

Monodispersed Particles

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Monodispersed Particles

Preface

The term "monodispersed particles" as the antonym of "polydispersed particles" means a group of particles made highly uniform in size and shape. If they are defined in terms of size distribution, one may expect the coefficient of variation (= standard deviation / mean size) to be within 10 %. The major significance of monodispersed particles is attributed to the uniformity in physico-chemical properties of individual particles in a dispersion system, which allows us to directly correlate the properties of a whole system with those of each particle and facilitates theoretical approaches. Their practical importance seems to be due to the potential capability for precise control of their own properties. Thus, they are of obvious importance not only in the fields of physical chemistry, dealing with the dynamic behavior and stability of particulate systems, but also in the industries including catalysts, ceramics, electromagnetic materials, photographic emulsions, pigments, medicines, etc. Complying with so many scientific and practical demands, great efforts have been devoted to the preparation of well-defined colloidal particles for a long time. One may be able to trace the history back to the beginning of the twentieth century. For example, uniform gold particles were prepared by Zsigmondy as early as in the 1900s using a seeding technique; monodispersed barium sulfate particles of different shapes by Andreasen *et al.* (1943); spherical sulfur particles by LaMer and Barnes (1946); polystyrene latex by Bradford and Vanderhoff (1955); cubic and octahedral silver bromide particles by Berry *et al.* in the early 1960s; spindle-like akaganeite (β -FeOOH) by Watson *et al.* (1962); spherical silica particles by Stöber *et al.* (1968); spherical chromium hydroxide particles by Demchak and Matijević (1969); platinum nanoparticles in microemulsions by Boutonnet *et al.* (1982); synthesis of hematite particles of different shapes in the gel-sol system (1992). However, the substantial progress in this field, including theory and practice, is rather recent and particularly remarkable for the last two decades.

While the fundamental and practical importance is generally accepted, it may not seem easy to attain monodisperse systems exactly serving individual purposes, because many factors have decisive influences on the monodispersity and other relevant characteristics. In fact, a large number of monodisperse particles have been prepared only by trial and error or by

optimization of preparation conditions, and it appears rather rare to find studies which genuinely shed light on the fundamental formation mechanisms, leading to general principles, or design synthetic systems on the basis of reasonable guidelines. Nevertheless, it is also true that steady efforts have been continued to investigate the underlying mechanisms of the formation of monodispersed particles, so that the formation processes are gradually being clarified. Such efforts will finally lead us to reasonable and more precise control of monodispersed systems. Moreover, in response to the persistent demand for the industrial use of monodispersed particles of enormous potential benefits, highly condensed monodisperse systems, so-called the "gel-sol systems," was invented in 1992 to resolve the essential problem, *the extremely low productivity*, in existing dilute monodisperse systems. The new method is based on an idea of using highly condensed precursor gels as a matrix of growing final particles for preventing their coagulation, which is eventually transformed into a condensed sol of the final particles through a dissolution-recrystallization process. This idea was first realized for the synthesis of monodisperse hematite particles, as referred to above. Since a monodispersed sol is formed from a gel, in contrast to the sol-gel process, the method has been named "gel-sol method." This invention is a kind of challenge to the conventional physical chemistry for colloidal systems, on which existing monodispersed systems have been fabricated. Since the backgrounds of the colloid chemistry in condensed systems essentially differ in a sense from those in dilute systems, establishment of the new colloid chemistry is an urgent issue. In view of these situations, it seems timely to publish a comprehensive book on the preparation, characterization, and application of monodispersed particles, which will be useful for systematic understanding of the underlying principles of general monodispersed systems and mechanisms of individual practical cases and for creating novel systems.

