

TABLE OF CONTENTS

1 Nanoparticles in the Environment

Jillian F. Banfield, Hengzhong Zhang

INTRODUCTION	1
NANOPARTICLES IN NATURAL SYSTEMS: WHERE DO THEY COME FROM?	2
Example: Predominantly inorganic nanoparticle formation in acid drainage	3
Other inorganic pathways for formation of nanoparticles	5
NANOPARTICLE FORMATION VIA BIOLOGICAL PATHWAYS	6
Example: Iron-oxidizing microbes and nanoparticle formation in AMD systems	6
Example: Nanoparticles formed by microbes in anoxic regions of AMD systems	10
Other examples of biological pathways that lead to nanoparticles in the environment	14
MICROBES, NANOPARTICLES, AND MINERALOGICAL BIOSIGNATURES	16
NANOPARTICLES: HOW AND WHY ARE THEY DIFFERENT?	16
Introduction	16
Surface free energy and surface stress	19
Surface energy and particle size	20
Surface "pressure" and structural responses in nanoparticles	21
THERMODYNAMICS OF NANOPARTICLE SYSTEMS	22
Minimization of the total free energy by phase transformation	23
Examples of phase stability in nanoparticle systems	29
Particle size and surface adsorption	35
Nanoparticles and organics	36
KINETICS IN NANOPARTICLE SYSTEMS	37
Brief review of kinetic models for macroscopic solids	37
Kinetics of amorphous-to-nanocrystalline transformations	38
Kinetics of crystalline transformations involving nanoparticles	39
Crystal growth of nanocrystalline particles	41
Aggregation and nucleation	44
Possible galvanic interactions in nanoparticle mixtures	46
Microstructure development in nanocrystals	47
SOME RESEARCH OPPORTUNITIES AND CHALLENGES	48
ACKNOWLEDGMENTS	51
REFERENCES	51

2 Nanocrystals as Model Systems for
Pressure-Induced Structural Phase Transitions

Keren Jacobs, A. Paul Alivisatos

INTRODUCTION	59
SINGLE-STRUCTURAL DOMAIN	60
SURFACE EFFECTS AND SHAPE CHANGE	62
THERMODYNAMIC SMEARING	62
TRANSFORMATION KINETICS: ACTIVATION VOLUME	65
TRANSFORMATION MECHANISM	68
Activation volume	69
Activation energy (enthalpic barrier)	70
Entropic factor (entropic barrier)	70
TEMPERATURE DEPENDENCE	70
ACKNOWLEDGMENTS	71
REFERENCES	71

INTRODUCTION	73
THERMODYNAMIC ISSUES	74
METHODS FOR DETERMINING NANOPARTICLE ENERGETICS	77
Equilibrium measurements	77
Calorimetric measurements	77
Computation, simulation, and modeling	79
SPECIFIC SYSTEMS	79
Aluminum oxides and oxyhydroxides	79
Iron oxides and oxyhydroxides	83
Manganese oxides	84
Titanium oxide	85
Zirconium oxide	89
Magnesium aluminate	91
Silica	92
Interfaces, dislocations, and nanocomposites	95
Mixed hydroxides and hydroxycarbonates:	
from surface adsorbates to nanoparticles to bulk phases	96
FUTURE DIRECTIONS AND UNANSWERED QUESTIONS	98
ACmOWLEDGMENTS	99
REFERENCES	99

4 Structure, Aggregation and Characterization of Nanoparticles

Glenn A. Waychunas

INTRODUCTION	105
Structural aspects of natural nanomaterials	105
Definitions	105
GROWTH AND AGGREGATION PROCESSES	106
Growth processes	106
Inorganic vs. organic (enzymatic)	106
NUCLEATION AND GROWTH	107
Classical nucleation theory (CNT)	107
Homogeneous nucleation	107
Heterogeneous nucleation	108
PROBLEMS WITH CLASSICAL MODELS	109
Dynamical nucleation processes: Smoluchowski's approach	109
Classical growth mechanisms vs. aggregation processes	110
Classical growth mechanisms and laws	110
Growth topologies	111
Inorganic vs. biologically produced crystallites	113
How do these growth considerations apply to nanoparticles and nanocrystals?	115
AGGREGATION MECHANISMS	117
Particle-particle interaction forces	117
Electrical double layer, Derjaguin approximation and DLVO theory	119
Aggregation kinetics and kernels in the Smoluchowski equation	122
Fractal dimensions of an aggregate	123
Aggregation topologies	123
Simulations and state of knowledge	126
STRUCTURE	126
Scales of structure	126
<u>Surface vs. bulk structure</u>	127

