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Applications of NMR to Food and Model Systems in Process Engineering

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Preface

Nuclear Magnetic Resonance (NMR) (Bloch et al. 1946; Purcell et al. 1946) and Nuclear Magnetic Resonance Imaging (MRI) (Lauterbur 1973) have a reputation for being exotic, expensive, academic and not appropriate for industrial applications, especially in engineering sciences. The aim of this thesis is to demonstrate the potential of NMR techniques and in particular MRI in food technology and process engineering. NMR can be used in order to study the structure, to characterise the composition (e. g. local moisture or solid concentration) and to quantify diffusive and convective transport processes in disperse systems including porous solid materials. These data are often not, or only in reduced quality, achievable with other measuring techniques.

The expression "potential" has to be taken seriously, as many applications of NMR and especially of MRI to materials in food technology and process engineering are often feasibility studies (Hills 1998). This is no disadvantage, but a challenge to break new ground in science, development and practice. Besides the academic interest (a) to produce impressive images of the interior of optically opaque materials, (b) to characterise the micro-structure and (c) to visualise micro-processes during the production, transportation and storage of foods and non-food products, in short, to understand "was die Welt im Innersten zusammenhält", there are very substantial arguments for using NMR methods in engineering. Heat, mass and momentum transport in disperse systems play an important role in many natural and industrial processes (chapter 2). Relevant structural parameters (e. g. geometry, permeability, tortuosity) are necessary for their understanding and the modelling of the corresponding production processes. NMR provides the possibility to characterise the structure and, furthermore, to quantify the flow inside the sample. Thus, (a) appropriate models can be developed and checked. The corresponding material-parameters can be determined for the studied material/process combinations as a function of the time and the spatial coordinates. (b) A precise description of the system can be developed which is a prerequisite for a reliable process design, process observation, quality and process control. Thus time-intensive trial-and-error can be forgone.

Based on the knowledge of the involved phenomena, new products and apparatus with improved process conditions can be developed. Furthermore, the following economically important objectives might be obtained: reduced cost of development, reduced cost of production due to a better understanding of the inner structure, increased product quality and as a result of the above mentioned a reduced time for introducing new developments to the market (Kretschmer 1995).

In order to limit the extent of the present work the basic ideas of NMR and MRI are not treated. I have to refer to existing brilliant textbooks (e. g. Abragam 1961; Farrar and Becker 1971; Ernst et al. 1987; Callaghan 1991; Grant and Harris 1996; Kimmich 1997; Hills 1998, Blümich 2000). Regarding the inclination in engineering sciences to develop and use vivid imaginations it has to be emphasised that they are not available for all types of NMR parameters. Due to the quantum mechanical character of NMR effects this is, however, not surprising. The interpretation of the parameters determined with NMR and MRI, respectively, and theoretically based or experimentally verified correlations with macroscopic measuring quantities (e. g. viscosity, molecular mass) are discussed in chapter 2, 3 and 5.

I, therefore, want to summarise numerous papers, which I have published during the last years, and want to put them into a common context.

Contents

List of Symbols

Latin	**Description**	**Units**
A	resolution	µm or mm/s
A_i	spatial resolution (per pixel/voxel) in x_i direction	mm
A_{F_i}	velocity resolution (velocity interval per pixel/voxel) in v_i direction	cm/s
a	activity	-
a	zero drift	a. u.
a	radius of spherical particles	m
a_W	activity	-
$\mathbf{B}_0$	magnetic field vector	Tesla
C	tracer concentration	- or kg/kg or kg/m^3
c	concentration	- or kg/kg or kg/m^3
D	diffusion coefficient	m^2/s
D_F	Fickian diffusion coefficient	m^2/s
D_S	self-diffusion coefficient	m^2/s
D_{Sf}	self-diffusion coefficient for free diffusion	m^2/s
D_{Sr}	self-diffusion coefficient for restricted diffusion	m^2/s
D_S^*	pseudo self-diffusion coefficients	m^2/s
d_i	fraction of spins in the state i	-
$\mathbf{E}$	electric field vector	V/m
$E_\Delta(\mathbf{q})$	spin-echo amplitude	m$^{9/4}$ or a. u.
F	moisture (water content of a gel, per dry mass)	kg/kg or kg/m^3
FOF	field of flow	m/s
FOF_i	field of flow in v_i direction	m/s
FOV	field of view	mm
FOV_i	field of view in x_i direction	mm
$\mathbf{G}$	gradient of magnetic field vector, gradient amplitude	Tesla/m
g	acceleration of gravity	m/s^2
G´	storage modulus	Pa
G´´	loss modulus	Pa
h	characteristic length due to the extension of the surface-interaction	m

I	intensity obtained by a specific NMR method	a. u.
I_g	spin-echo amplitude with gradient **G**	a. u.
I_0	spin-echo amplitude without gradient **G**	a. u.
k	Boltzmann constant	J/K
k_e	exchange rate	s^{-1}
m_{Wnw}	mass of non-washable water or serum	kg
m_W	total mass of water	kg
m_S	dry mass	kg
N_{F_i}	number of pixels (matrix size) in v_i direction	-
N, N_{x_i}	number of pixels (matrix size) in x_i direction	-
p	pressure	Pa
p_r	m_{Wnw}/m_W, averaged over all phases	-
$\overline{P}_S$	average propagator	$m^{-3/4}$
$\mathbf{q}$	wave vector	m^{-1}
$\mathbf{R}$	dynamic displacement vector	m
$\mathbf{r}$	position vector at $t = 0$	m
$\mathbf{r}'$	position vector at $t > 0$	m
r_p	hydraulic pore radius with $r_p = 2V/S$	m
r_c	critical radius	m
r_{ch}	characteristic length	m
S	surface area	m^2
$\mathcal{T}$	tortuosity	-
T	absolute temperature	K
T_1	T_1-relaxation (spin-lattice) or longitudinal relaxation time	ms
T_{1f}	free or bulk fluid	ms
T_{1s}	surface fluid with enhanced relaxation rate	ms
$T_{1\rho}$	$T_{1\rho}$-relaxation time (rotating frame relaxation time)	ms
T_2	T_2-relaxation (spin-spin) or transversal/transverse relaxation time	ms
$T_{2,i}$	T_2-relaxation time of spins in the state i	ms
T_{2m}	mean T_2-relaxation time	ms
T_{2obs}	observable T_2-relaxation time	ms
T_2^*	apparent (effective) T_2-relaxation time	ms
TE	echo time	ms
TR	recovery or repetition time	ms
t	time	s

t_0	time for cross-over from free to restricted diffusion	s
V	volume	m^3
v	volume	m^3
w	mass	kg
w	air velocity	m/s
WHC	water-holding capacity	kg/kg
WHC_{NMR}	water-holding capacity determined by the wash-out test	kg/kg
v_i	velocity in i-direction	m/s
X	ratio of diffusing substance and solid material	-
X_0	material-specific moisture	kg/kg
x_i	spatial variable in i-direction (i = 1 - 3)	m
Y_∞	air humidity	kg/m^3

Greek	**Description**	**Units**
β	parameter depending on fluid-solid interactions at the wall	m/s
γ	gyromagnetic ratio	s^{-1} Tesla^{-1}
Δ	time between gradient pulses **G**	ms
δ	gradient-pulse duration (of the gradient **G**)	ms
ε'	real part of the electrical permittivity	-
ε''	imaginary part of the electrical permittivity	-
θ	effective dimensionality	-
ϑ_∞	air temperature	K
η	dynamic viscosity	Pa s
η_0	zero-shear-rate viscosity	Pa s
η_∞	viscosity at high shear rates	Pa s
κ	shear rate	s^{-1}
ϕ	porosity	-
ρ	spin density	m^{-3}
ρ_1	relaxivity	m/s
τ_b	mean residence time in the "bound" state	ms

Abbreviation	**Description**
Al_2O_3	aluminium oxide
a. u.	arbitrary units
b	bound, immobilised

BSA	bovine serum albumin
c. f. u. or cfu	colony forming unit
^{13}C	carbon
Ca	calcium
CPMG	Carr Purcell Meiboom Gill sequence
^{133}Cs	caesium
CSI	chemical shift imaging
CO_2	carbon dioxide
CP-MAS	solid state cross polarization magic angle spinning
1D	one-dimensional
2D	two-dimensional
3D	three-dimensional
Da	Dalton
D_2O	deuterium oxide, heavy water
DSC	Differential Scanning Calorimetry
ECG	electrocardiography
ENMR	electrophoretic NMR
EPI	echo planar imaging
f	free
f	fraction of the fluid in contact with the solid
^{19}F	fluorine
FLASH	fast low-angle shot
^{1}H	hydrogen
HCl	hydrochloric acid
HDPE	high density polyethylene
HPLC	high pressure (performance) liquid chromatography
im	immobilised
K	potassium
LDPE	low density polyethylene
LR-NMR	Low Resolution NMR
M	mechandise
MAS	magic angle spinning
MRI	Magnetic Resonance Imaging
^{15}N	nitrogen
^{23}Na	sodium
NMR	Nuclear Magnetic Resonance

O_2	oxygen
OPP	oriented polypropylene
o/w	oil in water
P	yoghurt of pasteurised, homogenised milk
^{31}P	phosphorus
PC	yoghurt of pasteurised, homogenised milk with κ-carrageenan
PC	polycarbonate
PDMS	polydimethylsiloxane
PE	polyethylene
PEO	polyethylene oxide
PET	polyethylene terephthalate
PFG	pulsed field gradient
PGSE	pulsed field gradient spin-echo
PGSTE	pulsed field gradient stimulated echo
PMMA	polymethyl-methacrylate
PP	polypropylene
PS	polystyrene
PSMS	polydimethylsiloxane
PTFE	polytetrafluoroethylene
R	yoghurt of raw native milk
RARE	rapid acquisition with relaxation enhancement
RC	yoghurt of raw native milk with κ-carrageenan
^{87}Rb	rubidium
SEM	Scanning Electron Microscopy
SFC	solid fat content
SiO_2	silicon dioxide
^{29}Si	silicon
STRAFI	stray field imaging
TiO_2	titanium oxide
VR	vulcanised rubber
w/o	water in oil
^{129}Xe	xenon

Chapter 1

Summary

The overall objective of the present work (chapter 2.3) is to elucidate the possibilities to monitor and quantify transport phenomena and to characterise the structure of heterogeneous disperse media, which are non-matched and thus inaccessible to many optical techniques. MRI does not provide the spatial resolutions of other microscopic techniques like atomic force microscopy, electron microscopy (few nanometres) or even light microscopy (few micrometres) (Hills 1995). It offers, however, the possibility to perform measurements non-invasively and non-destructively in order to study the structure or to trace structural changes or transport processes inside the sample without preparations or unpredictable modifications caused by the measurement. Thus it is not only possible to detect and quantify the static structure, but also to monitor dynamic structural changes and processes during production, storage, transportation and even consumption of food-products with temporal, spatial and chemical resolution (multidimensional). NMR enables, therefore, repetitive testing of dynamic processes including enzymic and non-enzymic chemical reactions (Webb and Hall 1990). Samples may be studied several times under identical or changed conditions, which is a great advantage compared to other imaging preparative methods like optical or electron microscopy-methods.