This book covers diverse aspects of monodispersed particles, consisting of four parts: *i.e.*, Fundamentals, Preparation, Analyses, and Applications. In Part 1 (Fundamentals), I will introduce the fundamental concepts of nucleation, growth, habit formation, recrystallization, and solid-solution formation in its individual chapters, in each of which theories and the corresponding experimental results will be given. In Part 2 (Preparation), the general principles for the formation of monodispersed particles will be summarized in the first place, and then all examples of monodispersed or fairly uniform systems will be classified into homogeneous or heterogeneous systems, being reviewed systematically according to the characteristics of the individual reactions. In particular, considering the convenience for readers,

I tried to compile as many examples as possible from available literature for uniform inorganic and organic particles, with sizes ranging from a few nanometers to several hundreds of micrometers. As a result, even such particles as fairly uniform but not so complete as to be called "monodispersed particles" are also covered in this part, in accord with the comprehensive nature of this book. Also, the techniques and underlying principles for the control of particle characteristics, such as mean size, shape, internal homogeneous structure, composition, layered structure, hollow structure, porous structure, and heterojunction, will be described in detail. In Part 3 (Analyses), methods for the analysis of the formation processes of monodisperse particles and for the characterization of the products will be explained comprehensively. In Part 4 (Applications), applications of monodispersed particles as models of colloidal systems to fundamental studies and as advanced particulate materials for practical use will be delineated. For the practical use of monodispersed particles, special emphasis is placed on their potentialities and infinite possibilities in future rather than the current applications, since it is only the latest event that we have found some general clue to their manufacture for practical purposes.

I hope that this book, probably the first comprehensive book dealing with general aspects of monodispersed particles, will serve as a guide to the fascinating field of uniform colloidal systems for students of senior and graduate-level courses up to advanced specialists in both academic and industrial centers. Perhaps, the readers will find that this book is not an ordinary textbook, but a unique one which involves numerous new ideas of the author in every chapter, and may notice his implicit intention to lead the readers naturally to the essential principles ruling the wonderland of monodispersed particles. Particularly, I have developed a number of new theories for this book, whenever I felt it necessary.

A book such as this could not have appeared without the sustained help of many people. I am especially indebted to Prof. E. Matijević of Clarkson University in the United States for his inspiring encouragements and kind offer of his latest publications. Special thanks are also due to Drs. A. Muramatsu and H. Itoh in my laboratory for their help in searching for the literature and in the preparation of many electron micrographs and the name index.

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LIST OF SYMBOLS

A	surface area, Hamaker constant, or light absorption
$A(t)$	relative amplitude to the average level in dynamic light scattering
a	particle radius, or solid surface area divided by the number of the adsorbed particles
a_0	lattice parameter of a -axis
a_1	surface area of a monomer
a_n	surface area of a cluster consisting of n monomers (n -mer), or electric multipole moment
B	magnetic flux density
b_n	magnetic multipole moment
C	total concentration of all monomeric species
C_0	initial C
C_b	C in the bulk in the liquid phase of a particle growth system
C_{crit}	C at the critical supersaturation
C_i	C at the solid/liquid interface in a particle growth system
C_r	C in equilibrium with a particle of radius r
C_∞	C in equilibrium with a bulk solid
$C_{(n)}$	C in equilibrium with a n -mer
C_N	C in equilibrium with the stable nuclei at the end of nucleation
C^*	C close to C_{crit} but slightly below C_{crit}
ΔC^*	$C^* - C_\infty$
$C(\tau)$	autocorrelation function in dynamic light scattering
C_{ext}	extinction cross-section of a particle
C_{abs}	absorption cross-section of a particle
C_{sca}	scattering cross-section of a particle
c	concentration of monomers, or weight concentration of particles
c_0	lattice parameter of c -axis
$c_{(\infty)}$	concentration of monomers in equilibrium with a bulk solid
$c_{(n)}$	concentration of monomers in equilibrium with a n -mer
c_n	number concentration of n -mers
c_n^e	c_n in equilibrium with supersaturated monomers
c_r	number concentration of radicals in monomer-swollen polymer particles per unswollen unit volume
c^*	number concentration of precursor radicals in the aqueous phase of an

