

Paul Heitjans · Jörg Kärger

Diffusion in Condensed Matter

Methods, Materials, Models

With 448 Figures



Springer

Contents – In Detail

Part I Solids

1 Diffusion: Introduction and Case Studies in Metals and Binary Alloys

<i>Helmut Mehrer</i>	3
1.1 Introduction	3
1.2 Continuum Description of Diffusion	4
1.2.1 Fick's Laws for Anisotropic Media.....	4
1.2.2 Fick's Second Law for Constant Diffusivity	5
1.2.3 Fick's Second Law for Concentration-Dependent Diffusivity	6
1.3 The Various Diffusion Coefficients	7
1.3.1 Tracer Diffusion Coefficients	7
1.3.2 Chemical Diffusion (or Interdiffusion) Coefficient	8
1.3.3 Intrinsic Diffusion Coefficients	10
1.4 Experimental Methods	10
1.4.1 Direct Methods	11
1.4.2 Indirect Methods	15
1.5 Dependence of Diffusion on Thermodynamic Variables	17
1.5.1 Temperature Dependence	17
1.5.2 Pressure Dependence	18
1.6 Atomistic Description of Diffusion	19
1.6.1 Einstein-Smoluchowski Relation and Correlation Factor ..	19
1.6.2 Atomic Jumps and Diffusion	22
1.6.3 Diffusion Mechanisms	23
1.7 Interstitial Diffusion in Metals.....	27
1.7.1 'Normal' Interstitial Solutes	27
1.7.2 Hydrogen Diffusion.....	29
1.8 Self-Diffusion in Metals.....	31
1.8.1 Face-Centered Cubic Metals	32
1.8.2 Body-Centered Cubic Metals	34
1.9 Impurity Diffusion in Metals	35
1.9.1 'Normal' Impurity Diffusion in fcc Metals	36
1.9.2 Slow Diffusion of Transition-Metal Solutes in Aluminium ..	39
1.9.3 Fast Solute Diffusion in 'Open' Metals	40
1.10 Self-Diffusion in Binary Intermetallics	42

1.10.1	Influence of Order-Disorder Transition	43
1.10.2	Coupled Diffusion in B2 Intermetallics	44
1.10.3	The Cu ₃ Au Rule	47
1.11	Interdiffusion in Substitutional Binary Alloys	49
1.11.1	Boltzmann-Matano Method	49
1.11.2	Darken's Equations	51
1.11.3	Darken-Manning Relations	52
1.12	Multiphase Diffusion in Binary Systems	53
1.13	Conclusion	56
	References	60

2 The Elementary Diffusion Step in Metals Studied by the Interference of Gamma-Rays, X-Rays and Neutrons

	<i>Gero Vogl, Bogdan Sepiol</i>	65
2.1	Introduction	65
2.2	Self-Correlation Function and Quasielastic Methods	66
2.2.1	Quasielastic Methods: Mößbauer Spectroscopy and Neutron Scattering	68
2.2.2	Nuclear Resonant Scattering of Synchrotron Radiation	73
2.2.3	Neutron Spin-Echo Spectroscopy	74
2.2.4	Non-Resonant Methods	75
2.3	Experimental Results	77
2.3.1	Pure Metals and Dilute Alloys	77
2.3.2	Ordered Alloys	78
2.4	Conclusion	87
	References	89

3 Diffusion Studies of Solids by Quasielastic Neutron Scattering

	<i>Tasso Springer, Ruep E. Lechner</i>	93
3.1	Introduction	93
3.2	The Dynamic Structure Factor	94
3.3	The Rate Equation and the Self-Correlation Function	102
3.4	High Resolution Neutron Spectroscopy	106
3.5	Hydrogen Diffusion in Metals and in Metallic Alloys	115
3.6	Diffusion with Traps	121
3.7	Vacancy Induced Diffusion	124
3.8	Ion Diffusion Related to Ionic Conduction	126
3.9	Proton Diffusion in Solid-State Protonic Conductors	131
3.10	Proton Conduction: Diffusion Mechanism Based on a Chemical Reaction Equilibrium	139
3.11	Two-Dimensional Diffusion	143
3.12	Coherent Quasielastic Scattering	149
3.13	Conclusion	155
	References	159

