

Michael Quinten

Optical Properties of Nanoparticle Systems

Mie and Beyond



WILEY-VCH Verlag GmbH & Co. KGaA

Contents

	Preface	<i>XIII</i>
1	Introduction	<i>1</i>
2	Nanoparticle Systems and Experimental Optical Observables	<i>9</i>
2.1	Classification of Nanoparticle Systems	<i>10</i>
2.2	Stability of Nanoparticle Systems	<i>14</i>
2.3	Extinction, Optical Density, and Scattering	<i>21</i>
2.3.1	The Role of the Particle Material Data	<i>25</i>
2.3.2	The Role of the Particle Size	<i>26</i>
2.3.3	The Role of the Particle Shape	<i>29</i>
2.3.4	The Role of the Particle Concentration	<i>33</i>
2.3.4.1	Dilute Systems	<i>33</i>
2.3.4.2	Closely Packed Systems	<i>34</i>
3	Interaction of Light with Matter – The Optical Material Function	<i>37</i>
3.1	Classical Description	<i>37</i>
3.1.1	The Harmonic Oscillator Model	<i>38</i>
3.1.2	Extensions of the Harmonic Oscillator Model	<i>40</i>
3.1.3	The Drude Dielectric Function	<i>41</i>
3.2	Quantum Mechanical Concepts	<i>42</i>
3.2.1	The Hubbard Dielectric Function	<i>43</i>
3.2.2	Interband Transitions	<i>47</i>
3.3	Tauc–Lorentz and OJL Models	<i>50</i>
3.4	Kramers–Kronig Relations and Penetration Depth	<i>52</i>
4	Fundamentals of Light Scattering by an Obstacle	<i>55</i>
4.1	Maxwell’s Equations and the Helmholtz Equation	<i>56</i>
4.2	Electromagnetic Fields	<i>59</i>
4.3	Boundary Conditions	<i>61</i>
4.4	Poynting’s Law and Cross-sections	<i>62</i>
4.5	Far-Field and Near-Field	<i>65</i>

4.6	The Incident Electromagnetic Wave	66
4.7	Rayleigh's Approximation for Small Particles – The Dipole Approximation	69
4.8	Rayleigh–Debye–Gans Approximation for Vanishing Optical Contrast	71
5	Mie's Theory for Single Spherical Particles	75
5.1	Electromagnetic Fields and Boundary Conditions	76
5.2	Cross-sections, Scattering Intensities, and Related Quantities	83
5.3	Resonances	87
5.3.1	Geometric Resonances	88
5.3.2	Electronic Resonances and Surface Plasmon Polaritons	91
5.3.2.1	Electronic Resonances	92
5.3.2.2	Surface Plasmon Polariton Resonances	94
5.3.2.3	Multiple Resonances	101
5.3.3	Longitudinal Plasmon Resonances	104
5.4	Optical Contrast	108
5.5	Near-Field	112
5.5.1	Some Further Details	122
6	Application of Mie's Theory	123
6.1	Drude Metal Particles (Al, Na, K)	124
6.2	Noble Metal Particles (Cu, Ag, Au)	127
6.2.1	Calculations	127
6.2.2	Experimental Examples	129
6.2.2.1	Colloidal Au and Ag Suspensions	129
6.2.2.2	Gold and Silver Nanoparticles in Glass	131
6.2.2.3	Copper Nanoparticles in Glass and Silica	132
6.2.2.4	Ag _x Au _{1-x} Alloy Nanoparticles in Photosensitive Glass	134
6.2.2.5	Silver Aerosols	135
6.2.2.6	Further Experiments	137
6.3	Catalyst Metal Particles (Pt, Pd, Rh)	139
6.4	Magnetic Metal Particles (Fe, Ni, Co)	141
6.5	Rare Earth Metal Particles (Sc, Y, Er)	142
6.6	Transition Metal Particles (V, Nb, Ta)	145
6.7	Summary of Metal Particles	147
6.8	Semimetal Particles (TiN, ZrN)	148
6.9	Semiconductor Particles (Si, SiC, CdTe, ZnSe)	151
6.9.1	Calculations	151
6.9.2	Experimental Examples	154
6.9.2.1	Si Nanoparticles in Polyacrylene	154
6.9.2.2	Quantum Confinement in CdSe Nanoparticles	154
6.10	Carbonaceous Particles	156
6.11	Absorbing Oxide Particles (Fe ₂ O ₃ , Cr ₂ O ₃ , Cu ₂ O, CuO)	162
6.11.1	Calculations	162