	emulsion polymerization system
D	diffusion coefficient of solute molecules or particles
D_T	transverse diffusivity of particles
d	diameter of a monomer or a particle
E	electric field, or energy
E_c	magnetic energy of crystalline anisotropy
E_H	magnetic energy of external magnetic field
E_s	magnetic energy of shape anisotropy
E_σ	magnetic energy of strain anisotropy
e	electric charge of an electron
F	Faraday constant, or force
f	size distribution function, frequency of a laser beam, or activity coefficient
$G(\Gamma)$	distribution function of Γ in photon correlation spectroscopy
g	normalized size distribution function of embryos, or particle concentration in gram per one gram of the dispersion
H	external magnetic field, or peak height of a pyramid extrapolated from a two-dimensional nucleus in the form of a truncated pyramid
H_0	separation between the Stern layers of two particles
H_c	coercive force
$H_u(\theta)$	horizontal component of a Rayleigh ratio, $R_u(\theta)$
h	dimensionless size distribution function, dimensionless magnetic field, surface-to-surface interparticle distance, or height in general
I	magnetization, intensity of transmitted light, or initiator of polymerization
$I\cdot$	initiator radical
I_0	spontaneous magnetization per unit volume of a particle, or intensity of incident light
I_r	residual magnetization
I_s	saturation magnetization
J	nucleation rate
K	absorption coefficient of a particle
K_0	stability constant of initiator radicals
K_D	rate constant in the diffusion-controlled growth mode
K_d	constant in Nielsen's chronomal of diffusion-controlled growth
K_m	constant in Nielsen's chronomal of mononuclear-layer growth
K_R	rate constant in the reaction-controlled growth mode
K_r	constant in Nielsen's chronomal of (polynuclear-layer) reaction-controlled growth
K_s	magnetic shape-anisotropy constant

K_{sp}	solubility product
K_u	uniaxial magnetocrystalline anisotropy constant
K_G	magnetic strain-anisotropy constant
k	Boltzmann constant, or growth rate constant ($= k_d$)
k_0	reaction rate constant of initiator radicals with monomer
k_∞	k_n of a bulk solid ($n = \infty$)
k_∞^0	k_n^0 of a bulk solid ($n = \infty$)
k_d	overall deposition rate constant of all monomeric species per unit area
k_d^0	deposition rate constant of monomers per unit area
k_e	number of radicals entering a polymer particle per unit time
\bar{k}_e	averaged k_e for all polymer particles in a system
k_m	number of monomers polymerized by a radical per unit time in monomer-swollen polymer particles, or reaction rate constant of mononuclear-layer particle growth
k_n	absolute dissolution rate of a n -mer per unit area
k_n^0	absolute release rate of monomers from a n -mer per unit area in the absence of complexing agents
k_r	recombination rate constant of radicals in monomer-swollen polymer particles
k_s	rate constant of the surface process for the entry of radicals into a monomer-swollen polymer particle per unit area
L	ligand
L_0	circumference of a two-dimensional nucleus in the form of a truncated pyramid
l	length
M	magnetic dipole moment of a particle or monomer for polymerization
m	refractive index of a particle relative to that of the medium, magnetic pole strength, or mass of a particle
N	Avogadro number, or demagnetization factor
N_0	number of embryos generated per unit time ($= QV_m/v_0$)
N_p	number concentration of polymer particles
N^s	surface density of monomers
n	number of monomeric subunits of a n -mer, real part of the relative refractive index, m , of a particle, or number concentration of cations or anions of 1-1 electrolytes
n^*	number of monomeric subunits of a critical nucleus
n_{min}^*	n^* at the maximum supersaturation
n_0	$QRT/8\pi D\gamma V_m C_\infty$, or number concentration of particles in a sol at the ground level under the influence of gravity
n_+	number or number concentration of stable nuclei in a system

