



RSC Nanoscience & Nanotechnology

# Thermometry at the Nanoscale

Techniques and Selected Applications

Edited by Luís Dias Carlos and  
Fernando Palacio



# ***Thermometry at the Nanoscale Techniques and Selected Applications***

Edited by

**Luís Dias Carlos**

*University of Aveiro, Portugal*

*Email: lcarlos@ua.pt*

**Fernando Palacio**

*CSIC-University of Zaragoza, Spain*

*Email: palacio@unizar.es*



RSC Nanoscience & Nanotechnology No. 38

Print ISBN: 978-1-84973-904-7

PDF eISBN: 978-1-78262-203-1

ISSN: 1757-7136

A catalogue record for this book is available from the British Library

© The Royal Society of Chemistry 2016

*All rights reserved*

*Apart from fair dealing for the purposes of research for non-commercial purposes or for private study, criticism or review, as permitted under the Copyright, Designs and Patents Act 1988 and the Copyright and Related Rights Regulations 2003, this publication may not be reproduced, stored or transmitted, in any form or by any means, without the prior permission in writing of The Royal Society of Chemistry or the copyright owner, or in the case of reproduction in accordance with the terms of licences issued by the Copyright Licensing Agency in the UK, or in accordance with the terms of the licences issued by the appropriate Reproduction Rights Organization outside the UK. Enquiries concerning reproduction outside the terms stated here should be sent to The Royal Society of Chemistry at the address printed on this page.*

The RSC is not responsible for individual opinions expressed in this work.

The authors have sought to locate owners of all reproduced material not in their own possession and trust that no copyrights have been inadvertently infringed.

Published by The Royal Society of Chemistry,  
Thomas Graham House, Science Park, Milton Road,  
Cambridge, CB4 0WF, UK

Registered Charity Number 207890

For further information see our web site at [www.rsc.org](http://www.rsc.org)

Printed in the United Kingdom by CPI Group (UK) Ltd, Croydon, CR0 4YY, UK

# Thermometry at the Nanoscale

## Techniques and Selected Applications

## **RSC Nanoscience & Nanotechnology**

### *Editor-in-Chief:*

Professor Paul O'Brien FRS, *University of Manchester, UK*

### *Series Editors:*

Professor Ralph Nuzzo, *University of Illinois at Urbana-Champaign, USA*

Professor Joao Rocha, *University of Aveiro, Portugal*

Professor Xiaogang Liu, *National University of Singapore, Singapore*

### *Honorary Series Editor:*

Sir Harry Kroto FRS, *University of Sussex, UK*

### *Titles in the Series:*

- 1: Nanotubes and Nanowires
- 2: Fullerenes: Principles and Applications
- 3: Nanocharacterisation
- 4: Atom Resolved Surface Reactions: Nanocatalysis
- 5: Biomimetic Nanoceramics in Clinical Use: From Materials to Applications
- 6: Nanofluidics: Nanoscience and Nanotechnology
- 7: Bionanodesign: Following Nature's Touch
- 8: Nano-Society: Pushing the Boundaries of Technology
- 9: Polymer-based Nanostructures: Medical Applications
- 10: Metallic and Molecular Interactions in Nanometer Layers, Pores and Particles: New Findings at the Yoctolitre Level
- 11: Nanocasting: A Versatile Strategy for Creating Nanostructured Porous Materials
- 12: Titanate and Titania Nanotubes: Synthesis, Properties and Applications
- 13: Raman Spectroscopy, Fullerenes and Nanotechnology
- 14: Nanotechnologies in Food
- 15: Unravelling Single Cell Genomics: Micro and Nanotools
- 16: Polymer Nanocomposites by Emulsion and Suspension
- 17: Phage Nanobiotechnology
- 18: Nanotubes and Nanowires, 2<sup>nd</sup> Edition
- 19: Nanostructured Catalysts: Transition Metal Oxides
- 20: Fullerenes: Principles and Applications, 2<sup>nd</sup> Edition
- 21: Biological Interactions with Surface Charge Biomaterials
- 22: Nanoporous Gold: From an Ancient Technology to a High-Tech Material
- 23: Nanoparticles in Anti-Microbial Materials: Use and Characterisation
- 24: Manipulation of Nanoscale Materials: An Introduction to Nanoarchitectonics
- 25: Towards Efficient Designing of Safe Nanomaterials: Innovative Merge of Computational Approaches and Experimental Techniques
- 26: Polymer-Graphene Nanocomposites