Another advantage of MRI is the possibility to determine concentration distributions of a certain substance by material-specific excitation in sections or in the complete measuring volume in 1D, 2D or 3D experiments, dependent on the problem concerned. Thus materials cannot be studied only at their surfaces (partly created or modified by the preparation), but also in their interior. In contrast to X-ray tomography, NMR allows non-destructive imaging with various possibilities of contrast which can, furthermore, be combined (e. g. Morris 1986; Blümich and Kuhn 1992; Blümich et al. 1998; Gladden 2003; Mantle and Sederman 2003). The local concentrations of the observable nuclides (e. g. ^{1}H, ^{19}F), relaxation times like T_1, T_2 and $T_{1\rho}$ and the resonance frequencies (chemical shift) are available as measuring quantities and contrast giving parameters. Diffusion coefficients, also for multi-component diffusion (chapter 3.3), three-dimensional velocity-vectors (chapter 3.2), concentration distributions (chapter 3.1) and in some cases, partly by the addition of suitable tracers, temperature fields can also be determined (chapter 2.2). In combination with spectroscopic methods mass transport processes during chemical reactions are accessible.

NMR spectroscopic methods (chapter 3.4) enable the following to be obtained (a) molecular/microscopic properties of samples like the molecular mass (Götz et al. 2001a) and (b) macroscopic properties like the viscosity (Götz et al. 2001a, 2003c) or permeability (Watson and Chang 1997). The quantities can be determined volumetrically averaged or, in some cases, even spatially resolved. With the help of theoretical or empirical correlations or calibrations (Hills 1995) data can be derived to optimise production apparatus, processes and storing conditions of food and non-food products.

Besides academic interests a strong motivation for the development and application of tomographic methods arises from technical problems. The design of apparatus and processes are based on various models and simulations which generally include thermodynamics, reaction kinetics and rheology (Ronson 2002). Due to the complexity of many natural and industrial processes the corresponding models, for example computational fluid dynamics models for simulating realistic processes (Harding et al. 1997; Rombach et al. 1998; Sousa et al. 1999), need to be validated by comparison with experimental data in order to verify them and/or quantify the accuracy of their predictions. MRI allows in many cases the evaluation of mathematical-physical theories, the testing or development of constitutive equations or boundary and initial conditions. Existing MRI results, which will be presented in the present work, reveal that a professional design of products, processes and apparatus requires a reliable modelling of physical, chemical or biological phenomena and tests with the interesting materials instead of relying on eventually insufficient, oversimplistic models (descriptive, methodological or pertaining to a special apparatus) (Schrader et al. 1992). NMR is applicable under real and "difficult" industrial conditions. The measuring temperature can be varied up to 2500 °C (Müller 2002) and pressures from vacuum up to several hundreds of MPa (Zahl et al. 1994; Kärger and Fleischer 1994; Ballard and Jonas 1997) have been realised.

In combination with fast automated evaluation-procedures NMR and MRI measurements offer the possibility for an effective on-line quality and process control (e. g. chapter 3.4, Götz et al. 2003a, 2004a, b). The use of conventional NMR apparatus and the application of NMR techniques is well established in medicine, chemistry and physics, but not in engineering. Therefore, in many cases established NMR sequences and methods have to be identified or developed for, transferred or adapted to problems in engineering sciences.

The following topics have proved to be promising applications of NMR in food technology and process engineering:

- structure and structural changes of disperse media (chapter 3.1),
- convective transport processes (chapter 3.2),
- diffusive transport processes (chapter 3.3),
- spectroscopic material characterisation (chapter 3.4).

Chapter 2

Introduction

2.1 Motivation

In this chapter an example is given in order to illustrate how NMR and MRI are integrated into traditional material testing and how data relevant for the processing of disperse media can be derived. The design of filled polymers was chosen to demonstrate how to bridge the gap between the design of a tool-component and the design or selection of an appropriate raw material.

The material-class of filled polymers became recently more significant in comparison to pure polymers, polymer blends and copolymers in industry. Fillers are used for economic and technical reasons (up to 70 vol.%), for example to modify purposefully the process or the product properties (mechanical, chemical, thermal, magnetic or electrical). On a microscopic scale, polymeric pastes are multi-phase systems consisting of finely dispersed solid particles (filler), the polymer as fluid phase (capable of forming drops) and eventually gas inclusions or hollows. The fraction of hollows in industrial pastes is in many cases approx. zero. Exceptions are foams where gas can be considered as filler.

Besides the deformation of the polymer matrix further deformation mechanisms arise due to possible boundary layers between the surface of the solid fillers and the matrix (Hübner 1994). Important is the matrix-filler detachment which varies between ideal sticking and partial or complete detachment. Time- and deformation-dependent deformation behaviour are presumably caused by processes in the boundary layer between solid-surface and matrix. As materials with volume fractions of the disperse phase higher than 5 vol.% (Roco 1992) are usually opaque, detachment processes can only be detected with conventional material testing by a macroscopic increase of the total volume and the related decrease of the Poisson's ratio.

Problem

Up to now a great number of experiments have been necessary in order to design a filled polymer or a foam with defined properties in the hardened state. The reason is that it has not been possible yet to correlate the macroscopic flow- (fluid state) and deformation-behaviour (hardened state) with the micro-mechanical processes during the production (e. g. extrusion) and the deformation in the hardened state satisfactorily:

- Assuming macroscopic constitutive laws for materials in the hardened state the existing material testing enables one to derive the corresponding material parameters or material functions. Thus, a design of components is principally possible. Modifications (recipe, pretreatment) can only be evaluated after materials have been hardened.
- Micro-models, like elementary-cell model with matrix-sticking/detachment (for filled polymers) (Hübner et al. 1999; Gusev 2001) or rod model (for foams) allow only qualitative information on the influence of the micro-structure and micro-processes on the macroscopic material behaviour.

Many macroscopic properties of disperse systems cannot be predicted a priori from atomic or microscopic principles for multi-particle systems. On the contrary, it is necessary to derive physically established, phenomenological constitutive laws for industrial applications. This requires the knowledge of the micro-structure in the disperse system and the flow-induced micro-processes (e. g. demixing, matrix filler detachment, wall slip, wall zones, cross-linking and chain cleavage) which are accessible by means of NMR. Therefore, the conventional material testing will be expanded by NMR in order to build a bridge between the micro- and macro-mechanics (in the fluid and hardened state, respectively). A deeper understanding of the micro-structure and the involved micro-processes can stimulate the creation of practicable, but, nevertheless, intelligent micro-models. The main objective is to derive relevant information concerning the deformation behaviour in the hardened state from the flow-behaviour of the system in the previous fluid state and to modify the flow-behaviour by appropriate additives, production devices and process parameters during the production.

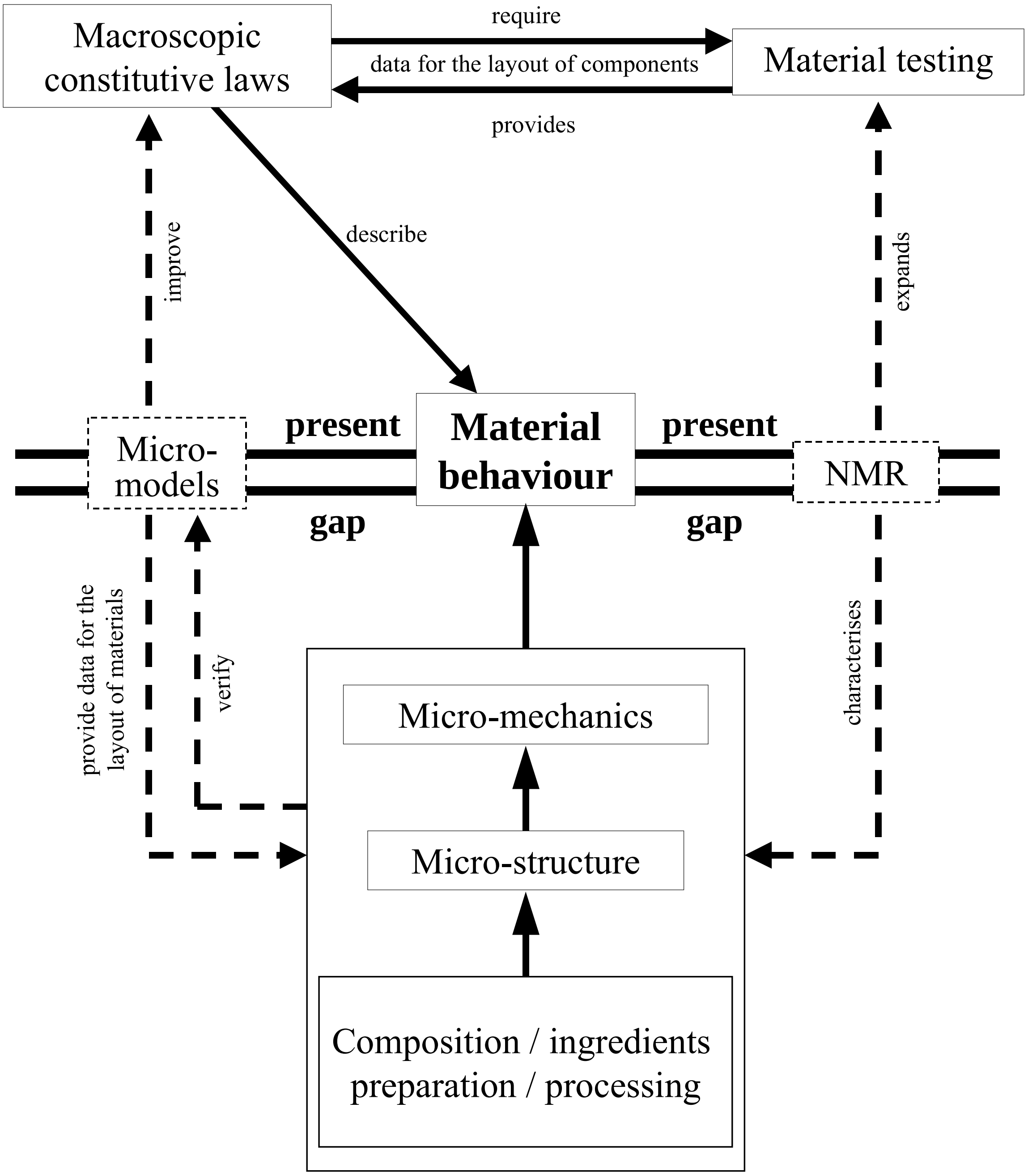


Fig. 2.1.1. Problem and solution.

The methodology of combining traditional material testing and NMR, or more generally spoken of non-destructive and non-invasive spectroscopic and tomographic measuring methods, is illustrated in Fig. 2.1.1. The above presented concept of the correlation between NMR and macroscopic material behaviour or parameters can easily be transferred to other applications. Further examples are given in chapter 5.

2.2 Disperse Systems

Disperse systems are mixtures of substances on a non-molecular level (Löffler and Raasch 1991). In many cases at least one component is disperse which means in the shape of solid-particles, drops or gas bubbles. Examples are suspensions, emulsions, packings and porous or inhomogeneous solid-systems. Mass transport processes play an important role in many natural and industrial applications. Examples are (Schubert 1982):

- biology (transport of water and sap in plants),
- drying technique,
- solid-fluid separation (de-watering of packings), filtration,
- agglomeration,
- fluidised bed,
- dispersing (dissolving of instant agglomerates),
- impregnation (clothing),
- diffusion-, migration- and permeation-processes in polymers,
- catalysis technique,
- soil mechanics (wetting and de-wetting of soils),
- oil production (multi-phase system consisting of solid-matrix, oil, water and gas),
- building materials technology,
- ground water and geological flows.