n_+^∞	final number or final number concentration of stable nuclei in a system after the nucleation period
n_-	number of unstable nuclei in a system
n_-^∞	final number of unstable nuclei in a system
n_c	number concentration of particles
n_h	number concentration of particles at a height h
n_i	number concentration of ion i
n_{max}	n of a nucleus at the front of a quasi-steady size distribution
n_r	average number of radicals in a polymer particle
n_s	number of bond-free open sites of a free monomer
n_s^σ	number of bond-free open sites of a surface monomer
P	molarity of precipitate
p	r_{111}/r_{100} , or r/r_p
p^*	r^*/r_p
Q	generation rate of monomeric species in a unit volume, feed rate of monomeric species, total electric surface charge of a particle, or capillary charge of a particle.
Q_0	generation rate or feed rate of monomeric species, assumed to be constant during the nucleation stage
q	magnitude of a scattering vector in dynamic light scattering
R	gas constant, or center-to-center interparticle distance
R_∞	infinite reflectivity
R_r	recombination rate of radicals in a polymer particle
$R_u(\theta)$	Rayleigh ratio for unpolarized incident light
r	particle radius, circle radius, distance from a particle center, or degree of ion exchange
r^*	radius of a particle in equilibrium with the monomeric species in a solution phase
r_{min}^*	r^* at the maximum supersaturation
\bar{r}	mean particle radius
r_0	mean radius of embryos or initial degree of ion exchange
r_{100}	distance from the center of a tetradehedral particle to a {100} surface
r_{111}	distance from the center of a tetradehedral particle to a {111} surface
\dot{r}_+	mean linear growth rate of a stable nucleus
r_∞	ultimate particle radius at the end of the growth
r_g	geometric mean radius
r_p	maximum radius of an embryo, or unswollen radius of a polymer particle swollen with the monomers

r_N	mean radius of stable nuclei at the end of a nucleation stage
r_n	number-average radius
r_s	surface-average radius
r_w	weight-average radius
S	supersaturation ratio ($= c/c_{(\infty)} = C/C_{\infty}$), surface area, or scattering coefficient of a particle
S_{max}	maximum supersaturation ratio
T	absolute temperature
t	time
t_N	nucleation period
U_m	magnetostatic energy of a particle
u_E	electric mobility of a particle
V	volume of a particle
V_0	molar volume of solvent molecules
V_A	London - van der Waals attractive energy
V_B	Born repulsive energy
V_E	Electric repulsive energy
V_M	magnetic energy
V_m	molar volume of a solid
V_t	total potential energy
$V_u(\theta)$	vertical component of a Rayleigh ratio, $R_u(\theta)$
v_m	volume of a monomer unit of a linear polymer chain
v_p	unswollen volume of a polymer particle swollen with the monomer
X	monomer in a liquid phase
X_i	species i
$[X_i]$	molarity of species i
X_n	cluster consisting of n monomers (n -mer)
X^s	monomer in a surface molecular layer
x	mole fraction of monomers in a liquid phase, or distance in general
x^*	fraction of the number of the embryos whose radius is greater than r^*
x_0^*	x^* at $t_+ = 0$ ($= v_0/v_p$)
x_i	mole fraction of monomeric species i in a liquid phase
x_n	mole fraction of n -mers in a liquid phase
$x_{(n)}$	mole fraction of monomers in equilibrium with n -mers
$x_{(\infty)}$	mole fraction of monomers in equilibrium with a bulk solid ($n = \infty$)
z_i	valency of ion i

Greek letters

α	$\gamma_{111}/\gamma_{100}$ ratio, aspect ratio of a prolate particle ($= l/w$), optical size parameter ($= 2\pi r/\lambda'$), magnetic energy parameter ($= MH/kT$), direction
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	cosine of saturation magnetization, or collision efficiency of particles to a solid in a magnetic field
β	shape factor of a particle defined by $4A^3/27V^2$, the ratio of the swollen volume of a polymer particle to its unswollen volume, or ratio of the equatorial radius to a half length of the revolution axis of an oblate particle
β_n	stability constant of complex ML_n ($= [ML_n]/[M][L]^n$)
β_s	ratio of the scattering cross section of a particle to its geometric cross section
Γ	half-width at the half-height of an amplitude peak as a function of frequency at a certain scattering angle in dynamic light scattering
γ	specific surface energy, or specific wall energy of a magnetic domain
δ	thickness of a Stern layer, or thickness of a diffusion layer
ϵ	optical extinction
ϵ	surface energy of a bond-free site, or molar optical absorption coefficient
ϵ_0	vacuum permittivity, or width parameter of a size distribution of embryos
ϵ_r	relative permittivity
ζ	zeta potential
η	viscosity
θ	scattering angle, diffraction angle, slope angle of the inscribed circular cone of a two-dimensional nuclei, or angle between magnetic field and primary axis of an anisometric particle
κ	Debye-Hückel parameter, or light absorption index of a particle
λ	n_s^0/n_s , or wavelength in vacuum
λ'	wavelength in a medium ($= \lambda/\mu_0$; μ_0 = refractive index of the medium)
μ	chemical potential of a monomer in liquid phase, refractive index of particles in vacuum, or magnetic permeability
$\underline{\mu}$	magnetic moment vector of a particle
$\bar{\mu}$	relative permeability ($= \mu/\mu_0$; μ_0 = vacuum magnetic permeability)
μ°	standard chemical potential of a monomer in a liquid phase
μ_0	refractive index of a medium in vacuum, or vacuum magnetic permeability
μ_{100}	surface chemical potential of the {100} face of a polyhedral particle
μ_{111}	surface chemical potential of the {111} face of a polyhedral particle
μ^0	chemical potential of a monomer in the interior of a pure bulk solid
$\mu_{(n)}^0$	chemical potential of a monomer in a n-mer
$\mu_{(n)}$	chemical potential of a monomer in a liquid phase in equilibrium with a monomer in a n-mer