- 27: Carbon Nanotube-Polymer Composites
- 28: Nanoscience for the Conservation of Works of Art
- 29: Polymer Nanofibers: Building Blocks for Nanotechnology
- 30: Artificial Cilia
- 31: Nanodiamond
- 32: Nanofabrication and its Application in Renewable Energy
- 33: Semiconductor Quantum Dots: Organometallic and Inorganic Synthesis
- 34: Soft Nanoparticles for Biomedical Applications
- 35: Hierarchical Nanostructures for Energy Devices
- 36: Microfluidics for Medical Applications
- 37: Nanocharacterisation, 2<sup>nd</sup> Edition
- 38: Thermometry at the Nanoscale: Techniques and Selected Applications

*How to obtain future titles on publication:*

A standing order plan is available for this series. A standing order will bring delivery of each new volume immediately on publication.

*For further information please contact:*

Book Sales Department, Royal Society of Chemistry, Thomas Graham House,  
Science Park, Milton Road, Cambridge, CB4 0WF, UK

Telephone: +44 (0)1223 420066, Fax: +44 (0)1223 420247

Email: [booksales@rsc.org](mailto:booksales@rsc.org)

Visit our website at [www.rsc.org/books](http://www.rsc.org/books)



# *Preface*

Sensing and measuring temperature is a crucial need for countless scientific investigations and technological developments. Consequently, as technology progresses into the nanoscale an increasing demand for accurate, non-invasive and self-referenced temperature measurements at sub-micrometric length scales has been observed. This is particularly so in microelectronics and micro/nanofluidics, for instance, where the comprehension of heat dissipation, heat transfer and thermal conductivity mechanisms can play a crucial role in areas as diverse as reliability and integration of electronic systems, energy transfer, and cell physiology.

The assortment of luminescent and non-luminescent nanothermometers proposed over the last decade clearly point to an emerging interest in nanothermometry in a large variety of fields, from electronic to photonic devices, from optoelectronic to micro/nanofluidics and nanomedicine. At the same time, nanothermometry is a multidisciplinary and challenging subject requiring new approaches and new techniques, since conventional thermometry is not valid at such scales.

Apart from a few pioneering works published at the very end of the past century, the subject of investigating and developing thermometric devices that work with sub-micrometre space resolution has exploded in the last 10 years. Particularly since 2010, the research on the field has been biased towards luminescent nanothermometry and its applications in photonics, electronics, fluids, and nanomedicine. For instance, luminescent nanothermometers have already been used to provide thermal readings during photothermal treatments in both culture cells and living organisms.

Several reviews have recently described the progress on high-resolution thermometers operating at the sub-micron scale, including luminescent and non-luminescent nanothermometers, intracellular measurements, ceramic phosphors that can withstand extreme temperatures, multiple optical



chemical sensors and temperature-stimuli polymers. Despite the coverage of the subject, we have arrived at the conclusion that this very multidisciplinary subject demands a more solid piece of work, half way between a monograph and a reference book, where specialists in each particular technique can cover it, discussing achievements and limitations as well as future trends and technological possibilities. This was exactly the original purpose of this book.

The book is organized in four quite independent sections (Fundamentals, Luminescence- and Non-Luminescence-Based Thermometry and Applications) comprising sixteen chapters. After a bird's-eye short review on nanoscale thermometry and temperature measurements, the remaining two chapters of the first section encourage the reader to reflect on the basics of nanothermometry, namely the minimal length scales for the existence of local temperature and heat transfer at the nanoscale.

Section II examines in detail luminescent thermometers based on different thermal nanoprobe: Quantum dots (Chapter 4), lanthanide phosphors (Chapter 5), organic dyes (Chapter 6), polymers (Chapter 7), and organic-inorganic hybrids (Chapter 8). Section III provides a comprehensive discussion about three important non-luminescent techniques to measure temperature: Scanning thermal microscopy (Chapter 9), near-field thermometry (Chapter 10) and nanotube thermometry (Chapter 11). Finally, Section IV explores some of the most exciting and intriguing nanothermometry applications, still limited in practice and results, such as cellular thermometers (Chapter 12), thermal issues in microelectronics (Chapter 13), heat transport in nanofluids (Chapter 14), temperature probes in micro/nanofluidics (Chapter 15) and multifunctional platforms for dual-sensing (Chapter 16).

The book renders lucid explorations of a number of significant and difficult problems in nanothermometry providing readers new to the field with a clear overview of this expanding topic, being simultaneously an inspiration to those already well versed in the field. The book is presented in a format that aims to be accessible to postgraduate students and researchers in physics, chemistry, biology and engineering interested in nanothermometry.