6.11.2	Experimental Examples	163
6.11.2.1	Aerosols of Fe_2O_3	163
6.11.2.2	Aerosols of Cu_2O and CuO	165
6.11.2.3	Colloidal Fe_2O_3 nanoparticles	167
6.12	Transparent Oxide Particles (SiO_2 , Al_2O_3 , CeO_2 , TiO_2)	168
6.13	Particles with Phonon Polaritons (MgO , NaCl , CaF_2)	170
6.14	Miscellaneous Nanoparticles (ITO , LaB_6 , EuS)	172
7	Extensions of Mie's Theory	177
7.1	Coated Spheres	177
7.1.1	Calculations	177
7.1.1.1	Metallic Shells on a Transparent Core	180
7.1.1.2	Oxide Shells on Metal and Semiconducting Core Particles	184
7.1.2	Experimental Examples	187
7.1.2.1	Ag–Au and Au–Ag Core–Shell Particles	187
7.1.2.2	Multishell Nanoparticles of Ag and Au	189
7.1.2.3	Optical Bistability in Silver-Coated CdS Nanoparticles	190
7.1.2.4	Ag and Au Aerosols with Salt Shells	193
7.1.2.5	Further Experiments	196
7.2	Supported Nanoparticles	198
7.3	Charged Nanoparticles	206
7.4	Anisotropic Materials	210
7.4.1	Dichroism	210
7.4.2	Field-Induced Anisotropy	211
7.4.3	Gradient-Index Materials	211
7.4.4	Optically Active Materials	213
7.5	Absorbing Embedding Media	214
7.5.1	Calculations	214
7.5.2	Experimental Examples	219
7.5.2.1	Absorption of Scattered Light in Ag and Au Colloids	219
7.5.2.2	Ag and Fe Nanoparticles in Fullerene Film	220
7.6	Inhomogeneous Incident Waves	223
7.6.1	Gaussian Beam Illumination	223
7.6.2	Evanescent Waves from Total Internal Reflection	226
8	Limitations of Mie's Theory—Size and Quantum Size Effects in Very Small Nanoparticles	233
8.1	Boundary Conditions—the Spill-Out Effect	233
8.2	Free Path Effect in Nanoparticles	234
8.3	Chemical Interface Damping—Dynamic Charge Transfer	240
9	Beyond Mie's Theory I—Nonspherical Particles	245
9.1	Spheroids and Ellipsoids	247
9.1.1	Spheroids (Ellipsoids of Revolution)	247
9.1.1.1	Electromagnetic Fields	248

9.1.1.2	Scattering Coefficients	251
9.1.1.3	Cross-sections	252
9.1.1.4	Resonances	252
9.1.1.5	Numerical Examples	254
9.1.1.6	Extensions	254
9.1.2	Ellipsoids (Rayleigh Approximation)	255
9.1.3	Numerical Examples for Ellipsoids	259
9.1.3.1	Metal Particles	259
9.1.3.2	Semimetal and Semiconductor Particles	265
9.1.3.3	Carbonaceous Particles	266
9.1.3.4	Particles with Phonon Polaritons	267
9.1.3.5	Miscellaneous Particles	267
9.1.4	Experimental Results	268
9.1.4.1	Prolate Spheroidal Silver Particles in Fourcault Glass	268
9.1.4.2	Plasma Polymer Films with Nonspherical Silver Particles	269
9.1.4.3	Further Experiments	272
9.2	Cylinders	273
9.2.1	Electromagnetic Fields and Scattering Coefficients	273
9.2.2	Efficiencies and Scattering Intensities	277
9.2.3	Resonances	279
9.2.4	Extensions	281
9.2.5	Numerical Examples	282
9.2.5.1	Metal Particles	283
9.2.5.2	Semimetal and Semiconductor Particles	288
9.2.5.3	Carbonaceous Particles	291
9.2.5.4	Oxide Particles	292
9.2.5.5	Particles with Phonon Polaritons	293
9.2.5.6	Miscellaneous Particles	294
9.3	Cubic Particles	296
9.3.1	Theoretical Considerations	296
9.3.2	Numerical Examples	298
9.3.2.1	Metal Particles	299
9.3.2.2	Semimetal and Semiconductor Particles	299
9.3.2.3	Particles with Phonon Polaritons	300
9.3.2.4	Miscellaneous Particles	301
9.4	Numerical Methods	302
9.4.1	Discrete Dipole Approximation	302
9.4.2	T-Matrix Method or Extended Boundary Condition Method	305
9.4.3	Other Numerical Methods	307
9.4.3.1	Point Matching Method	307
9.4.3.2	Discretized Mie Formalism	307
9.4.3.3	Generalized Multipole Technique	307
9.4.3.4	Finite Difference Time Domain Technique	307
9.5	Application of Numerical Methods to Nonspherical Nanoparticles	308