Surface features	128
Bulk nanoparticle features	130
STRUCTURE AND SHAPE/SIZE DETERMINATION	133
Atomic structure-TEM, X-ray scattering and diffraction	133
Bragg peak broadening	134
Bragg analysis and Rietveld method	134
Debye equation and scattering from small crystallites	137
Short range order: X-ray absorption spectroscopy (XANES and EXAFS)	142
Disorder problems in EXAFS analysis	147
Empirical and <i>ab initio</i> XANES analysis	148
Determination of particle size distributions	152
Rate of growth/aggregation experiments with SAXS	153
Small-angle neutron scattering (SANS)	154
Light scattering techniques	155
"INDIRECT" STRUCTURAL METHODS	156
Optical spectroscopy (IR, visible, UV, Raman, luminescence, LfifD)	156
Soft X-ray spectroscopy	158
Mossbauer/NMR spectroscopy	159
SOME OUTSTANDING ISSUES	160
Can crystal chemistry systematics be applied to nanoparticles?	160
Can we meaningfully compare nanoparticle surfaces with bulk crystal surfaces (i.e., are nanoparticles just like small units of a bulk crystal surface)?	160
Is the local structure of water different near nanoparticles? Is this significant in defining nanoparticle surface/bulk structure and perhaps stability?	160
Do highly defective structures have aspects in common with nanoparticles? For example: Do "nanoporous materials" have similarities to clustered nanoparticles either structurally or energetically?	161
Outstanding problems that need to be addressed	161
REFERENCES	162

5 Aqueous Aluminum Polynuclear Complexes and Nanoclusters: A Review

William H. Casey, Brian L. Phillips, Gerhard Furrer

INTRODUCTION	167
METHODS FOR DETERMINING STRUCTURES	168
X-Ray diffraction	168
Nuclear magnetic resonance spectroscopy	168
Potentiometry	169
STRUCTURES	169
Aluminum monomers	169
Aluminum dimers	169
Baker-Figgis Keggin-like structures	173
The flat aluminum tridecamers	174
Al ₃₀ polyoxocations	175
REACTIVITIES OF KEGGIN-LIKE ALUMINUM POLYOXOCATIONS	178
Rates of oxygen-isotopic exchange in E-Keggin molecules	178
Decomposition of the E-Keggin Molecules	183
Mechanisms of formation of the E-Keggin molecules	184
Mechanisms of formation of the Al ₃₀ molecules	184
CATALYSIS BY OXIDE NANOCLUSTERS	184
CONCLUSIONS	186
ACKNOWLEDGMENTS	187
REFERENCES	187

6 Computational Approaches to Nanomineralogy

James R. Rustad, Witold Dzwiniel, David A. Yuen

INTRODUCTION	191
MULTISCALE DESCRIPTION OF COMPLEX SURFACES	193
Scaling concepts	194
Wavelets and multiscale description of surfaces and interfaces	196
MULTISCALE SIMULATION METHODS FOR SOLIDS	199
Large-scale molecular dynamics methods	200
Coupling methods	201
Transition state searching and kinetic Monte Carlo techniques	203
MULTISCALE COMPUTATIONAL METHODS FOR FLUIDS	204
Dissipative particle dynamics	205
Agglomeration of particles	206
Coarse-graining dissipative particle dynamics: fluid particle model.	208
OUTLOOK	211
ACKNOWLEDGMENTS	212
REFERENCES	213