4 Diffusion in Semiconductors

<i>Teh Yu Tan, Ulrich Gösele</i>	165
4.1 Introduction	165
4.2 Diffusion Mechanisms and Point Defects in Semiconductors	165
4.3 Diffusion in Silicon	166
4.3.1 Silicon Self-Diffusion	166
4.3.2 Interstitial-Substitutional Diffusion: Au, Pt and Zn in Si ..	168
4.3.3 Dopant Diffusion	172
4.3.4 Diffusion of Carbon and Other Group IV Elements	177
4.3.5 Diffusion of Si Self-Interstitials and Vacancies	180
4.3.6 Oxygen and Hydrogen Diffusion	182
4.4 Diffusion in Germanium	183
4.5 Diffusion in Gallium Arsenide	184
4.5.1 Native Point Defects and General Aspects	185
4.5.2 Gallium Self-Diffusion and Superlattice Disordering	187
4.5.3 Arsenic Self-Diffusion and Superlattice Disordering	194
4.5.4 Impurity Diffusion in Gallium Arsenide	196
4.5.5 Diffusion in Other III-V Compounds	203
4.6 Conclusion	203
References	205

5 Diffusion in Oxides

<i>Manfred Martin</i>	209
5.1 Introduction	209
5.2 Defect Chemistry of Oxides	210
5.2.1 Dominating Cation Disorder	212
5.2.2 Dominating Oxygen Disorder	215
5.3 Self- and Impurity Diffusion in Oxides	216
5.3.1 Diffusion in Oxides with Dominating Cation Disorder ...	216
5.3.2 Diffusion in Oxides with Dominating Oxygen Disorder ...	222
5.4 Chemical Diffusion	226
5.5 Diffusion in Oxides Exposed to External Forces	228
5.5.1 Diffusion in an Oxygen Potential Gradient	229
5.5.2 Diffusion in an Electric Potential Gradient	236
5.6 Conclusion	242
5.7 Appendix	243
References	245

6 Diffusion in Metallic Glasses and Supercooled Melts

<i>Franz Faupel, Klaus Rätzke</i>	249
6.1 Introduction	249
6.2 Characteristics of Diffusion in Crystals	250
6.3 Diffusion in Simple Liquids	251
6.4 General Aspects of Mass Transport and Relaxation in Supercooled Liquids and Glasses	254

6.5	Diffusion in Metallic Glasses	259
6.5.1	Structure and Properties of Metallic Glasses	259
6.5.2	Possible Diffusion Mechanisms	262
6.5.3	Isotope Effect	265
6.5.4	Pressure Dependence	268
6.5.5	Effect of Excess Volume on Diffusion	269
6.6	Diffusion in Supercooled and Equilibrium Melts	270
6.7	Conclusion	276
	References	278

Part II Interfaces

7 Fluctuations and Growth Phenomena in Surface Diffusion

	<i>Michael C. Tringides, Myron Hupalo</i>	285
7.1	Introduction	285
7.2	Surface Diffusion Beyond a Random Walk	286
7.2.1	The Role of Structure and Geometry of the Substrate	286
7.2.2	The Role of Adsorbate-Adsorbate Interactions	288
7.2.3	Diffusion in Equilibrium and Non-Equilibrium Concentration Gradients	290
7.3	Equilibrium Measurements of Surface Diffusion	297
7.3.1	Equilibrium Diffusion Measurements from Diffraction Intensity Fluctuations	297
7.3.2	STM Tunneling Current Fluctuations	306
7.4	Non-Equilibrium Experiments	313
7.4.1	Uniform-Height Pb Islands on Si(111)	313
7.4.2	Measurements of Interlayer Diffusion on Ag/Ag(111)	320
7.5	Conclusion	331
	References	333