Many model systems have been developed in order to describe the transport processes in porous materials. It is problematic to quantify structural properties of the solid-matrix relevant for the transport processes in the pore system (Pel 1995; Baldwin et al. 1996; Glantz 1997; Valckenborg 2001). Serious difficulties arise when observing processes in the interior of a packing with traditional measuring techniques:

1 Optical methods require refraction-index adapted transparent model systems combined with great experimental expenditure (Rottschäfer 1997; Giese et al. 1998; Winterberg 2000). Due to temperature-dependent refraction-indices even model systems can usually only be studied near the walls.

2 Experiments with systems containing microscopically small particles cannot be substituted by model packed beds with bigger particle dimensions, because for bigger particle sizes the effect of the gravity dominates the effect of surface tension.

3 In model systems with smaller outer dimensions (decreased macroscopic scale) boundary effects cannot be neglected.

To summarise the findings, it is important to perform experiments on real systems (with regard to dimensions and materials) and under real process conditions (with regard to flow rate and temperature).

A solution for many problems relevant in process engineering is NMR (e. g. Morris 1986; Callaghan 1991; Gladden 1994; Gladden et al. 1995; Günther 1995; Gladden and Alexander 1996; Blümler and Blümich 1996; Grant and Harris 1996; Blümler and Blümich 1997; Kimmich 1997; Blümler et al. 1997; Blümich and Blümler 1998; Hills 1998; Manz et al. 1999b;

Blümich 2000; Gladden 2003; Mantle and Sederman 2003). NMR provides a non-destructive, non-invasive and non-adulterating measuring technique with various applications which allows measurements with resolution in energy, time and space, independent of the optical properties of the studied materials. In chemistry and biology it is used to elucidate the structure and the dynamics of complex compounds. In physics NMR is applied for the detection of solid-state structures and the study of molecular dynamics. In medical science NMR allows a non-destructive imaging with many possibilities of contrast (e. g. Morris 1986; Blümich and Kuhn 1992; Blümich et al. 1998). The only restriction for the selection of the samples and the materials of the devices is that they cannot be ferromagnetic or electrically conducting and may contain only small amounts of paramagnetic substances.

The local concentrations of the observable nuclides [e. g. ^{1}H, ^{19}F (Ilg et al. 1990)], the relaxation times like T_1, T_2 and $T_{1\rho}$ and the resonance frequencies (chemical shift) are available as measuring quantities and contrast giving parameters. Selective excitation according to the chemical shift allows for example to differentiate water and oil. Diffusion coefficients (even for multi-component diffusion), three-dimensional velocity-vectors and concentration distributions and in some cases, partly by the addition of suitable tracers, also temperature fields can be determined. If the excitation frequency is equal to the resonance frequency of defined molecule-group (in combination with a small half-width), molecular-specific flow processes, both diffusive and convective, can be traced (Chemical Shift Imaging: CSI). In MRI terminology experiments to measure velocity distributions in flowing systems are usually called flow experiments (Callaghan 1991). In contrast to most other techniques even the flow inside complex structures and disperse or opaque materials can be analysed (chapter 3.2 and 3.3).

To summarise the findings, NMR is applicable to disordered, optically opaque materials and can be used for in-situ characterisation of heterogeneous, porous or, generally, disperse media. As NMR is a highly selective and non-invasive technique suitable for the study of materials in different phases or generally states of aggregation, there is a wide field of applications for NMR.

2.3 Objectives

Within the scope of this habilitation thesis the potential of NMR techniques and especially MRI in food technology and process engineering will be demonstrated. Using NMR techniques it is possible to study the structure and the composition (e. g. local moisture or solid concentration) and to detect and quantify diffusive and convective transport processes in disperse systems (food and model systems) including porous solid materials. The main objectives of the thesis are

(1) to illustrate the application of NMR techniques, which are either already established in physics, chemistry and medicine or especially developed, to problems in engineering (Gladden and Alexander 1996; Gibbs and Hall 1996; Tallarek et al. 1999; Gladden 2003; Mantle and Sederman 2003; Götz et al. (2002a-f, 2004d), Hinrichs et al. 2003),

(2) to determine structural parameters like geometry (Götz et al. 2002e), permeability (Friedmann 1999), tortuosity (e. g. Heil 1999) which are necessary for the understanding and modelling of flow processes in disperse media,

(3) to correlate the NMR measuring quantities theoretically or empirically with relevant macroscopic parameters (e. g. viscosity (Bloembergen et al. 1947, 1948; Roessler 1990a, b; Götz et al. (2000, 2001a, 2003b), molecular mass (Götz et al. 2001a), denaturation fraction (Götz et al. 2004b), solid concentration in filtration or extrusion (Götz et al. 2002c), moisture and water-holding capacity (Götz et al. 2001b) or reaction orders and rate constants (Götz et al. 2004b)).

The following options result from the objectives mentioned above:

(a) Appropriate models including boundary and initial conditions can be developed and tested and, furthermore, the corresponding material-parameters can be determined for the studied material/process combinations with spatial and temporal resolution (Götz et al. 2000a, 2001d).

(b) A precise description of the system with the help of appropriate models is a prerequisite for a reliable process design, quality and process control. Based on the knowledge of the involved and thus observable phenomena new products and apparatus with improved process conditions can be developed (Götz et al. 2002c, 2003c, d).

(c) If reliable correlations between NMR quantities and macroscopic parameters are established or if the sufficiently selective spectra are detected, non-destructive on-line measurements (as process and quality control) to characterise quantitatively and directly the reaction kinetics and the equilibrium states of chemical/physical reactions (Hahnenstein et al. 1995) may be performed. Examples are thermal protein denaturation (Götz et al. 2004b), synthesis of silicone oils (Götz et al. 2001a) or dewatering of bulk solids (Korger et al. 1994). Thus, a direct reaction monitoring with continuous-flow NMR (Dachtler et al. 2001; Nordon et al. 2001) can be realised.

Therefore, I want to summarise numerous papers, which were published during the last years, and want to put them into a common context.

Chapter 3

Applications of NMR in Engineering

As previously mentioned the following topics have proved to be promising applications of NMR in food technology and process engineering:

3.1 structure and structural changes of disperse media,
3.2 convective transport processes,
3.3 diffusive transport processes,
3.4 spectroscopic material characterisation.

Both foods and model systems which are relevant in process engineering are taken into consideration in the following chapters (3.1) to (3.4). Model systems are often chosen with regard to special features which enable or simplify the interpretation of NMR experiments. The study of model systems is, nevertheless, helpful and in many cases inevitable. Foods have to be built up step by step from simple ingredients to complex real systems in order (a) to study effects of single constituents on relevant phenomena and (b) to quantify possible interactions between the present constituents.

The pore structure of solid matrices (in general: the spatial distribution of the volume concentrations of the constituents) and the composition have obviously a strong impact on the convective and diffusive transport phenomena. In order to model or simulate numerically transport processes in disperse media geometrical data of the matrix as detailed as possible are necessary for the discretisation of the region in question (1D, 2D or 3D) and the generation of the required numerical grids. Therefore, on the one hand the analysis of the pore structure (chapter 3.1) is an important prerequisite for a better understanding of transport processes in disperse materials (chapter 3.2-3). On the other hand it has become obvious that the knowledge of velocity distributions (chapter 3.2) and time-dependent diffusion-coefficients (chapter 3.3) provide information concerning the pore-structure, like for example characteristic pore-radii and tortuosity (Glantz 1997; Heil 1999; Frosch et al. 2000). The possibilities to derive information with regard to molecular/microscopic properties like molecular mass (Götz et al. 2001a) or gelation/denaturation fraction (Götz et al. 2004b) and macroscopic properties like the structure and water-holding capacity (Götz et al. 2002d, f), the flow-behaviour (Bloembergen et al. 1947, 1948; Götz et al. 2000b, 2001a, 2003b), the permeability (Friedmann 1999) and other material-specific parameters relevant for disperse systems obtained by means of MRI (chapter 3.1-3) and NMR spectroscopy (chapter 3.4) are discussed in chapter 3. Several strategies have been developed in order to map the temperature distribution in three dimensions. Dynamic processes can be tracked by all four topics (chapter 3.1-4).

3.1 Structure and Structural Changes of Disperse Media

The applications of NMR in this chapter are focussed to MRI with relevant disperse systems in order (a) to analyse their structure and composition and (b) to size up the potential of NMR techniques to detect structural modifications caused by appropriate processes or process conditions. Most initial and final food or non-food products are disperse multi-phase systems, like pasta, dairy and chocolate products or suspensions in general (e. g. highly filled polymers), foams, emulsions, porous solid-structures, dry and wet bulk solids. Aspects of the material properties essential for both consumer and producer are the structure on different length-scales and the flow behaviour. The flow behaviour is important for the design of process unit operations and for the sensorial behaviour of the final food product (Windhab 2002). The structure is correlated with various macroscopic properties like the storage-/ageing-behaviour (shelf-life: microbiological stability), the tendency to phase-separation [e. g. syneresis, sedimentation: physical stability (Lelievre and Creamer 1978; Gerhards 1994)], the firmness/crispness, the deformation/flow behaviour (sensorial behaviour) and the filtration-behaviour. Correlations between the evolution of the shear stress and the porosity, agglomeration processes and the type of flow can be established for foods, like starch solutions (Dolan and Steffe 1990), wheat dough-types (Schluentz et al. 2000) and ceramic pastes (Götz et al. 2001c, 2002f) in shear or extensional flows. It is, therefore, plausible to assume that the correlation between the structure and the rheology is generally valid. This means that the structure determines the stress tensor and its temporal evolution for a certain process. The deformation-history on the other hand, for example during the preparation, defines the structure of the material as illustrated in Fig. 2.1.1.

In MRI-experiments (chapter 3.1) including flow (chapter 3.2) and diffusion experiments (chapter 3.3) (if spatially resolved) the sample is divided into a grid (matrix) of three-dimensional voxels (volume element). The size of each voxel is given by the chosen, so-called field of view (FOV), which means by the dimensions of the measuring volume in the magnet, and the matrix size N (number of voxels according to the relevant spatial dimensions). Generally FOV (Field of View) is the detectable spatial region (to be exact it is the measuring size of the image), and FOF (Field of Flow) the analogous in the velocity range. The three-dimensional spatial resolution A is, for the spatial coordinates x_i, A_i (spatial extension per pixel or voxel)

$$A_i = FOV_i/N_{x_i} \qquad (3.1.1)$$

FOV_i Field of View in x_i direction
N_{x_i} number of pixels (matrix size) in x_i direction

and for the velocity directions A_{F_i} (velocity interval per pixel or voxel)

$$A_{F_i} = FOF_i/N_{F_i} \qquad (3.1.2)$$

FOF_i Field of Flow in v_i direction
N_{F_i} number of pixels (matrix size) in v_i direction

$(FOF)_z$ is the FOF in z direction, $(FOF)_{rec}$ the FOF perpendicular to the main flow direction, $(FOV)_r$ the FOV in r direction and $(FOV)_z$ the FOV in z direction. N_r means the number of pixels perpendicular to the z direction, N_z the number of pixels in z direction and N_F the number of pixels for the presentation of the velocity. A $(FOV)_z$ together with N_z, number of pixels in z direction, means that the coordinate z is screened from 0 to $(FOV)_z$. The corresponding resolution is $A_z = (FOV)_z/N_z$. Analogous means a $(FOF)_z$ with N_F that the velocities can be detected from $-(FOF)_z/2$ to $(FOF)_z/2$ with a resolution of $(FOF)_z/N_F$. In Fig. 3.1.1 the relation between the Field of View FOV, the number of pixels N and the realised spatial resolution A is illustrated. An analogous relation holds for the Field of Flow FOF, the number of pixels N_F and the realised spatial resolution A_F.

