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Tim Still

High Frequency Acoustics in Colloid-Based Meso- and Nanostructures by Spontaneous Brillouin Light Scattering

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High Frequency Acoustics in Colloid-Based Meso- and Nanostructures by Spontaneous Brillouin Light Scattering

Doctoral Thesis performed at Max Planck Institute for Polymer Research and accepted by Johannes Gutenberg University, Mainz, Germany

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Der Klügere gibt nach! Eine traurige Wahrheit,
sie begründet die Weltherrschaft der Dummheit.

(*The wiser man gives in! A distressing truth,*
it establishes the world domination of stupidity.)

Marie von Ebner-Eschenbach

Parts of this thesis have been published in the following journal articles:

T. Still, W. Cheng, M. Retsch, R. Sainidou, J. Wang, U. Jonas, N. Stefanou, G. Fytas, *Phys. Rev. Lett.* 2008, **100**, 194301. Copyright 2008 APS.

T. Still, W. Cheng, M. Retsch, U. Jonas, G. Fytas, *J. Phys. Condens. Matt.* 2008, **20**, 404203. Copyright 2008 IOP.

T. Still, R. Sainidou, M. Retsch, U. Jonas, P. Spahn, G. P. Hellmann, G. Fytas, *Nano Lett.* 2008, **8**, 3194. Copyright 2008 American Chemical Society.

T. Still, M. D'Acunzi, D. Vollmer, G. Fytas, *J. Coll. Interf. Sci.* 2009, **340**, 42. Copyright 2009, Elsevier, Inc. All rights reserved.

K. Kearns, T. Still (equal contribution), G. Fytas, M. D. Ediger, *Adv. Mater.* 2010, **22**, 39. Copyright 2010 Wiley-VCH.

T. Still, M. Retsch, U. Jonas, R. Sainidou, P. Rembert, K. Mpoukouvalas, G. Fytas, *Macromolecules* 2010, **43**, 3422. Copyright 2010 American Chemical Society.

Supervisor's Foreword

Materials that can mold the flow of elastic waves of certain energy in certain directions are called *phononic* materials. The present thesis deals essentially with such phononic systems, which are structured in the *mesoscale* (<1 μm), and with their individual components. Such systems show interesting phononic properties in the *hypersonic* region, i.e., at frequencies in the GHz range. It is shown that *colloidal systems* are excellent model systems for the realization of such phononic materials. Therefore, different structures and particle architectures are investigated by Brillouin light scattering, the inelastic scattering of light by phonons.

Both the mechanical properties of the individual colloidal particles, which manifest in their resonance vibrations (*eigenmodes*), as well as the acoustic propagation in colloidal structures have been investigated. The measurement of the eigenmodes allows for new insights into physical properties at the mesoscale, e.g., confinement effects, copolymer behavior, or the non-destructive determination of nanomechanical properties of core–shell particles, supporting the working groups aim to achieve a deeper understanding of 'soft mechanics' at small length scales. Another novel contribution assigned to this thesis is the first experimental realization of a phononic band gap arising from the interaction of these particle eigenmodes with the effective medium band (*hybridization gap*). This finding already gave new impulses to the whole field of phononics.

The thesis was performed between 03/2007 and 08/2009 at Max Planck Institute for Polymer Research, leading to several publications and presentations in international conferences, and was honored *summa cum laude* by the University of Mainz.

Mainz, March 2010 Prof. Dr. H.-J. Butt

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When reading this thesis, it becomes clear that nearly all presented results are based on diverse cooperations, since the success of my studies was up to the continuous supply with all kinds of high quality samples. The most fruitful and longest lasting of these cooperations was with Dr. Markus Retsch and Dr. Uli Jonas. I really enjoyed our work together, since both of them came up with a great deal of improvements and completely new ideas. Markus was the best conceivable ‘colloid cook’, who always delivered requested samples or realized just discussed ideas incredibly shortly and with impressive quality. Beyond science, he became a good friend.

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And finally, I want to express my deepest thankfulness to the woman I love, who gave me so much joy and happiness in the last years. Danke!