8 Grain Boundary Diffusion in Metals

	<i>Christian Herzig, Yuri Mishin</i>	337
8.1	Introduction	337
8.2	Fundamentals of Grain Boundary Diffusion	338
8.2.1	Basic Equations of Grain Boundary Diffusion	338
8.2.2	Surface Conditions	339
8.2.3	Methods of Profile Analysis	340
8.2.4	What Do We Know About Grain Boundary Diffusion?	343
8.3	Classification of Diffusion Kinetics	347
8.3.1	Harrison's Classification	348
8.3.2	Other Classifications	351
8.4	Grain Boundary Diffusion and Segregation	353
8.4.1	Determination of the Segregation Factor from Grain Boundary Diffusion Data	353

8.4.2	Beyond the Linear Segregation.....	357
8.5	Conclusion.....	359
	References	364

9 NMR and β -NMR Studies of Diffusion in Interface-Dominated and Disordered Solids

	<i>Paul Heitjans, Andreas Schirmer, Sylvio Indris</i>	<i>367</i>
9.1	Introduction	367
9.2	Influence of Diffusion on NMR Spin-Lattice Relaxation and Linewidth	369
9.3	Basics of NMR Relaxation Techniques.....	375
9.4	Method of β -Radiation Detected NMR Relaxation	380
9.5	Intercalation Compounds	384
	9.5.1 Lithium Graphite Intercalation Compounds	384
	9.5.2 Lithium Titanium Disulfide – Hexagonal Versus Cubic ...	386
9.6	Nanocrystalline Materials.....	390
	9.6.1 Nanocrystalline Calcium Fluoride	391
	9.6.2 Nanocrystalline, Microcrystalline and Amorphous Lithium Niobate	394
	9.6.3 Nanocrystalline Lithium Titanium Disulfide	397
	9.6.4 Nanocrystalline Composites of Lithium Oxide and Boron Oxide	399
9.7	Glasses.....	402
	9.7.1 Inhomogeneous Spin-Lattice Relaxation in Glasses with Different Short-Range Order.....	403
	9.7.2 Glassy and Crystalline Lithium Aluminosilicates	405
9.8	Conclusion	408
9.9	Appendix.....	409
	References	411

10 PFG NMR Studies of Anomalous Diffusion

	<i>Jörg Kürger, Frank Stallmach.....</i>	<i>417</i>
10.1	Introduction	417
10.2	The Origin of Anomalous Diffusion	418
10.3	Fundamentals of PFG NMR	421
	10.3.1 The Measuring Principle	421
	10.3.2 The Mean Propagator	422
	10.3.3 PFG NMR as a Generalized Scattering Experiment	424
	10.3.4 Experimental Conditions.....	425
10.4	PFG NMR Diffusion Studies in Regular Pore Networks.....	427
	10.4.1 The Different Regimes of Diffusion Measurement	428
	10.4.2 Intracrystalline Self-Diffusion	430
	10.4.3 Correlated Diffusion Anisotropy.....	431
	10.4.4 Transport Diffusion Versus Self-Diffusion	432
	10.4.5 Single-File Diffusion	434

