)](mol/cm^2 sec)
γ	Expansion ratio c_p/c_v; exponent in power-law form of size distribution; stoichiometric ratio in flames
Δ_a	Rainfall parameter [Eq. (7.13)]
Δ_{ij}	Fuch's concentration depletion factor [Eq. (3.51)]
δ	Fluid boundary layer thickness (cm)
ε_o	Permittivity of gas
ε_p, ε_s, ε_f	Dielectric constant of particles or collectors
ε_ν	Rainout efficiency
ε_t	Turbulent energy dissipation rate (cm^2/sec^3)
ε_v	Void fraction
ζ_a	Refill factor [Eq. (3.56)]
ζ_o	Filter pressure loss coefficient [Eq. (10.30)]
η, η_v	Collection efficiency (%); self-preserving spectrum size scale, vN/V
κ	Debye reciprocal length (cm^{-1})
Λ	Washout rate coefficient or scavenging coefficient
λ	Wavelength of light (cm)
λ_p, λ_i, λ_g	Mean free path for particles or gas (cm)
λ_ν	Latent heat of vaporization
μ_g	Dynamic viscosity
μ^*_ν	Dimensionless moment of size distribution, $\int_0^\infty \eta^\nu \Psi(\eta) d\eta$
$\hat{\mu}$	Chemical potential (cal/molecule or cal/embryo)
ν	Kinematic viscosity μ/ρ
ξ	Sound intensity; washout ratio; packing density $(1 - \varepsilon_v)$ of filters or packed beds
ρ_ν	Mass density (gm/cm^3) or concentration (gm/cm^3)
σ	Surface free energy or surface tension (dyn/cm)
σ_{cg}, σ_{cl}	Surface energy between substrate (c), gas (cg), or liquid (cl)(dyn/cm)
σ_g	Standard deviation (geometrical)
σ_{AB}	Coefficient as a function of m_ν and d_ν [Eq. (2.18)]

Symbol	Meaning
σ_y, σ_z	Dispersion coefficients in Gaussian plume model, $2D_t x/\bar{u}$
τ	Particle relaxation time $\mathcal{C}^{-1}$; residence time in atmosphere (sec;hr)
τ, τ_a	Optical depth (thickness) for aerosols (m)
τ^+	Dimensionless relaxation time $\tau u^*2/\nu$
$\hat{\tau}$	Thermal force factor [Eq. (2.11)]
Φ	Rate of exchange or transfer, jS(g/sec)
ϕ	Contact angle
χ	Condensation–coagulation similarity ratio [Eq. (3.65)]
χ_ν	Rainwater concentration of species ν (mg/liter)
Ψ	Self-preserving size distribution function nV/N^2
Ω_{ij}	Electrical correction factor for coagulation [Eq. (3.47)]
ω	Angular rotation speed (sec^{-1})
$\bar{\omega}_o$	Single light-scattering albedo

Subscripts	Meaning
A,B, . . . ,ν	Molecular component
g	Gas
l	Liquid
s	Surface property
∞	Free-stream condition

Named dimensionless numbers	Meaning
Br	Brown number $(\bar{q}_i/\bar{q}_g)$
Kn	Knudsen number (λ_g/R_p)
La	Langmuir number $(\mu_l\bar{q}_p/\sigma)$
Le	Lewis number $(k/\rho_g c_p D_{AB})$
Ma	Mach number $(\lvert q_i - q_g \rvert/\bar{q}_g)$
Nu	Nusselt number $(2\mathcal{h}R/k_g)$
Pe	Peclet number $(U_\infty a/D_\nu)$
Pr	Prandtl number $(c_p\mu_g/k_g)$
Re	Reynolds number $(qR_p/\nu_g;\ U_\infty a/\nu_g)$
Sc	Schmidt number (ν_g/D_ν)
Sh	Sherwood number $(2\mathcal{k}R/D_{AB})$
Stk	Stokes number $(2U_\infty\rho_p R^2/9\mu_g a)$
We	Weber number $(\rho_g q_p^2 R_p/\sigma)$

CONTENTS

CHAPTER 1

INTRODUCTION

Contained in one corner of man's storehouse of knowledge is an expanding collection of information about the behavior of tiny particles dispersed in gases. Generically such suspensions have been called *aerosols, aerocolloids,* or *aerodisperse* systems. They include clouds of suspended matter ranging from dust and smoke to mists, smogs, or sprays. The science and technology of aerosols has matured rapidly in the twentieth century as part of the increasing interest in their chemistry and physics. But the history of this part of colloidal chemistry dates back to much earlier times. One might guess that man has been concerned about airborne particles since the time he first choked on smoke from his campfires; indeed, particulate matter has played a major role in the development of the knowledge of air pollution. The optical experiments of Tyndall in 1869, followed by Rayleigh's (1871) theory of light scattering, may have signaled the beginnings of modern aerosol science. This work was followed by Aitken's (1884) studies of particle mechanics, and Wilson's (1897) classical work on nucleation. At the turn of the century came Einstein's (1905) theories of Brownian motion, which bridged the link between a microscopic approach to particle behavior akin to that of large molecules and the evolution of a continuum theory of fluids. Since then, the science has progressed rapidly as described in reviews such as Whytlaw-Gray and Patterson (1932), Fuchs (1964), and Hidy and Brock (1970).

Aerial dispersions vary widely in physical and chemical properties, depending on the nature of the suspended particles, their concentration in the gas, their size and shape, and the spatial homogeneity of dispersion. Both