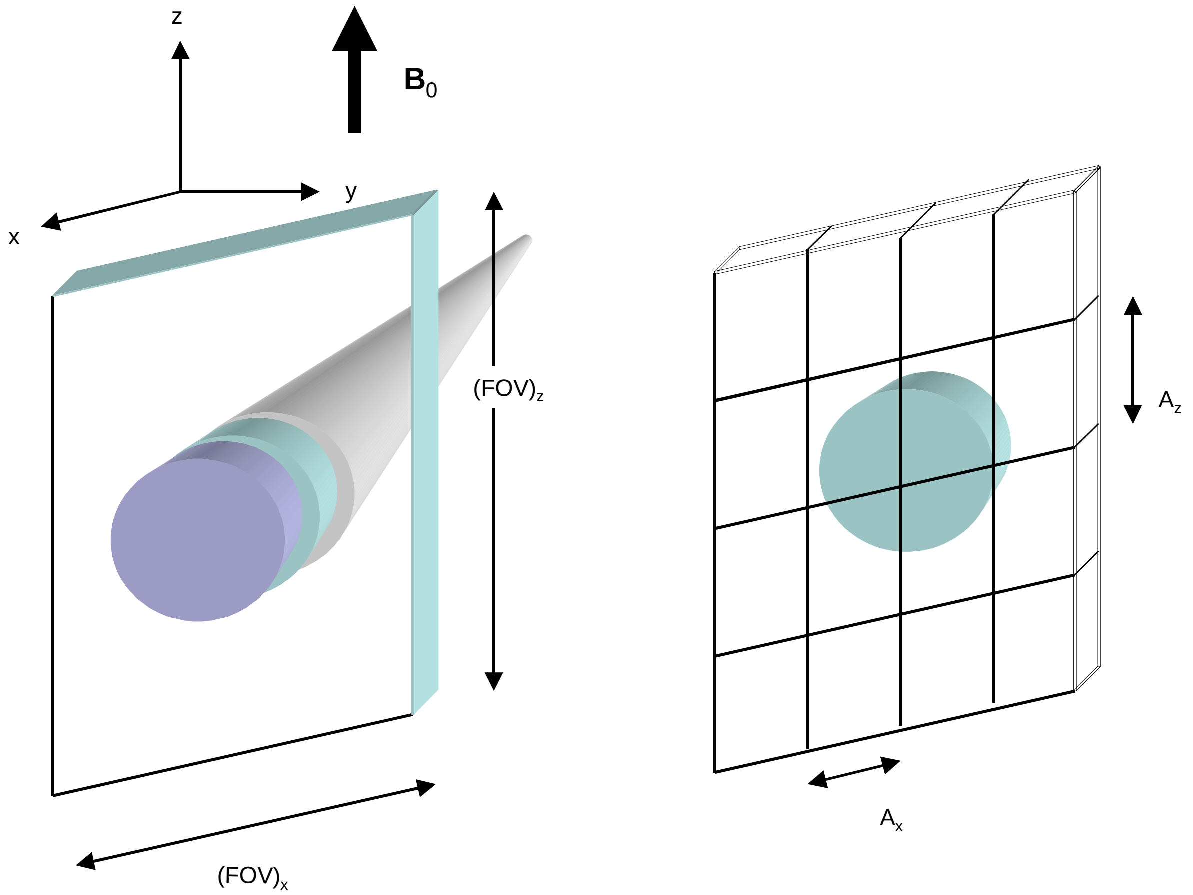


Fig. 3.1.1. Relation between the Field of View FOV, the number of pixels N and the realised spatial resolution A.

The local intensity I(**r**) of the MRI images shown below (e. g. Fig. 3.1.2) is due to the various possibilities of contrast techniques (e. g. Callaghan 1991) generally a complex function of the applied method. It depends on the sequence parameters (e. g. the echo time TE and the repetition time TR), the spin-density ρ, the material properties (e. g. T_1-, $T_{1\rho}$-, T_2-, T_2^*-relaxation times, chemical shift, self-diffusion coefficient D) and the velocity field **v**(**r**). Using gradient- and spin echoes the local intensity I(**r**) is, under several assumptions (Callaghan 1991), given by

$$I \sim f(\rho, T_1/TR, T_2/TE, T_2^*/TE, D, \mathbf{v}, \ldots) \qquad (3.1.3)$$

f	function dependent on the applied measuring sequence
ρ	spin density
T_1	T_1-relaxation (spin-lattice) or longitudinal relaxation time
T_2	T_2-relaxation (spin-spin) or transversal/transverse relaxation time
TE	echo time
TR	repetition time
T_2^*	apparent T_2-relaxation time

There are sequences available for the quantitative determination of specific material-parameters mentioned above. The local intensity of the MRI images shown below, for example, is, in good approximation, proportional to the local volume concentration of ^{1}H nuclei, that means proportional to the local ^{1}H concentration. Usually, dark stands for non-detectable material and the brighter the intensity, the higher is the local ^{1}H concentration. If one material-parameter is predominant and I(**r**) does not exclusively depend on this parameter, the sequence is considered, for example, as T_1- or T_2-weighted. Generally I(**r**), however, does not represent specific material-parameters. In many medical investigations, for example, the used sequences and the corresponding parameters are optimised with regard to maximal contrast inside the studied organs or tissues.

Possible applications of MRI in engineering are

(a) to determine the distribution of local moisture (generally: fluid phase) or of the solid concentration (for example in a suspension) in a sample or of products, in general, in apparatus containing one-component or multi-component systems,

(b) to analyse the structure of optically opaque, heterogeneous materials that means the differentiation between the present components in a heterogeneous sample. Examples are fruit and vegetables (Chen et al. 1989; Schrader et al. 1992; Hall et al. 1998), cheese (Rosenberg et al. 1991: ripening, microbial contamination), initial food materials (e. g. fruits, Fig. 3.1.2), final food products (pasta; chocolate products, Fig. 3.1.3-4; ham or meat products (Guiheneuf et al. 1997), bread or cake doughs (Götz et al. 2003a), cracker (Yan et al. 1996)), wood, bones (Oerther 2002), filter cakes, ceramics (Hayashi 1988, Götz 1994), building materials (Beyea et al. 1998; Pel 1995), sandstone (Merrill 1994; Bobroff 1995), catalyst pellets (Hollewand and Gladden 1993, 1994), rock (Guillot et al. 1989), porous silica (Behr et al. 1998), polymer foams (Fig. 3.1.5), and, in combination with (a) and (b),

(c) to detect and quantify spatially resolved structural changes or reactions caused for example by process unit operations, storage/ageing or transportation.

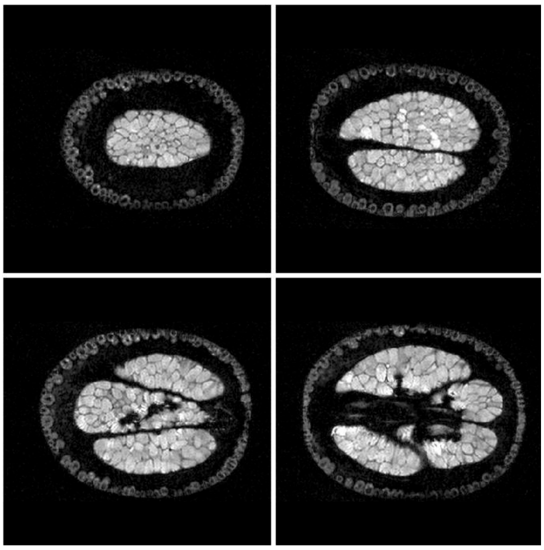


Fig. 3.1.2. MRI image of a cumquat (Groß and Lehmann 1998). Measuring sequence: Spin Echo 3D with the sequence-parameters: FOV = 30x15x15 mm; number of pixels N = 512x256x256; A = 59 µm/pixel; TE = 3.0 ms; TR = 200 ms; averages: 1, total measuring time: 3.6 h, 300 MHz. Fruit flesh in the centre is surrounded by the peel. The subepidermal tissue in between cannot be visualised due to short T_2-relaxation times. Spherical structures visible in the peel typically contain flavour substances.

The determination of the local concentration of detectable spins (a) and the analysis of the structure (b) are often different aspects of the same study. The examples in the following are assigned to (a) or (b) according to the main purpose of the experiments.

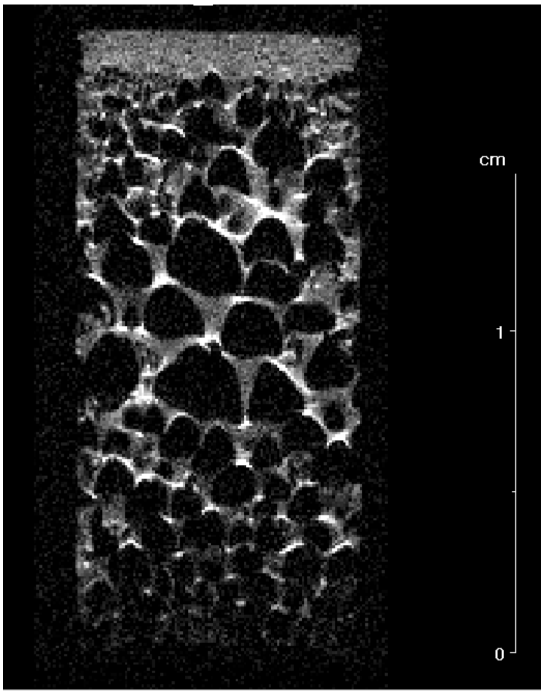


Fig. 3.1.3. MRI image of a aerated countline (Götz et al. 1998). Measuring sequence: Spin Echo 3D with the sequence-parameters: FOV = 22x11x11 mm; number of pixels N = 256x128x128; A = 86 µm/pixel; TE = 3.3 ms; TR = 300 ms; averages: 8, total measuring time: 11 h, 300 MHz