10.4.6	Diffusion in Ordered Mesoporous Materials	437
10.5	Anomalous Diffusion by External Confinement	439
10.5.1	Restricted Diffusion in Polystyrene Matrices	440
10.5.2	Diffusion in Porous Polypropylene Membranes	441
10.5.3	Tracing Surface-to-Volume Ratios	444
10.6	Anomalous Diffusion due to Internal Confinement	447
10.6.1	Anomalous Segment Diffusion in Entangled Polymer Melts	448
10.6.2	Diffusion Under the Influence of Hyperstructures in Polymer Solutions	450
10.6.3	Diffusion Under the Influence of Hyperstructures in Polymer Melts	453
10.7	Conclusion	455
	References	456
11 Diffusion Measurements by Ultrasonics		
	<i>Roger Biel, Martin Schubert, Karl Ullrich Würz, Wolfgang Grill</i>	461
11.1	Introduction	461
11.2	Diffusion of Hydrogen in Single-Crystalline Tantalum	462
11.3	Observation of Diffusion of Heavy Water in Gels and Living Cells by Scanning Acoustic Microscopy with Phase Contrast	466
11.4	Conclusion	468
	References	469
12 Diffusion in Membranes		
	<i>Ilpo Vattulainen, Ole G. Mouritsen</i>	471
12.1	Introduction	471
12.2	Short Overview of Biological Membranes	473
12.3	Lateral Diffusion of Single Molecules	477
12.3.1	Lateral Tracer Diffusion Coefficient	477
12.3.2	Methods to Examine Lateral Tracer Diffusion	479
12.3.3	Lateral Diffusion of Lipids and Proteins	482
12.4	Rotational Diffusion of Single Molecules	491
12.5	Lateral Collective Diffusion of Molecules in Membranes	493
12.5.1	Fick's Laws	493
12.5.2	Decay of Density Fluctuations	494
12.5.3	Relation Between Tracer and Collective Diffusion	495
12.5.4	Methods to Examine Lateral Collective Diffusion	497
12.5.5	Lateral Collective Diffusion in Model Membranes	498
12.6	Diffusive Transport Through Membranes	500
12.7	Conclusion	503
	References	505

Part III Liquids

13 Viscoelasticity and Microscopic Motion in Dense Polymer Systems

<i>Dieter Richter</i>	513
13.1 Introduction	513
13.2 The Neutron Scattering Method	514
13.2.1 The Neutron Spin-Echo Technique Versus Conventional Scattering	516
13.2.2 Neutron Spin Manipulations with Magnetic Fields	516
13.2.3 The Spin-Echo Principle	518
13.3 Local Chain Dynamics and the Glass Transition	519
13.3.1 Dynamic Structure Factor	521
13.3.2 Self-Correlation Function	527
13.4 Entropic Forces – The Rouse Model	529
13.4.1 Neutron Spin-Echo Results in PDMS Melts	531
13.4.2 Computer Simulations	534
13.5 Long-Chains Reptation	537
13.5.1 Theoretical Concepts	537
13.5.2 Experimental Observations of Chain Confinement	538
13.6 Intermediate Scale Dynamics	540
13.7 The Crossover from Rouse to Reptation Dynamics	543
13.8 Conclusion	550
References	552

14 The Molecular Description of Mutual Diffusion Processes in Liquid Mixtures

<i>Hermann Weingärtner</i>	555
14.1 Introduction	555
14.2 Experimental Background	558
14.3 Phenomenological Description of Mutual Diffusion	559
14.4 Thermodynamics of Mutual Diffusion	564
14.5 Linear Response Theory and Time Correlation Functions	567
14.6 The Time Correlation Function for Mutual Diffusion	569
14.7 Properties of Distinct-Diffusion Coefficients	571
14.8 Information on Intermolecular Interactions Deduced from Diffusion Data	573
14.9 Conclusion	576
References	577