This book would have not been possible without the support and contributions from a significant number of people. In the first place it is our pleasure to acknowledge Prof. João Rocha, Series Editor of the *RSC Nanoscience & Nanotechnology Series*, for encouraging us to submit a book proposal to the Royal Society of Chemistry. We are also extremely grateful to the Royal Society of Chemistry for continuous and always stimulating support without which our work would have been much more difficult. Last but not least, we want to deeply thank to all the contributing authors for enthusiastically accepting our invitation and embracing the book's scope and vision. Their time, work and dedication deserve our most profound acknowledgement.

Luís Dias Carlos and Fernando Palacio  
Aveiro and Zaragoza

# Contents

## Section I Fundamentals

<b>Chapter 1</b>	<b>Nanoscale Thermometry and Temperature Measurement</b>	<b>3</b>
	<i>Peter R. N. Childs</i>	
1.1	Introduction	3
1.2	Methods	6
1.2.1	Infrared	7
1.2.2	Raman Scattering	7
1.2.3	Luminescence	8
1.2.4	Thermoreflectance	10
1.2.5	Interferometry	10
1.2.6	Non-luminescent	11
1.3	Selection	13
1.4	Conclusions	15
	References	15
<b>Chapter 2</b>	<b>Minimal Length Scales for the Existence of Local Temperature</b>	<b>23</b>
	<i>Michael J. Hartmann</i>	
2.1	Introduction	23
2.2	Definition of Temperature	25
2.2.1	Definition in Thermodynamics	25
2.2.2	Definition in Statistical Mechanics	26
2.2.3	Local Temperature	26

2.3	General Theory for the Existence of Local Temperature	28
2.3.1	The Model	29
2.3.2	Thermal State in the Product Basis	29
2.3.3	Conditions for Local Thermal States	31
2.4	Harmonic Chain	32
2.5	Estimates for Real Materials	34
2.6	Discussion of the Resulting Length Scales	36
	References	37
<b>Chapter 3</b>	<b>Introduction to Heat Transfer at the Nanoscale</b>	<b>39</b>
	<i>Pierre-Olivier Chapuis</i>	
3.1	Introduction	39
3.2	Heat Conduction Equations	40
3.2.1	Establishing the Heat Equation	40
3.2.2	Phase Change Phenomena	42
3.2.3	Review of the Main Limitations of the Heat Conduction Equation	42
3.2.4	Non-local Heat Conduction Equations	47
3.3	Beyond the Heat Equation	48
3.3.1	Characteristic Scales	48
3.3.2	Heat Carriers	50
3.4	Heat Conduction at the Nanometre Scale	59
3.4.1	Thermal Boundary Resistances	59
3.4.2	Confinement in Nanoscale Objects	62
3.4.3	Other Effects	67
3.5	Thermal Radiation at the Nanoscale	68
3.5.1	At the Macroscale	68
3.5.2	Interbody Distances Smaller than the Thermal Wavelength	69
3.5.3	Bodies Smaller than the Thermal Wavelength	73
3.6	Characterization of Heat-transfer Properties in Nanomaterials	74
3.6.1	Electrical Measurements	74
3.6.2	Optical Measurements	75
3.7	Conclusions	77
	Acknowledgements	77
	References	78

## Section II Luminescence-based Thermometry

<b>Chapter 4</b>	<b>Quantum Dot Fluorescence Thermometry</b>	<b>85</b>
	<i>Daniel Jaque García and José García Solé</i>	
4.1	Quantum Dots: An Introduction	85
4.2	Fluorescent Properties of Quantum Dots	87
4.2.1	Basic Principles: Quantum Confinement Effects	87
4.2.2	Temperature Dependence of Quantum Dot Luminescence	94
4.2.3	The Importance of Surface Coating	104
4.3	Quantum Dots as Thermal Sensors: Applications	107
4.3.1	Intracellular Thermal Sensing	107
4.3.2	Thermal Characterization of Microelectronic Devices	113
4.3.3	Sub-tissue Thermal Sensing	115
4.3.4	Heterostructures	117
4.4	Conclusions and Perspectives	120
	References	120
<b>Chapter 5</b>	<b>Luminescent Nanothermometry with Lanthanide-doped Nanoparticles</b>	<b>124</b>
	<i>Marta Quintanilla, Antonio Benayas, Rafik Naccache and Fiorenzo Vetrone</i>	
5.1	Introduction	124
5.2	Some Insight into the Properties of the Lanthanides	126
5.2.1	Lanthanide Ions as Luminescent Probes	126
5.2.2	Cooperative Processes between Lanthanide Ions: Energy Transfer and Upconversion	128
5.3	Sensing Temperature with Lanthanides	132
5.3.1	Nanothermometers based on One Emission Intensity	134
5.3.2	The Ratiometric Technique based on more than One Emission Intensity	135
5.3.3	Luminescence Lifetime for Thermal Sensing	146
5.3.4	Other Possibilities for Lanthanide-based Nanothermometry	150
5.4	Applications	153
5.5	Conclusions and Perspectives	159
	References	161