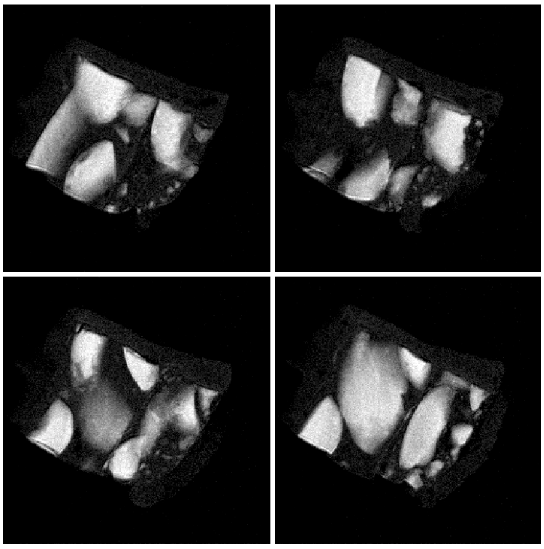


Fig. 3.1.4. MRI image of a chocolate bar (Fang et al. 2000). Measuring sequence: MSME (Multi Slice Multi-Echo) with the sequence-parameters: FOV = 25x25x30 mm; number of pixels N = 256x256x16; A = 98·98 µm/pixel in plane and 1875 µm slice thickness; TE = 3.6 ms; TR = 1002 ms; averages: 16, total measuring time: 11 h 39 min, 200 MHz

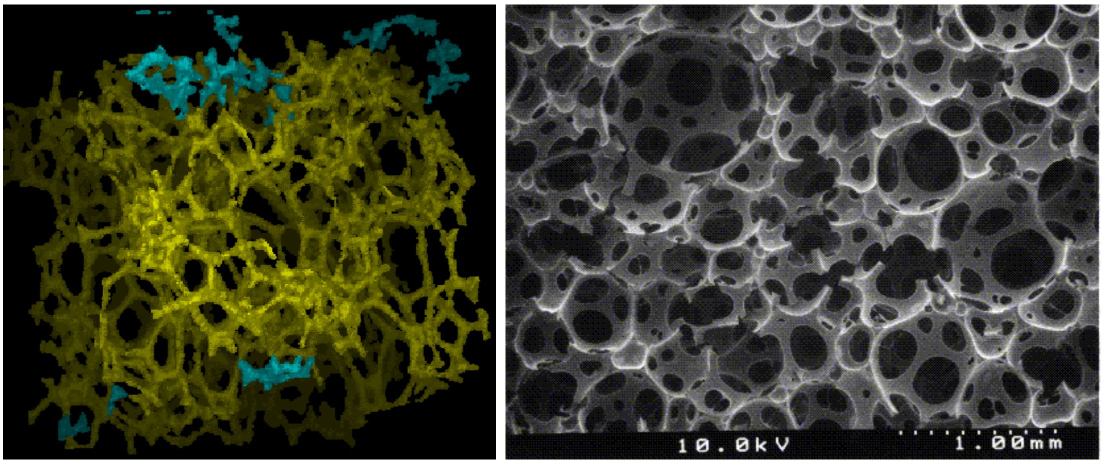


Fig. 3.1.5. Polyethylene (PE) foam. Left: MRI image (Groß and Lehmann 1998). The blue marked regions are not connected with the yellow part. Measuring sequence: Spin Echo 3D with the sequence-parameters: FOV =10x5x5 mm; number of pixels N = 256x128x128; A = 39 µm/pixel; TE = 3.8 ms; TR = 300 ms; averages: 8, total measuring time: 11 h, 300 MHz. Right: Scanning Electron Microscopy (Völkel 1998). 10 kV

Ad (a) **Distribution of Concentration**. The structure, the quality and the sensorial behaviour of many foods depend on the state and distribution of food components like water, oil or hydrocolloids including proteins. The single components are often distinguished by chemical shift (CSI) or relaxation times weighted imaging. In CSI chemical shift data are added as a fourth dimension to the three spatial dimensions of imaging (Callaghan 1991). Thus NMR provides an approach to characterise the food structure, interactions between food components and possible induced structural changes. Winkler et al. (1991) and Duce et al. (1995) studied the local concentration of water and oil in a model-emulsion. CSI of cheese reveals that the fat distribution varies less than the water distribution (Ruan et al. 1998). McCarthy and Kauten (1990) quantified the water and fat concentrations in trout samples.

CSI enables, furthermore, the analysis of the pore-structure and the distribution of water and oil in rocks (Horsfield et al. 1990; Davies et al. 1994) and sandstones (Bobroff et al. 1995). Thus the evolution of the spreading of oil or other contaminants in ground water, soils or rocks can be monitored, processes to decontaminate the affected areas can be checked or measures to exploit oil can be evaluated.

Hydrocolloids are used for the production of many dairy products (e. g. jellied products, desserts and puddings, yoghurt, cocoa and ice-cream) in order to modify the textural properties of the product in a predetermined manner, for thickening, gelling or increasing the physical stability. It is possible to determine the local concentration of hydrocolloids in gels by a calibration relating the T_2-relaxation time to the concentration of the hydrocolloid (Potter al. 1993).

The comparison of extrudates with circular cross-section of ceramic masses in the green state shows that the moisture-distribution changes dramatically after adding cellulose (Götz 1994). The regions with the highest moisture are in ceramic masses without cellulose at the outer surface of the extrudates. After addition of cellulose the maximum of the moisture is in the middle of extrudates. It is commonly assumed that the compressive and tensile strength of the extruded material in the green state and after the drying/sintering process can be improved by increasing the homogeneity of the structure of the material after extrusion. MRI allows one to optimise the extrusion by variation of the composition and the pretreatment of the paste, the die-geometry and the process parameters. It is, furthermore, possible to detect cracks and other imperfections in the extrudates which often reduce the quality of the final product. By studying the processes in the interior of the extruder, including the die, the evolution of cracks can be observed.

Analogous experiments are imaginable in order to determine the local moisture content in extruded pasta like maccheroni for optimisation of the production processing. As shown by Götz (1994) the flow of pastes around an installed stick in the die leads to increased moisture-contents of volume elements which have passed the internal fittings. As dies used for the maccheroni-production possess installations, the moisture content in the extruded pasta is presumably not homogeneous. Depending on the local moisture the corresponding regions may tend towards spoilage.

Ad (b) **Analysis of the Structure**. There are principally two possibilities to study the pore-system of porous materials or, more generally, the structure of solid systems:

- direct imaging of the solid matrix, if the matrix material can be imaged,
- indirect imaging of the pore-system, when it is or after it has been saturated with a fluid which contains protons, thus revealing the inverse inner structure.

Direct Imaging. Fig. 3.1.5 shows images of a polyethylene foam obtained by MRI (Groß and Lehmann 1998) and by Scanning Electron Microscopy (SEM) (Völkel 1998). MRI provides a 3D representation of foams (Szayna and Völkel 1999; Szayna et al. 1999), whereas SEM is only capable of monitoring the structure at the surface of the sample. In order to study the interior of foams by means of SEM the sample has to be destroyed. MRI allows, furthermore, to image the foam again after or even during the deformation. Thus, the evolution of the pore-system, influenced by reversible and irreversible deformations and an eventual breaking of the polymer matrix (bars, cells), can be monitored during the treatment.

Direct imaging has been applied to aerated countlines (Fig. 3.1.3). A dense layer of chocolate is visible at the outer surface (at the top of Fig. 3.1.3). The diameters of the pores are not homogeneous. In the middle of the sample the pores are greater than those near the surface. The inhomogeneous pore-size distribution of the countline causes a spatial variation of the firmness and - in combination - of the sensorial behaviour. In Fig. 3.1.4 the MRI image of a chocolate bar is shown. Two zones can be differentiated: The inner zone where peanuts can clearly be distinguished from the surrounded chocolate matrix due to the mobile oil contained in the peanuts. The outer zone with pure chocolate which can hardly be detected due to a small signal/noise ratio. Miquel et al. (1998) found that nuts and fat fillings produce good contrast, whereas dried fruit and biscuit can hardly be observed due to their low signal intensities. MRI can, furthermore, be used to determine the local fat concentration and to identify spatially resolved the present polymorphic states of cocoa butter (Duce et al. 1990; Lipp and Anklam 1998). Thus it is possible to quantify the influence of thermal treatments on the composition of the obtained fat phases (conformations) and to detect water and fat migration during storing.

Guiheneuf et al. (1997) visualised the migration of liquid triacylglycerol in composite chocolate confectionary by MRI. Dependent on the storage temperature completely different concentration profiles evolve during storage. The higher the temperature, the higher is the total migration of liquified cocoa butter towards the surface, where a recrystallisation in the form of fat bloom can occur (Jana and Thakar 1993). Thus fat bloom can be detected, before the migrated butter components have recrystallised at the outer surface of the confectionary. MRI provides, therefore, a rapid test for the study of fat bloom and optimisation of the production process, the recipe and the storage conditions.

Rosenberg et al. (1994) and Duce et al. (1995) demonstrated the potential of MRI in studying dairy products during production and storage. Several types of cheese are imaged. Holes, cracks and seams of mould can be localised. It is, furthermore, possible to differentiate the local grade of ripening within the cheese.

Short relaxation times in solids cause, in many cases, problems for tomography with typical echo times longer than 1 ms. The signal decays after the excitement, before it can be detected. With the help of the so-called SPI (Single Point Imaging) a signal can already be recorded 50 μs after the excitation. That means at least some solids can be imaged which are inaccessible with other NMR methods. SPI is optimal for relaxation times between approx. 0.1 and 3 ms (Nauerth and Gewiese 1993a, b; Chudek and Hunter 2002; Oerther 2002). A great disadvantage of this sequence are the long measuring times, which are eventually several hours depending on the required spatial resolution.

Indirect Imaging. In contrast to materials which can be visualised directly (e. g. with SPI), a prerequisite for the application of the indirect method is that (a) all pores are or can be filled with the proton-containing fluid (Kose 1996) and (b) the pore-system is not changed due to the hydration, for example due to swelling. Isolated pores and the inner structure of the solid matrix cannot, however, be analysed. Examples for the indirect method, are glass beads or glass fibres in a polymer matrix (Götz et al. 2002a, b). Fillers are used in order to modify the properties of the polymer during the production and of the final product. Filled polymers are used for attenuation elements, seals, coatings, tubes, foams, extrudates and energetic materials. The local firmness and, therefore, the macroscopic firmness of the considered component depends on (i) the local filler concentration, (ii) the position and orientation of reinforcements consisting of fibres and tissues and (iii) gas inclusions. An inhomogeneous distribution of the solid particles might be caused by the extrusion and pumping process during the production (Götz 1994, 2002a, b, 2003d). In many cases single particles cannot be observed due to the limited spatial resolution, whereby isotropic spatial resolutions better than 10 μm are difficult to realise using existing MRI methods and hardware (Groß 2002).

It is, nevertheless, possible to detect agglomerates and matrix filler detachment by means of the local concentration of the solid particles. Especially NMR imaging, possibly in combination with spatially resolved spectroscopic techniques, offers new aspects of examining the ageing behaviour of polymeric systems (e. g. Kuhn et al. 1992; Knörgen et al. 1997). The key to the understanding of ageing processes induced by UV irradiation, heat, oxygen or chemical treatment (Blümich 2000; Götz et al. 2002a, b) is the detection and quantification of matrix filler detachment (e. g. local spin density), cross-link density [e. g. T_2 (Knörgen et al. 1997), $T_{1\rho}$ (Kuhn et al. 1992; Barth and Hafner 1997)] and chain cleavage or molecular mass (e. g. T_2). Defects in technical polymer products due to insufficient mixing or flow-induced phase-separation (inhomogeneous cross-link density), unintentional hollow spaces or wrong positioning of reinforcements cause inhomogeneous macroscopic properties concerning the mechanical, thermal or electrical behaviour. Ageing processes can produce heterogeneities in initially homogeneous samples. Sufficiently high temperatures (for thermoplastics) or incomplete hardening of the curing (for duroplasts) improve the signal-to-noise ratio due to increased mobilities of molecules or segments of molecules. Examples of MRI applications to polymers including the applied measuring sequences are given by Blümich and Blümler (1993, 1997), Weigand et al. (1994), Fülber (1996), Bovey and Mireau (1996), Klei and Koenig (1997), Mori and Koenig (1998), Traub et al. (1998) and Blümich (2000).