15 Diffusion Measurements in Fluids by Dynamic Light Scattering

<i>Alfred Leipertz, Andreas P. Fröba</i>	579
15.1 Introduction	579

15.2	Basic Principles	580
15.2.1	Spectrum of Scattered Light	580
15.2.2	Correlation Technique	582
15.2.3	Homodyne and Heterodyne Techniques	587
15.3	The Dynamic Light Scattering Experiment	589
15.3.1	Setup	589
15.3.2	Signal Statistics and Data Evaluation	594
15.4	Thermophysical Properties of Fluids Measured by Dynamic Light Scattering	597
15.4.1	Thermal Diffusivity	597
15.4.2	Mutual Diffusion Coefficient	600
15.4.3	Dynamic Viscosity	601
15.4.4	Sound Velocity and Sound Attenuation	604
15.4.5	Landau-Placzek Ratio	606
15.4.6	Soret Coefficient	606
15.4.7	Derivable Properties	607
15.5	Related Techniques	608
15.5.1	Surface Light Scattering	608
15.5.2	Forced Rayleigh Scattering	613
15.6	Conclusion	615
	References	617
 16 Diffusion in Colloidal and Polymeric Systems		
	<i>Gerhard Nägele, Jan K. G. Dhont, Gerhard Meier</i>	619
16.1	Introduction	619
16.2	Principles of Quasielastic Light Scattering	620
16.2.1	The Scattered Electric Field Strength	620
16.2.2	Dynamic Light Scattering	624
16.2.3	Dynamic Structure Factors	626
16.3	Heuristic Considerations on Diffusion Processes	628
16.3.1	Very Dilute Colloidal Systems	629
16.3.2	Diffusion Mechanisms in Concentrated Colloidal Systems	636
16.4	Fluorescence Techniques for Long-Time Self-Diffusion of Non-Spherical Particles	660
16.4.1	Fluorescence Recovery After Photobleaching	661
16.4.2	Fluorescence Correlation Spectroscopy	669
16.5	Theoretical and Experimental Results on Diffusion of Colloidal Spheres and Polymers	675
16.5.1	Colloidal Spheres	676
16.5.2	Polymer Blends and Random Phase Approximation	697
16.6	Conclusion	709
	References	712

17 Field-Assisted Diffusion Studied by Electrophoretic NMR

<i>Manfred Holz</i>	717
17.1 Introduction	717
17.2 Principles of Electrophoretic NMR	719
17.2.1 Electrophoresis	719
17.2.2 Pulsed Field Gradient NMR for the Study of Drift Velocities	720
17.3 NMR in Presence of an Electric Direct Current. Technical Requirements, Problems and Solutions	725
17.4 ENMR Sample Cells	727
17.5 ENMR Experiments (1D, 2D and 3D) and Application Examples	728
17.5.1 1D ENMR Applications	729
17.5.2 2D and 3D Experiments	734
17.5.3 Mobility and Velocity Distributions. Polydispersity and Electro-Osmotic Flow	737
17.6 Conclusion	738
References	741

Part IV Theoretical Concepts and Models

18 Diffusion of Particles on Lattices*Klaus W. Kehr, Kiaresch Mussawisade, Gunter M. Schütz, Thomas*

<i>Wichmann</i>	745
18.1 Introduction	745
18.2 One Particle on Uniform Lattices	748
18.2.1 The Master Equation	748
18.2.2 Solution of the Master Equation	749
18.2.3 Diffusion Coefficient	751
18.2.4 Extensions	752
18.3 One Particle on Disordered Lattices	753
18.3.1 Models of Disorder	753
18.3.2 Exact Expression for the Diffusion Coefficient in $d = 1$...	755
18.3.3 Applications of the Exact Result	757
18.3.4 Frequency Dependence in $d = 1$: Effective-Medium Approximation	758
18.3.5 Higher-Dimensional Lattices: Approximations	762
18.3.6 Higher-Dimensional Lattices: Applications	766
18.3.7 Remarks on Other Models	769
18.4 Many Particles on Uniform Lattices	771
18.4.1 Lattice Gas (Site Exclusion) Model	771
18.4.2 Collective Diffusion	772
18.4.3 Tracer Diffusion for $d > 1$	773
18.4.4 Tagged-Particle Diffusion on a Linear Chain	774
18.5 Many Particles on Disordered Lattices	778

18.5.1	Models with Symmetric Rates	778
18.5.2	Selected Results for the Coefficient of Collective Diffusion in the Random Site-Energy Model	780
18.6	Conclusion	783
18.7	Appendix	784
18.7.1	Derivation of the Result for the Diffusion Coefficient for Arbitrarily Disordered Transition Rates	784
18.7.2	Derivation of the Self-Consistency Condition for the Effective-Medium Approximation	787
18.7.3	Relation Between the Relative Displacement and the Density Change	789
	References	790