<b>Chapter 6</b>	<b>Organic Dye Thermometry</b>	<b>167</b>
	<i>Guoqiang Yang, Xuan Liu, Jiao Feng, Shayu Li and Yi Li</i>	
6.1	Introduction	167
6.2	Temperature-sensitive Organic Dyes	168
6.2.1	Thermal Quenching Dyes	168
6.2.2	Intramolecular Excimer/Exciplex Dyes	174
6.2.3	Intermolecular Excimer/Exciplex Dyes	175
6.2.4	Intersystem Crossing Dyes	178
6.2.5	Twisted Intramolecular Charge-transfer Compounds	179
6.3	Conclusions and Perspectives	187
	References	187
<b>Chapter 7</b>	<b>Polymeric Temperature Sensors</b>	<b>190</b>
	<i>Gertjan Vancoillie, Qilu Zhang and Richard Hoogenboom</i>	
7.1	Introduction	190
7.2	Dye Incorporation and Positioning in the Polymer Chain	192
7.2.1	Dye-functionalized Monomers	194
7.2.2	Dye-functionalized Initiators/Terminators/ Transfer Agents	195
7.2.3	Post-polymerization Modification	196
7.3	Polymers used for Temperature Sensors	198
7.3.1	Classification of Polymers used for Temperature Sensors	199
7.3.2	Chemical Structures of Thermoresponsive Polymers for Thermometers	201
7.3.3	Architectures of Thermoresponsive Polymers for Thermometers	204
7.4	Dyes used for Polymeric Temperature Sensors	206
7.4.1	Changes in Polarity: Solvatochromic Dyes	208
7.4.2	Changes in Interchain Distance: Förster Resonance Energy Transfer	216
7.4.3	Changes in Rigidity/Viscosity	219
7.4.4	Excimer Formation/Deformation	220
7.5	Potential Applications of Polymeric Temperature Sensors	223
7.5.1	Intracellular Temperature Detection	223
7.5.2	Dual Temperature and pH Sensors	225



7.5.3	Ion Sensors	226
7.5.4	Logic Gates	229
7.6	Conclusion and Outlook	229
	References	230

## **Chapter 8 Organic–Inorganic Hybrids Thermometry** 237

*Angel Millán, Luís D. Carlos, Carlos D. S. Brites,  
Nuno J. O. Silva, Rafael Piñol and  
Fernando Palacio*

8.1	Introduction	237
8.2	Classification	238
8.3	Optical Thermometers	239
8.3.1	Trivalent Lanthanides	240
8.3.2	Molecular Hybrids	244
8.3.3	Polymer Nanocomposites	248
8.3.4	Semiconductor Quantum Dots	250
8.3.5	Core–Shell Nanoparticles	253
8.4	Non-optical Thermometers	258
8.4.1	Magnetic Resonance Imaging	258
8.4.2	Thermosensitive Liposomes	259
8.4.3	Spin-transition Molecular Materials	261
8.4.4	Miscellaneous Systems	262
8.5	Perspectives: Hybrids Joining Nanothermometry and Nanoheating	262
	References	264

## **Section III Non-luminescence-based Thermometry**

## **Chapter 9 Scanning Thermal Microscopy** 275

*Séverine Gomès, Ali Assy and Pierre-Olivier Chapuis*

9.1	Introduction	275
9.2	Instrumentation and Associated Setups	276
9.2.1	General Layout	276
9.2.2	Main Techniques	278
9.2.3	Other Probes	285
9.2.4	Other Methods	286
9.3	SThM Measurement Approaches	287
9.3.1	Probe Calibration	287
9.3.2	Heat Transfer between the Probe and the Sample	297

9.4	Applications	302
9.4.1	Characterization of Devices	302
9.4.2	Measurement of the Thermal Conductivity	303
9.4.3	Phase-transition Temperature Measurement	305
9.5	Conclusions and Perspectives	306
	Acknowledgements	307
	References	307