MRI is used to characterise the porosity distribution in water-saturated bulk solids and filter-cakes and their evolution during mechanical and mechanical-thermic dewatering like filtration and expression (Horsfield et al. 1989; Fordham and Hall 1993; Kopinga and Pel 1994; Korger et al. 1994; Korger 1995; Yao et al. 1995a, b; La Heij et al. 1996; Pope et al. 1996; Yao et al. 1997; Airey et al. 1998). The indirect method was applied to salt-water ice systems. Menzel et al. (2000) studied the pore-structure of samples varying the preparation-conditions (e. g.

shock-freezing). Shock-freezing (-40 °C) induces an MRI-detectable pore-network (up to diameters of 300 μm and lengths of 8 mm), whereas after freezing at -20 °C to -2 °C comparable structures cannot be observed. Eicken et al. (2000) analysed natural and artificial ice grown and stored under different conditions as a function of the measuring temperature. Decane was used to replace pore-fluid in order to alleviate the MRI measurements. The shape, the density and connectivity of the pores in the ice depends on the measuring temperature. Further possibilities to characterise the pore-system in sea ice by means of NMR-diffusion experiments are presented in chapter 3.3.

The indirect method was used for example to examine the porous network of tablets filled with gadolinium doped silicone oil (Nebgen 1995; Nebgen et al. 1995). The tablets were produced by compressive and build-up agglomeration. The structure was studied in order to optimise the agglomeration process [process parameters (e. g. machine speed, pressure), composition of the solid particles and the fluid component] with regard to the design of the tablets (for example with or without coating) and to the controlled release of active ingredients. 3D images enable one to determine the density or the porosity of the tablet, to characterise the homogeneity of the agglomerate and to detect possible cracks. Porosity changes of approx. 3 % can de determined. The structure of the tablet determines the kinetics of the dissolving of the tablet and the drug release which will be discussed in (c).

The possibilities to study porous systems with the indirect method can essentially be improved by using hyperpolarized gases like ^{3}He or ^{129}Xe (Wittig and Kauczor 1997; Gregory et al. 1998; Moudrakovski et al. 2000). The used gas molecules saturate the pore-system more effectively than fluids. The use of hyperpolarized ^{129}Xe does not only allow one to characterise the pore-system, but also the corresponding nuclei at the surface of the pore-system can be detected and quantified by a polarization transfer from ^{129}Xe to other nuclei (e. g. ^{1}H, ^{13}C, ^{15}N, ^{29}Si) (Appelt et al. 1998, 2001). Ceramics in the green-state produced by extrusion or slip-casting can often directly be studied (Götz 1994; Blümich 2000). After sintering, however, ceramics have to be impregnated with detectable fluids or gases.

Applications in Food-Packaging. MRI was also applied to study packaging materials or food in packages. Segre et al. (1993) used MRI to characterise multi-component polymeric packaging materials like polymer blends and multi-layer films with regard to their structure and composition. It is possible to detect delamination in multi-layer films. Commercial food-products can often be studied without removal of their packages. Schenz et al. (1999) and Mermelstein (2000) describe on-line MRI systems used to detect spoilage in aseptic packages. The goal of the development is to reduce the spoilage rate of distributed products. The method is based on the dependence of T_2 and the signal extrapolated to the time zero on the degree of bacterial spoilage in liquid nutritional products (Schenz et al. 1993). Schenz et al. (1999) observed, furthermore, that the patterns in T_2-weighted MR images of the same matrix are characteristic for bacteria contaminating the sample. Wright and Hall (1994) checked the applicability of MRI to several types of packaging. Packages of plastic, paper or glass are appropriate for MRI. Even the content in glass jars with a polypropylene screw (peanut butter) and in polypropylene cartons with an aluminium foil top (yoghurt) can be imaged without any significant artefact. Problems are caused by papers with aluminium foil coating (camembert) and glass jars with ferrous metal top (jam) which distort the image due to shielding of the radio-frequency field and modifying the static magnetic field $\mathbf{B}_0$, respectively.

Ad (c) **Structural Changes and Reactions**. Dynamic processes with temporal changes that are small compared to the measuring time of a single image can be studied by a series of MRI images. Presently, the measuring time of one image with 64·32 pixels cannot be decreased below 60 ms/image (Müller 2002) despite newly developed hardware and new pulse sequences like Snapshot-FLASH (fast low-angle shot) (Haase et al. 1986; Haase 1990), EPI (Echo Planar

Imaging) (Mansfield 1977) and Turbo-RARE (rapid acquisition with relaxation enhancement) (Hennig et al. 1986). In the following chapter several examples concerning multi-phase systems of food and non-food products are given.

MRI has already been used in many cases to characterise the texture of foods, especially of fruits and vegetables, due to storage/ageing (e. g. ripening), damage (e. g. bruising), processing and pathogen infection, which generally cannot be detected without peeling (Ishida et al. 1989; Hall et al. 1998). The local concentration of water and oil was studied in a model-emulsion (Winkler et al. 1991) and in milk (Duce et al. 1995; Gibbs and Hall 1996). Phase-separation caused by creaming can be observed. Lipid is enriched in the upper layer and water is depleted with increasing settling time. Recent reviews of various MRI experiments applied to foods (initial, intermediate or final products) in processes of mechanical (flow: extrusion, pumping, stirring, mixing; solid-liquid separation, dust separation, liquid-gas separation), thermal (drying, freeze-drying, heating, cooking, melting, freezing, cooling, thawing, solidifying, crystallisation, baking, extraction, distillation) and chemical engineering (chemical reactions: distribution of the yield, composition and reaction kinetics) are given by Schrader et al. (1992), McCarthy (1994), McCarthy and McCarthy (1994), Corbett et al. (1995), Watanabe et al. (1995), Yan et al. (1996), Belton et al. (1998b), Hills (1998) and Webb et al. (2000).

Serial imaging based on various MRI techniques has been used in order to track solvent diffusion phenomena (ingress, permeation or migration of fluid components, drying) in heterogeneous materials (Watson and Chang 1997). In food the diffusion of water, fat, solutes and solids plays an important role. Most of the applied methods for analysing transport phenomena in disperse materials including food systems are based on integral experiments (McCarthy et al. 1994), for example the determination of the total weight in order to characterise the drying process of a product. These techniques enable, in many cases, an effective control of industrial processes. Integral data, however, are generally not sufficient for modelling of the corresponding process and deriving product and process parameters necessary for an effective design of the apparatus and the process. MRI allows one, on the other hand, to observe the solvent concentration in solid materials, to detect heterogeneities like internal defects, cracks or voids in the matrix (e. g. Rothwell et al. 1984; Koenig 1992) and to determine self-diffusion coefficients (chapter 3.3) or further NMR-quantities (Watson and Chang 1997) spatially and temporally resolved. Inhomogeneities can be observed directly by MRI or indirectly by serial MRI mapping the uptake of a penetrant (Webb and Hall 1990). Assuming a material law for the diffusion the corresponding material parameters (e. g. the dependence of the diffusion coefficient on the solvent concentration) can be derived from the monitored solvent concentration profiles. The knowledge of the network-structure and of eventual modifications of the pore-network dependent on the local concentration of the diffusing substances (and thus the local composition of the sample) can be used to improve the modelling of transport processes in heterogeneous media.

Imaging of dewatering/filtration processes reveal the structure of filter-cakes as a function of time (e. g. Horsfield et al. 1989; Fordham and Hall 1993; Wandelt 1993; Kopinga and Pel 1994; Korger et al. 1994; Korger 1995; La Heij et al. 1996). During filtration La Heij et al. (1996) observed a porosity gradient which disappears during expression forming a homogeneous cake. Kaulisch (1995) determined the evolution of the thickness of the surface layer of solid particles at the filter-tube in a cross-flow filtration device during the filtration and the subsequent detachment of the surface layer. Significant differences can be observed for laminar and turbulent flow of the suspension. In turbulent flow the layer grows faster and achieves a higher limiting thickness than in laminar flow. Korger et al. (1994, 1995) analysed the so-called vapour pressure dewatering, a combination of mechanical differential pressure dewatering of a wet bulk and contact drying. It was possible to confirm the concept of a migrating dewatering front.

Serial MRI could, furthermore, be applied to study the evolution of filter-cakes or sediments built up in centrifugal fields and the effect of additional mechanical deformation (like shear-deformation or ultrasonic) or of additives (flocculating and dispersing agents) on the structure of filter-cakes or sediments. The determined porosity profiles are required for an appropriate modelling of solid/liquid separation processes and the design of the corresponding apparatus. Rembor (2001) characterised the structure of fibrous filters used for dust separation by means of MRI after the filter had been saturated with water. In order to observe the local loading of the filter with solid particles during filtration spores of club moss (lycopodium bisdepuratum) were used. These spores can be imaged directly with NMR. It was possible to determine the local loading in the filter medium. The spatial distribution of the deposited spores is not homogeneous in the flow direction of the gas.

Another example for multi-phase apparatus are trickle-bed reactors with gas/liquid two-phase flows. Sederman and Gladden (2001) and van Buren et al. (2001) determined the local porosity, the local saturation and the surface local wetting as a function of the gas and liquid superficial velocities. Image analysis enables one to derive data on the droplet separation kinetics, the evolution of fluid hold-up and the extent of the surface wetting within packed beds. For single-phase flows in fixed-bed reactors the MRI results agree well with numerical simulations (lattice-Boltzmann) (Manz et al. 1999b; Mantle et al 2001). Mantle et al. (2001) used MRI, furthermore, to visualise the evolution of the liquid concentration for gas/liquid two-phase flows in a trickle-bed reactor.

The stability of different foams (cream, egg white and beer) have been analysed by MRI (German et al. 1991). Drainage and collapse of the foams were observed without disturbing the process or having to prepare the foams. Flow-induced structural changes in disperse, heterogeneous systems are described in detail in chapter 3.2. MRI experiments concerning bulk solids could, furthermore, be helpful for the understanding of fluidised beds, pneumatic conveying and mixing, the storage behaviour in silos, the dissolving or agglomeration including coating.

Gibbs and Hall (1996) observed the freezing and thawing of carrageenan gels. Two phase changes and at least three different phases are detectable. Hills et al. (1997) realised a rapid MR imaging method in order to study the freezing of raw potatoes. A sharply defined front processing through the potato cannot be observed. There is rather a region with several phases of liquid water and ice existing simultaneously. The extension of this region increases faster than linearly with time. Guiheneuf et al. (1997) were able to authenticate the effect of freezing, storing and thawing of pork by quantitative MRI of T_1, T_2 and the diffusion coefficient. Especially T_2 is sensitive to damaging effects of freezing and thawing cycles. The duration of storage, however, does not dramatically influence the studied NMR quantities.