19 Diffusion on Fractals

	<i>Uwe Renner, Gunter M. Schütz, Günter Vojta</i>	793
19.1	Introduction: What a Fractal is	793
19.2	Anomalous Diffusion: Phenomenology	797
19.3	Stochastic Theory of Diffusion on Fractals	802
19.4	Anomalous Diffusion: Dynamical Dimensions	803
19.5	Anomalous Diffusion and Chemical Kinetics	806
19.6	Conclusion	809
	References	810

20 Ionic Transport in Disordered Materials

	<i>Armin Bunde, Wolfgang Dieterich, Philipp Maass, Martin Meyer</i>	813
20.1	Introduction	813
20.2	Basic Quantities	816
20.2.1	Tracer Diffusion	816
20.2.2	Dynamic Conductivity	817
20.2.3	Probability Distribution and Incoherent Neutron Scattering	817
20.2.4	Spin-Lattice Relaxation	818
20.3	Ion-Conducting Glasses: Models and Numerical Technique	819
20.4	Dispersive Transport	822
20.5	Non-Arrhenius Behavior	832
20.6	Counterion Model and the “Nearly Constant Dielectric Loss” Response	835
20.7	Compositional Anomalies	839
20.8	Ion-Conducting Polymers	843
20.8.1	Lattice Model of Polymer Electrolytes	843
20.8.2	Diffusion through a Polymer Network: Dynamic Percolation Approach	846
20.8.3	Diffusion in Stretched Polymers	849
20.9	Conclusion	850
	References	852

21 Concept of Mismatch and Relaxation for Self-Diffusion and Conduction in Ionic Materials with Disordered Structure

<i>Klaus Funke, Cornelia Cramer, Dirk Wilmer</i>	857
21.1 Introduction	857
21.2 Conductivity Spectra of Ion Conducting Materials	861
21.3 Relevant Functions and Some Model Concepts for Ion Transport in Disordered Systems	864
21.4 CMR Equations and Model Conductivity Spectra	867
21.5 Scaling Properties of Model Conductivity Spectra	871
21.6 Physical Concept of the CMR	874
21.7 Complete Conductivity Spectra of Solid Ion Conductors	877
21.8 Ion Dynamics in a Fragile Supercooled Melt	880
21.9 Conductivities of Glassy and Crystalline Electrolytes Below 10 MHz	883
21.10 Localised Motion at Low Temperatures	887
21.11 Conclusion	891
References	892

22 Diffusion and Conduction in Percolation Systems

<i>Armin Bunde, Jan W. Kantelhardt</i>	895
22.1 Introduction	895
22.2 The (Site-)Percolation Model	895
22.3 The Fractal Structure of Percolation Clusters near p_c	897
22.4 Further Percolation Systems	901
22.5 Diffusion on Regular Lattices	903
22.6 Diffusion on Percolation Clusters	904
22.7 Conductivity of Percolation Clusters	905
22.8 Further Electrical Properties	906
22.9 Application of the Percolation Concept: Heterogeneous Ionic Conductors	908
22.9.1 Interfacial Percolation and the Liang Effect	908
22.9.2 Composite Micro- and Nanocrystalline Conductors	910
22.10 Conclusion	912
References	913

23 Statistical Theory and Molecular Dynamics of Diffusion in Zeolites

<i>Reinhold Haberlandt</i>	915
23.1 Introduction	915
23.2 Some Notions and Relations of Statistical Physics	916
23.2.1 Statistical Thermodynamics	916
23.2.2 Statistical Theory of Irreversible Processes	919
23.3 Molecular Dynamics	922
23.3.1 General Remarks	922
23.3.2 Procedure of an MD Simulation	923

23.3.3 Methodical Hints	925
23.4 Simulation of Diffusion in Zeolites	925
23.4.1 Introduction.....	925
23.4.2 Simulations	926
23.4.3 Results	928
23.5 Conclusion.....	942
References	944
List of Contributors	949
Index	955