## **Chapter 10 Near-field Thermometry** **315**

*Kenneth D. Kihm and Seonghwan Kim*

10.1	Introduction	315
10.2	Nano-optical Surface Plasmon Resonance Imaging Thermometry	316
10.2.1	Working Principles of SPR Imaging Thermometry	316
10.2.2	Experimental Setup for Near-field SPR Imaging Thermometry	320
10.2.3	Temperature Dependence of Refractive Index Values	320
10.2.4	Example Applications of SPR Thermometry	324
10.3	Nanomechanical Cantilever Thermometry	326
10.3.1	Working Principles of Nanomechanical Thermometry	326
10.3.2	Proof-of-concept Measurements using Nanomechanical Thermometry	330
10.3.3	Measurement Resolution of Nanomechanical Thermometry	334
10.4	Conclusion and Perspectives	336
	References	336

## **Chapter 11 Nanotube Thermometry** **339**

*Koji Takahashi*

11.1	Introduction	339
11.2	Structure and Mechanical Properties of CNTs	340
11.3	Thermal Conductivity of CNTs	341
11.4	Temperature Measurement using CNT Probes	342
11.5	Fabrication Techniques	346
	References	349

## Section IV Applications

<b>Chapter 12 Cellular Thermometry</b>	<b>355</b>
<i>Seiichi Uchiyama and Noriko Inada</i>	
12.1 Background	355
12.2 Tools for Measuring Cellular Temperature	357
12.2.1 Fluorescent and Luminescent Molecular Thermometers	357
12.2.2 Others	377
12.3 Closing Remarks	379
References	380
 <b>Chapter 13 Thermal Issues in Microelectronics</b>	 <b>383</b>
<i>X. Perpiñà, M. Vellvehi and X. Jordà</i>	
13.1 Introduction	383
13.2 Heat Generation and Testability Issues at the Chip Level for Signal Processing	385
13.2.1 Shrinkage and High-density Integration Effects in Heat Generation at the Chip Level	385
13.2.2 Heterogeneous Integration in the Low-voltage Scenario	387
13.2.3 Figure of Merit Monitoring in Radiofrequency/Analog Integrated Circuits	389
13.3 Heat Generation and Testability Issues at the Chip Level in Energy Processing	390
13.3.1 Power Semi-conductor Devices	390
13.3.2 Light-emission Devices	392
13.3.3 Heterogeneous Integration in Energy Management Systems	393
13.4 Thermal Characterization Techniques at the Chip Level	395
13.4.1 Time <i>versus</i> Frequency Domain Thermal Characterization	396
13.4.2 Temperature Measurements	397
13.5 Thermal Studies at the Chip Level in Microelectronics	417
13.5.1 Signal Processing Electronics: Digital Processing and RF/Analog ICs	417
13.5.2 Energy Processing Electronics: Power Devices and Light-emitting Devices	419



13.6	Conclusions	422
	List of Acronyms	423
	References	425
<b>Chapter 14</b>	<b>Heat Transport in Nanofluids</b>	<b>437</b>
	<i>Efstathios E. Michaelides</i>	
14.1	Thermal Conductivity Enhancement	437
14.1.1	Experimental Data	437
14.1.2	Analytical Expressions and Correlations	440
14.2	Mechanisms of Thermal Conductivity Enhancement	441
14.2.1	Particle Conductivity	441
14.2.2	Particle Shape and Orientation	442
14.2.3	Formation of an Interfacial Solid Layer	444
14.2.4	Electric Surface Charge and pH	445
14.2.5	Brownian Movement	446
14.2.6	Transient Motion of Particles	447
14.2.7	Particle Distribution and Aggregation	447
14.2.8	Preparation and Surfactants	448
14.2.9	Other Mechanisms	448
14.3	Additional Augmentation of the Convective Heat-transfer Coefficients	449
14.4	Natural Convection	451
14.5	Boiling with Nanofluids	452
14.5.1	Pool Boiling	452
14.5.2	Convective Boiling	453
14.5.3	Critical Heat Flux	455
14.6	Conclusions and General Observations	456
	Acknowledgements	457
	References	457
<b>Chapter 15</b>	<b>Thermometry in Micro and Nanofluidics</b>	<b>461</b>
	<i>C. Bergaud</i>	
15.1	Thermal Issues in Micro and Nanofluidics: General Context	461
15.1.1	Inducing Heat for Chemical and Biological Applications	462
15.1.2	Unexpected Heat in Micro and Nanofluidics	464
15.2	Contact Methods	469