Drying processes in several material systems with different drying techniques are studied with MRI: limestone (Guillot et al. 1989), corn during steeping (Ruan and Litchfield 1992), model gel at room temperature (Schrader et al. 1992), corn and cellulose/agar gels with contact drying (Song and Litchfield 1993), catalyst support pellets partially saturated with water with dry air (Hollewand and Gladden 1994), model-gel (Nott et al. 1999) and carrots or apples with micro-waves (Regier et al. 2000, 2002). Song and Litchfield (1993) found that the moisture distribution in gels is nearly homogeneous during the drying. In corn, however, MRI provides an inhomogeneous moisture-distribution revealing the morphology of the corn.

The decrease of the integral moisture content is usually combined with a shrinkage of the sample. The spatial extension of cracks correlates, as expected, with the magnitude of the moisture gradients. Leisen et al. (1998) observed the distribution of water during drying of carpets by air flow. The evolution of the moisture-distribution and the local drying rate depend on the orientation of the air flow. Nott et al. (1999) observed the three-dimensional distribution of both the moisture and the temperature in a model gel varying the salt concentration. As expected, the pore-structure strongly influences the drying process in all systems studied, that means the evolution of the moisture-distribution within the sample. Aims of the studies were to characterise the pore-system, to detect possible structural changes of the matrix, to discriminate different mechanisms of drying due to different moisture mobility within the pore matrix and to analyse the crack behaviour of the materials during drying.

Further applications could be the drying of materials with a two- or multi-component fluid system, the evolution of swelling (Douglas 1996) or shrinkage and the formation of cracks. The effect of freeze-thawing on the structure including the moisture distribution of meat, poultry and fish (Hall et al. 1998) or vegetables like courgettes (Duce et al. 1992) can be quantified by MRI. Hall et al. (1998) assumed that the change of the relaxation times in meat, poultry and fish after freezing and thawing is caused by protein denaturation and aggregation processes or cross-linking. The signal patterns in vegetables alter dramatically after freezing and thawing. The structural changes of the tissue morphology in courgettes is caused by the rupture of cell walls and the subsequent decrease of the turgor. As a result intracellular fluid drains into hollows and the firmness of the fruit decreases. Simoneau et al (1992) used MRI to measure the kinetics of melting of fat and crystallisation by determining the liquid-to-solid ratio of lipids (McCarthy et al. 1991).

Gonzalez et al. (2000) observed textural and structural changes in lasagna for various cooking and holding times by MRI. With increasing cooking time the moisture in the pasta increases inducing a swelling of the pasta. Simultaneously the firmness of the lasagna decreases caused by a moisture redistribution during holding. MRI allows one to determine the optimal holding conditions (temperature and relative humidity) and to modify the composition and the production process in order to lengthen the holding with constant material properties. Wheat grains were cooked by two different processes (Stapley et al. 1997): Whereas in boiled grains a front of moisture progresses towards the centre of the grains, steamed grains show a homogeneous distribution of the moisture content.

The theoretical understanding and hence the design of baking processes is rather difficult due to a complex combination of heat and mass transfer (water, gas and eventual fat), chemical/biological reactions and a change of the pore-structure caused by shrinkage or expansion during fermentation or baking. The final pore-structure is, furthermore, related to the sensorial behaviour of the baked product. Therefore, a deeper insight into the processes during fermentation and baking are required in order to optimise the complete production process with regard to (a) the sensorial and ageing behaviour, (b) minimising the demand of energy or production costs in general and (c) increasing the output at sufficient quality.

McCarthy and Kauten (1990) observed the structure of biscuits before and after baking. Heil et al. (1993) applied localised spectroscopy (chapter 3.4) and MRI to study void formation, lipid and water migration and water loss during baking of cookies. Duce et al. (1995) quantified the water loss in biscuits. Ruan et al. (1996) observed in starch-based foods the migration from moisture from the crumb to the crust combined with a firming of the crumb. MRI was also used to characterise the architecture of baked breads (Ishida et al. 2001). The baked bread-samples were saturated with acetone. Possible structural changes caused by the acetone are not investigated. Furthermore, the fermentation processes in yeasted wheat flour doughs was monitored by serial MRI in order to study the effect of dough handling on the properties of the doughs (Takano et al. 2002). The increase of the loaf volume was clearly demonstrated in this study, however, an exact measurement of the volume of the dough was not carried out.

In order to monitor on-line the fermentation without preparations or interruptions, dough samples were placed in PTFE (polytetrafluoroethylene) tubes. PTFE enables one to decrease the disturbing influence of the wall friction on the fermentation process, that means the formation of voids and the evolution of the dough-volume [14]. The evolution of (i) the amount of CO_2

which leaves the fermenting dough and of (ii) the volume of the dough were determined by two independent non-NMR experiments and compared to the MRI data. The MRI results correlate well with the volumetric measurements (ii). The MRI experiments provide, furthermore, structural information concerning the spatial distribution of the void formation, their homogeneity and the evolution of the mass density by determining the signal intensity in an area of interest and deriving the corresponding standard deviation. The ratio of the free CO_2 (which has permeated out of the dough) and the dough volume characterises the connectivity of the pores inside the dough matrix. MRI images clearly reveal slices of higher mass density and with, therefore, presumably lower gas-permeability at the outer surface of the fermenting dough (Götz et al. 2003a).

Potter et al. (1993, 1994) and Duez et al. (2000) studied the gelation of sodium alginate induced by calcium. A sol/gel boundary is migrating through the sample during the gelation. The progress of the calcium-ions depends on the initial ion concentration, the ionic strength of the alginate sol and the pore-system of the gel. The experimental data correlate in the short-time behaviour well with known reaction-diffusion models. Deviations for long times are probably caused by syneresis, which describes the progress of phase-separation of serum in disperse food-systems (e. g. cheese and yoghurt). McCarthy and Kauten (1990) used CSI to analyse the effect of syneresis. Serum was detected at the outside of the skim milk samples after coagulation. It is still not clarified, if (a) serum is expelled out of the cut cheese curd due to a contraction of the pore-matrix or if (b) the water-holding capacity of the gel decreases caused by physical/chemical/biological processes due to ageing of the gel. Syneresis in partly consumed foods like dairy products or mustards is presumably caused by the destruction of close pores in the network containing serum.

Many dried food-products are rehydrated before consuming. Examples are pasta, legumes, potato-powder for puree, dried milk, instant products (coffee, chocolate, cocoa, sauces), puddings and other desserts. The rehydration is possibly combined with dissolution, swelling or gelling after sufficient mixing, homogenisation, heating or cooling. Duce and Hall (1995) visualised in various foods (like butter bean, rigatoni and a snack food) the hydration and rehydration together with the subsequently induced structural changes.

As mentioned above in section (b) the structure of a tablet determines the kinetics of the dissolving of the tablet (Snaar et al. 1998, 2001) and thus the drug release (Korsmeyer et al. 1985, 1986; Rajabi-Siahboomi et al. 1994; Bowtell et al. 1994; Mäder et al. 1997; Black et al. 1998; Fahie et al. 1998). Tablets with hydrophilic matrices are dissolved in gastric juice and saliva of patients. This process was simulated by dissolving a tablet in a 0.5 mol HCl solution (Groß and Lehmann 1998; Fig. 3.1.6). Liquid diffuses into the tablet matrix, polymers present in the matrix hydrate and eventually build up a gel layer. This layer acts as a barrier for further liquid ingress and, thus, for the drug release. Depending on the matrix-composition the tablet swells. MRI shows the zones of the solid core, the gel and the outside liquid. In coated tablets the coating can also be observed as a further zone. The evolution of the drug release is controlled by the polymer (acting as gelling agent or increasing the viscosity and thus diminishing the mobility of water in the tablet) and the structure and composition of the matrix (hydration, swelling and crack behaviour).

In order to record the migration of brine into fresh meat ^{23}Na was imaged (Guiheneuf et al. 1997). The uptake of brine is a good approximation of a Fickian diffusion process with an Na^+-concentration-dependent diffusion coefficient. Blackband and Mansfield (1986) used MRI to study the diffusion of water into polyamide. Polyamide is often used as an oxygen-barrier in plastic packages, but only, if the water content in the polyamide is zero. Gil et al. (2000) observed the imbibition of water in differently prepared types of cork. Suberin is quantitatively the main component in cork of cork oaks (Quercus suber L.) and is believed to be a biopolyester. Suberin seems to be principally responsible for slowing down the uptake of water. Webb and Hall (1991) and Gibbs and Hall (1996) showed that the ingress of some organic fluids used as model-petrol into vulcanised rubber is a Fickian process. In superabsorbing polymers local differences in the cross-link density (T_2) can be detected (Traub et al. 2000). T_2 is longer in the centre than at the outside, this means the minimum of the cross-link density is in the centre. Besides the water uptake the swelling process can also be monitored as a function of time. Prado et al. (1999) studied the water uptake of water in pellets of zeolite using SPI. This was necessary due to the small T_2-relaxation times of water in micro-porous materials. Zeolites are used in separation processes, as catalysts and drying agents.

Bohris et al. (1998) observed three types of water in Portland cement pastes during curing. These are chemically bound, gel and capillary water. The effect of the water to cement ratio and of the cure conditions on the water migration and the distribution of the three phases during curing is discussed.

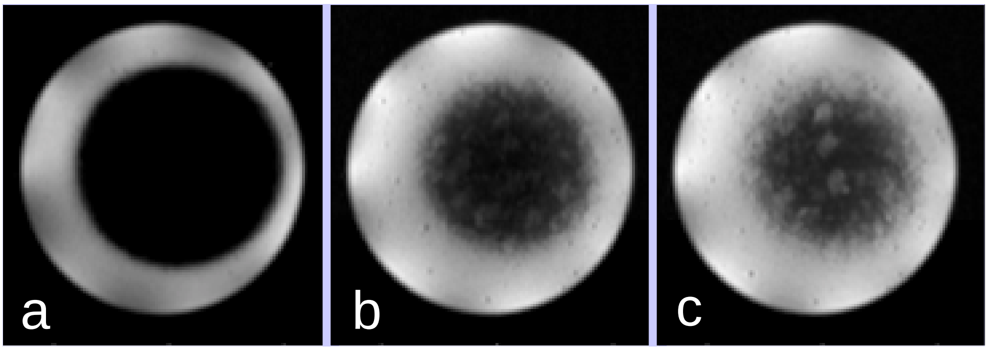


Fig. 3.1.6. Serial MRI (interval between two images: 1 h) of the dissolving of a tablet in a 0.5 mol HCl solution (Groß and Lehmann 1998). Measuring sequence: Spin Echo 3D with the sequence-parameters: FOV = 15x15x15 mm; number of pixels N = 128x128x16; A = 117·117 µm/pixel in plane and 9375 µm slice thickness; TE = 2 ms; TR = 200 ms; averages: 1, total measuring time of a single experiment: 7 min, time a: 7 min; time b: 10 h 7 min; time c: 17 h 7 min; 300 MHz

In many polymers cross-linking is observed after the extrusion and the die-casting. The mobility of specific segments correlates with the cross-link density (Fülber 1996; Blümich 2000; Götz et al. 2002a, b). This has a strong influence on the T_2-relaxation. Thus the evolution of the polymerisation/vulcanisation can be observed by T_2-weighted MRI methods. Prado et al. (2000) used SPI to localise the vulcanised boundary in rubber. Jackson et al. (1991) and Jezzard et al. (1992) studied the polymerisation of methylmethacrylate to polymethylmethacrylate in a mould which is temperature-controlled.