9.5.1	Nonmetallic Nanoparticles	308
9.5.2	Metallic Nanoparticles	310
10	Beyond Mie's Theory II—The Generalized Mie Theory	317
10.1	Derivation of the Generalized Mie Theory	318
10.2	Resonances	321
10.3	Common Results	325
10.3.1	Influence of Shape	325
10.3.2	Influence of Length	327
10.3.3	Influence of Interparticle Distance	327
10.3.4	Enhancement of Scattering and Extinction	329
10.3.5	The Problem of Convergence	331
10.4	Extensions of the Generalized Mie Theory	335
10.4.1	Incident Beam	335
10.4.2	Nonspherical Particles	336
11	The Generalized Mie Theory Applied to Different Systems	341
11.1	Metal Particles	342
11.1.1	Calculations	342
11.1.2	Experimental Results	346
11.1.2.1	Extinction of Light in Colloidal Gold and Silver Systems	346
11.1.2.2	Total Scattering of Light by Aggregates	353
11.1.2.3	Angle-Resolved Light Scattering by Nanoparticle Aggregates	355
11.1.2.4	PTOBD on Aggregated Gold and Silver Nanocomposites	358
11.1.2.5	Light-Induced van der Waals Attraction	360
11.1.2.6	Coalescence of Nanoparticles	361
11.1.2.7	Further Experiments with Gold and Silver Nanoparticles	363
11.2	Semimetal and Semiconductor Particles	364
11.3	Nonabsorbing Dielectrics	367
11.4	Carbonaceous Particles	369
11.5	Particles with Phonon Polaritons	372
11.6	Miscellaneous Particles	375
11.7	Aggregates of Nanoparticles of Different Materials	376
11.8	Optical Particle Sizing	379
11.9	Stochastically Distributed Spheres	382
11.10	Aggregates of Spheres and Numerical Methods	387
11.10.1	Applications of the Discrete Dipole Approximation	387
11.10.2	Applications of the T-Matrix approach	389
11.10.3	Other Methods	389
12	Densely Packed Systems	393
12.1	The Two-Flux Theory of Kubelka and Munk	394
12.2	Applications of the Kubelka–Munk Theory	397
12.2.1	Dense Systems of Color Pigments: Cr ₂ O ₃ , Fe ₂ O ₃ , and Cu ₂ O	398
12.2.2	Dense Systems of White Pigments: SiO ₂ and TiO ₂	399

12.2.3	Dense Systems of ZrN and TiN Nanoparticles	400
12.2.4	Dense Systems of Silicon Nanoparticles	401
12.2.5	Dense Systems of IR Absorbers: ITO and LaB ₆	403
12.2.6	Dense Systems of Noble Metals: Ag and Au	404
12.2.7	The Lycurgus Cup	406
12.3	Improvements of the Kubelka–Munk Theory	407
13	Near-Field and SERS	411
13.1	Waveguiding Along Particle Chains	412
13.2	Scanning Near-Field Optical Microscopy	416
13.3	SERS with Aggregates	420
14	Effective Medium Theories	427
14.1	Theoretical Results for Dielectric Nanoparticle Composites	431
14.2	Theoretical Results for Metal Nanoparticle Composites	433
14.3	Experimental Examples	437
	References	441
	Color Plates	479
	Index	485