$\mu_{(\infty)}$	chemical potential of a monomer in a liquid phase in equilibrium with a monomer in a bulk solid ($n = \infty$)
μ_i	chemical potential of species i , or surface chemical potential of the i th face of a polyhedral particle
μ_n	chemical potential of a n -mer in a liquid phase
μ_n^0	chemical potential of a n -mer in the interior of a bulk solid
μ_n^\ominus	standard chemical potential of a n -mer in a liquid phase
μ^σ	chemical potential of a monomer in a surface molecular layer
$\mu^{0,\sigma}$	standard chemical potential of a monomer in a surface molecular layer
ν_i	number of adsorption sites occupied by an adsorbate molecule i
ξ	degree of reaction in Nielsen's chromomals
π_n	angular distribution of a field radiated from electric multipoles in light scattering
ρ	space charge density, or density of a solid
ρ'	overall density of a particle dispersion
ρ_0	density of a medium
$\rho_u(\theta)$	polarization ratio ($= H_u(\theta)/V_u(\theta)$)
σ	surface charge density, mass specific magnetic moment, standard deviation of a size distribution, or collision parameter
σ_0	mass-specific spontaneous magnetization, or breadth parameter of a particle size distribution
σ_g	geometric standard deviation of a size distribution
σ_M	modal value of the optical size parameter α
σ_p	mass-specific magnetic moment
τ	$RT\nu_p/8\pi D\gamma V_m C_\infty$ (a time constant), time constant in autocorrelation function, or turbidity
τ_n	angular distribution of the field radiated from magnetic multipoles in light scattering
v	volume, or velocity
v_0	molecular volume of a solvent, or mean volume of embryos
v_1	volume of a monomer
v_+	mean volume of stable nuclei
v_+^0	initial v_+ , equivalent to the v_{\max} at the maximum supersaturation
\dot{v}_+	mean volumic growth rate of stable nuclei
v_{\max}	volume of a nucleus at the front of a quasi-steady size distribution
v_n	volume of a n -mer
v_p	maximum volume of an embryo
ϕ	work for transferring a monomer from a bulk solid ($n = \infty$) into a liquid phase and dispersing it to a mole-fraction level ($= kT\ln S$), or angle between the directions of magnetization and a magnetic field

ϕ_n	supersaturation energy parameter of the solubility of a n-mer against that of the bulk solid ($= kT \ln(c_{(n)}/c_{(\infty)})$)
χ	magnetic susceptibility
$\bar{\chi}$	relative magnetic susceptibility ($= \chi/\mu_0$)
ψ	ψ_n per $n^{2/3}$ for a n-mer ($= \psi_n/n^{2/3}$), or angle between the direction of magnetization and the primary axis of an anisometric particle
ψ_0	potential difference between the bulk solid and the solution phase in an inhomogeneous system
ψ^0	surface energy of a free monomer
ψ_n^0	intrinsic surface energy of a n-mer
ψ_n	surface energy of a n-mer
ψ_δ	Stern potential
$\psi^{0,\sigma}$	intrinsic surface energy of a surface monomer
ψ^σ	surface energy of a surface monomer

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