7 Magnetism of Earth, Planetary, and Environmental Nanomaterials

Denis G. Rancourt

INTRODUCTION	217
Magnetism in the Earth sciences	217
Relation to other books and reviews	217
Organization and focus of this chapter	218
Symbols and acronyms	219
MAGNETIC NANOPARTICLES EVERYWHERE	222
In our brains, the animals, space, everywhere	222
Applications of magnetic nanoparticles	223
Towards function and mechanisms	223
MAGNETISM OF THE CRUST AND SURFACE ENVIRONMENTS	224
Diamagnetic and paramagnetic ions	224
Magnetism from crustal ions in surface minerals	224
Magnetism from crustal and surface mineralogy	226
MEASUREMENT METHODS FOR MINERAL MAGNETISM	227
Constant field (dc) magnetometry	228
Alternating field magnetometry (ac susceptometry)	229
Neutron diffraction	230
Mossbauer spectroscopy	231
Electron spin resonance	232
TYPES OF MAGNETIC ORDER AND UNDERLYING MICROSCOPIC INTERACTIONS	232
Intra-atomic interactions and moment formation	232
Inter-atomic exchange interactions	233
Magnetic order-disorder transitions	233
Collinear and noncollinear ferromagnetism	234
Collinear and noncollinear antiferromagnetism	235
Ferrimagnetism	235
Weak ferromagnetism, canted antiferromagnetism	236
Metamagnetism of layered materials	236
Spin glasses, cluster glasses, and multi-configuration states	236
Spin-orbit coupling and magneto-crystalline energy	238
Dipole-dipole interactions and magnetic domains	239
FROM BULK TO NANOPARTICLE VIA SUPERPARAMAGNETISM	240
<u>Phenomena induced by small size and sequence of critical particle sizes</u>	<u>240</u>

Magneto-sensitive features of magnetic nanoparticles	244
MICROSCOPIC AND MESOSCOPIC CALCULATIONS	
OF MAGNETISM IN MATERIALS	252
Methods of calculation in solid state magnetism	252
Calculations of superparamagnetism and inter-particle interactions	257
INTERPLAYS BETWEEN MAGNETISM AND OTHER SAMPLE FEATURES	258
Chemistry and structure via $\{\mu_i, K_i, J_{ij}(r_{ij})\}$	258
Chemical coupling to magnetism in nanoparticles	258
Structural coupling to magnetism in nanoparticles	259
MAGNETIC AND RELATED TRANSITIONS AFFECTED BY PARTICLE SIZE	260
Defining the size effect question	260
Classic order-disorder, spin flops, electronic localization, and percolation	261
Frustration and magneto-strain effects	261
Magneto-volume effects	261
Exotic effects and transitions	262
OVERVIEW OF RECENT DEVELOPMENTS	262
Main recent developments in magnetic nanoparticle systems	262
Measurements on single magnetic nanoparticles	263
Synthetic model systems of magnetic nanoparticles	264
Inter-particle interactions and collective behavior	265
Noteworthy attempts at dealing with nanoparticle complexity	266
Interpreting the Mossbauer spectra of nanoparticle systems	269
Needed areas of development	271
EXAMPLES: CLUSTERS, BUGS, METEORITES, AND LOESS	273
Two-dimensional nanomagnetism of layer silicates and layered materials	273
Abiotic and biotic hydrous ferric oxide and sorbed-Fe on bacterial cell walls	274
Hydroxymagnetite, nanohematite, and the Morin transition	275
Mineral magnetism of loess/paleosol deposits	275
Synthetic and meteoritic nanophase Fe-Ni and Earth's geodynamo	276
NEW DIRECTIONS: ENVIRONMENTAL MODELLING	277
ACKNOWLEDGMENTS	278
REFERENCES	278

8 Atmospheric Nanoparticles

C. Anastasio, S. T. Martin

INTRODUCTION	293
BACKGROUND CONCEPTS	294
Size distributions of atmospheric particles	294
Sources and sinks of atmospheric particles	296
Visibility reduction	298
Radiative forcing and climate change	299
Health effects	301
Chemical reactions of atmospheric particles	303
NUCLEATION	307
Theoretical treatment of critical germ formation	308
Chemical composition of critical germ	310
New particle formation in the atmosphere	311
Primary emissions	315
GROWTH	317
CHARACTERIZATION	319
Number concentrations	319
Chemical composition	319
Morphology	324

PROPERTIES	325
Motion	325
Hygroscopic behavior	326
Chemical reactivity	331
OUTLOOK	336
ACKNOWLEDGMENTS	337
REFERENCES	338