Mainz Tim Still

Contents

Abbreviations

2D	Two-dimensional
3D	Three-dimensional
α	Angle incident laser/sample
α_η	Mark–Houwink parameter
$\beta_{(T,S)}$	(Isothermal, adiabatic) compressibility
ϵ	Dielectric constant
ϵ	Extinction coefficient
ϕ	Glancing angle
φ, ψ, χ	Scalar functions
Γ	Central point of *fcc* BZ
η	Viscosity
λ	Wave length
λ	Lamé coefficient
Λ	Phonon periodicity
μ	Lamé coefficient
v	Velocity of light in vacuum
θ	Scattering angle
ϱ	Mass density
σ	Poisson's ratio
σ	Scattering cross section
$\hat{\sigma}$	Normalized scattering cross section
σ_{ik}	Stress tensor
τ	Correlation time
ζ	Tandem FP angle
ω	Angular frequency
A	Free energy
A	Area under the curve
A	Absorbance
$A_{lml'm'}$	Structure constants
BLS	Brillouin light scattering
*n*BA	*n*-Butyl acrylate

BG	Bragg gap
c_F	Coefficient of finesse
$c_{l/t/\mathrm{eff}}$	(Longitudinal/transverse/effective) sound velocity
$C_{p/T}$	Specific heat (at constant p/T)
C_{ik}	Components of the stiffness matrix
CCD	Charge-coupled device
d	Diameter
$d_{1/2}$	FP mirror distances
D	Diffusion coefficient
DOS	Density of states
DSC	Differential scanning calorimetry
DTA	Differential thermo analysis
DVB	Divenyl benzene
E	Young's modulus
$\boldsymbol{E}$	Electric field
E_0	Field amplitude
EMT	Effective medium theory
f	Frequency
F	Finesse
$\boldsymbol{F}$	Force
$f_{lm}(r, \theta, \phi)$	Solution of the scalar Helmholtz equation
fcc	Face centered cubic
FP	Fabry–Pérot interferometer
FSR	Free spectral range
G	Green's function
$\boldsymbol{G}$	Reciprocal space vector
$G(q, \tau)$	Time–correlation function
$g^2(q, \tau)$	Second order autocorrelation
GPC	Gel permeation chromatography
h, $\hbar$	Planck quantum ($/2\pi$)
hcp	Hexagonal close packing
HG	Hybridization gap
I	(Scattering) intensity
$\boldsymbol{I}$	Unit tensor
IMC	Indomethacin
k_B	Boltzmann's constant
KPS	Potassium persulfate
K	Gordon–Taylor parameter
K	Bulk modulus
K_η	Mark–Houwink parameter
$\boldsymbol{k}_{(i/sc)}$	(Incident/scattered) Wave vector
l	Longitudinal
L	Distinct point in reciprocal *fcc* lattice
L	Shear modulus
$\boldsymbol{l}, \boldsymbol{m}, \boldsymbol{n}$	Three independent vectors

LMS	Layer multiple scattering method
M	Distinct point in reciprocal *fcc* lattice
MMA	Methyl methacrylate
MPIP	Max Planck Institute for Polymer Research
MS	Multiple scattering method
m	Mass
m_e	Electron mass
M_n	Number averaged molecular weight
M_w	Weight averaged molecular weight
n	Refractive index
$\boldsymbol{n}_i$	Unit vector
NaPSS	Sodium sulfonated polystyrene
Nd:YAG	Neodym doped yttrium aluminium garnet (laser)
OG	Ordinary glass
p	Pressure
p	Momentum
P*n*BA	Poly (*n*-butyl acrylate)
PCS	Photon correlation spectroscopy
PDI	Polydispersity
PS	Polystyrene
PW	Plane wave method
PMMA	Poly (methyl methacrylate)
$\boldsymbol{q}$	Scattering wave vector
q	Absolute value of $\boldsymbol{q}$
$\boldsymbol{q}_{\mathrm{para}}$	$\boldsymbol{q}$ Parallel to the sample plane
$\boldsymbol{q}_{\mathrm{perp}}$	$\boldsymbol{q}$ Perpendicular to the sample plane
Q	Heat
r	Radius
$\boldsymbol{r}$	Space vector
R	Reflectivity
R	Rigidity
$\boldsymbol{R}$	Position vector
R	Absolute value of $\boldsymbol{R}$
R_h	Hydrodynamic radius
$R_l(k, r)$	Spherical Bessel functions
$\boldsymbol{R}_n$	Bloch's vector
RS	Raman scattering
S	Entropy
SCC	Supercooled liquid
SEM	Scanning electron microscope
SG	Stable glass
$\boldsymbol{T}$	T-Matrix
t	Time
t	Transverse
T	Temperature