As described in chapter 2.1 the main motivation of this work is to demonstrate how NMR and MRI can be used for a better understanding of technical or natural processes. In drying technology for example it is assumed that a reliable prediction of the temporal evolution of the drying is impossible for real products (Gnielinski 1998). In order to find suitable dryers for a certain product, practical drying experiments still cannot be forgone. The main reason is that the distribution of water or other fluids, which should be removed, and - in combination - the character of the mass and heat transport cannot be derived from the total vaporised amount of fluid (Harding et al. 1997; Gnielinski 1898). That means that the knowledge of the evolving concentration distribution (or distributions) is required to characterise the drying process, to derive relevant material or system parameters for theoretical or numerical calculations of the drying process or for the development or improvement of existing constitutive equations. Examples of combinations between NMR results and modelling are already given for freezing (Kerr et al. 1996), rehydration (Hills et al. 1996a), characterising of pore systems (Klemm et al. 1997) and drying (Sousa de and Engelsberg 1999). Klemm et al. (1997) enlarged the set of parameters for the characterisation of the pore-system in disperse media. These parameters (e. g. fractal dimension, correlation length, percolation probability (Stauffer and Aharony 1985)) can be derived by means of conventional MRI, after the pore-system has been saturated with water. The procedure was tested for model objects with known pore-system and afterwards transferred to glass beads and natural materials like pumice, sponge and quartz sand.

MRI images can, furthermore, be used as a basis for the generation of grids for numerical simulations, for example to model the microscopic deformation behaviour of foams or filled polymers in mechanical load experiments (e. g. compression, torsion) (e. g. Gusev 2001). The comparison of numerical simulation and experimental MRI results might help to verify and improve the theoretical understanding of micro-structures and micro-processes in disperse materials undergoing a macroscopic deformation. Mechanical load causes a deformation of polymer chains combined for example with an eventual change of the corresponding T_2-relaxation times (Blümler and Blümich 1993; Blümich 2000). In simple deformation types it is possible to correlate the local T_2-relaxation time with the corresponding local mechanical stress or strain (Klinkenberg et al. 1996, 1997). Another application of MRI could be the generation of grids for the simulation of the flow in beds reactors, trickle-bed reactors or, generally, complex disperse pore-systems.

Structural changes due to convective and diffusive transport processes or spectroscopic properties are described in chapter 3.2, 3.3 and 3.4, respectively.

3.2 Convective Transport Processes

The applications of NMR presented in this chapter are essentially attributed to convective flow phenomena:

(a) the flow of disperse multi-phase materials (e. g. emulsions, suspensions, pastes, bulk solids, foams, aerosol, gas-liquid flow) or of other complex liquid systems (e. g. low molecular weight solutions, gels, entangled polymer solutions, micellar solutions, polymer melts, liquid crystalline polymers) (e. g. Callaghan and Gil 1999, 2001),

(b) transport processes in porous media or complex structures, including the separation of particles and/or drops out of flowing multi-phase materials, for example in filters or trickle-bed reactors.

A review concerning non-invasive tomographic methods for the analysis of multi-phase flow has been given by Chaouki et al. (1997). Capacitance tomography (e. g. Williams and Beck 1995; Plaskowski et al. 1995; Reinecke and Mewes 1997) has a high temporal resolution (0.1 s) at low costs compared to other tomographic techniques. The spatial resolution of capacitance tomography is, however, in the order of millimetres. Important advantages of MRI are the chemical sensitivity, the high spatial resolution and the possibility to determine three-dimensional velocity distributions. In MRI terminology experiments to measure velocity distributions in flowing systems are usually called flow experiments (Callaghan 1991). Various flow-imaging methods have been developed which can be classified into the following three groups (Pope and Yao 1993):

- Inflow/outflow methods: Changes of intensity due to motions of spins into or out of a defined slice can be determined.
- Time-of-flight methods: Frequency encoding correlates with displacements (in three dimensions) and thus with the corresponding velocity components, averaged over the total measuring time of the flow experiment. A special form are the so-called tagging experiments (Mosher and Smith 1990).
- Phase-encoding methods: Flow-dependent phase shifts provide the complete velocity data.

The tagging procedure is only in special cases appropriate for exact quantification of flow processes. Nevertheless, it is very useful for estimating qualitative properties of complex flow fields (Gibbs and Hall 1996). Phase-based or time-of-flight velocity imaging techniques provide exact velocity data. NMR flow experiments are especially appropriate for the following flow-types:

- Movements which can be interrupted for the MRI tests and continued afterwards [extrusion of pastes (e. g. Götz 1994, 2002c), Couette-experiments (Götz et al. 2001d)].
- Periodic flows: The NMR experiment has to be triggered with an external signal like electrocardiography (ECG) (e. g. Ruff et al. 2000), the phase of a shaft or another signal (Han et al. 2001b).
- Steady-state flows [examples in Götz et al. 2003d].

Fast imaging methods like EPI enable the study of thermal convection (Gibbs et al. 1993; Weis et al. 1996), of the flow in packed beds (Götz et al. 2002e) and even of turbulent flows (e. g. Kuethe 1989; Gatenby and Gore 1994). The statistical fluctuations in flows which might be present after the onset of turbulence can be characterised by NMR flow experiments. Velocity fluctuations and turbulent intensities (Batchelor 1953) can be derived spatially resolved. Kose (1992, 2003) used a combination of EPI with a spatial tagging sequence to visualise instationary flow processes (e. g. Taylor-Couette) or turbulent motion. The flow and actual flow pattern of disperse systems like emulsions can be characterised with snapshots (Götz et al. 2003c). By means of flow experiments it is, furthermore, possible to determine local acceleration vectors (e. g. Callaghan 1991; Pope and Yao 1993; Han et al. 2000a, b).

Flow experiments provide the complete, spatially resolved three-dimensional velocity field in the measuring volume. Not only an averaged value of the corresponding velocity component, but the whole frequency distribution at each position (more exactly within each voxel with finite, non-vanishing volume) can be obtained. Thus dispersion coefficients can be derived from the velocity profiles of the corresponding velocity components (Götz et al. 2002e). All detectable spins contribute to these frequency distributions which have passed the considered voxel during the measuring time. The frequency distribution in a voxel has several reasons:

- *Spatial gradients* of the velocity fields in a voxel due to the limited spatial resolution: The magnitude of the velocity-gradients are for the flow in porous media, due to the highly structured solid matrix, higher than in simple tubes at the same total flow rate (Saffman 1959; Scheidegger 1961; Bear 1969; Riquarts 1977; Ackermann et al. 1983; Jorgensen 1997).
- *Temporal fluctuations* like eddies and dispersion (Daszkowski 1991): The velocity field is averaged over the total measuring time.
- *Molecular diffusion* and
- *measuring errors*.

Due to the diffusion-similar behaviour of these processes these fluctuations are often compared to the movement of molecules in a one-phase fluid. The combined transport processes are called hydrodynamic dispersion and phenomenologically modelled like molecular diffusion (Bird et al. 1960). In contrast to diffusion coefficients dispersion coefficients are not pure material parameters, but quantities which depend on the local flow pattern of the present phases, like the flow of a fluid in porous matrix. Dispersion coefficients characterise the distribution and mixing of the present phases.

Ad (a) **Flow of Disperse Multi-Phase/Complex Materials**. In contrast to most other techniques even the flow inside of complex structures and disperse or opaque materials can be analysed. For a homogeneous sample its velocity profile can be obtained, for samples with several phases the velocity profiles of the single components can be determined (e. g. Laukamper-Ostendorf et al. 1997a, b; Götz et al. 2002e, 2003c). Flow experiments provide model-free velocity data, especially phase-encoding methods, in arbitrary directions, even in optically opaque materials.

Flow experiments with disperse multi-phase materials or of other complex liquid systems (Callaghan and Gil 1999, 2001) in viscometric flows [e. g. plate-plate, cone-plate, tube flow, extruder (capillary rheometer), Couette] offer the possibility to characterise quantitatively the flow behaviour or the mixing/demixing behaviour (with the help of the evolution of the volume-concentrations or the corresponding dispersion coefficient) of the present phases in the tested material. The application of MRI to determine material functions, i. e. flow and wall slip functions, was proposed and described in Götz (1994), Gibbs et al. (1997) and Cheung et al. (1997). For this application NMR flow-experiments are combined with further measurements like the differential pressure (tube flow, capillary rheometry) or the torque (Couette flow). Advantages of flow experiments are the possibility to detect eventual separation processes (homogeneity with regard to the moisture, hollow spaces or cracks), to control the supposed flow pattern, e. g. shear flow (Kuethe and Herfkens 1989; Götz et al. 1994a), or the degree of filling in the test device (Götz et al. 2001d). For heterogeneous multiphase systems it does not seem to make sense to realise viscometric flows in rheometers where the homogeneity of the material is assumed for the evaluation. Flow and wall-slip functions of homogeneous and quasi-homogeneous materials, i. e. one-phase fluids in good approximation, however, can be determined in one single experiment (Götz et al. 2001b).

NMR flow experiments have already been applied to study the flow in several set-ups. Not only suspensions or pastes have been studied, but also water and for example watery solutions of sugars, polysaccharides and hydro-colloids (McCarthy et al. 1992a, b, 1994, 1998; Gibbs et al. 1994; Manz et al. 1997; McCarthy and Kerr 1998; Yeow and Taylor 2002), tomato juice (Britton and Callaghan 1997), butter and margarine (Britton and Callaghan 2000), egg-white and polymer solutions (Rofe et al. 1994, 1996; Xia and Callaghan 1991), suspensions (Ding et al. 1993; Gibbs et al. 1996a, b; Han et al. 1999), fibrous suspensions (Seymour et al. 1993, 1995), blood (Han et al. 2001a) and granular materials saturated with fluid (Abbott et al. 1991; Graham et al. 1991).

Tube Flow

Assuming appropriate material laws the corresponding material functions can be derived from the velocity profiles in a tube flow determined with MRI. The flow of polymer solutions, particle dispersions and aqueous polysaccharide solutions was analysed with MRI velocimetry by several authors (e. g. Altobelli et al 1991, 1997; Sinton and Chow 1991; Ding et al. 1994a, b; Gibbs et al. 1994, 1997a, b; Arola et al. 1998; Götz et al. 2003c, d) in order to characterise the flow behaviour and to detect apparent wall slip for these materials in Poiseuille flow. Götz et al. (1994) used MRI to study the flow of PSPB-water pastes (polystyrene-polybutadiene copolymer) in steady-state flows. The velocity profiles and volume concentrations of free water and the solid matrix of flowing pastes could be mutually independently determined via MRI flow experiments. This supplies direct proof of the relative displacement of free water in flowing pastes. It was possible to measure the wall-slip of the two phases and, therefore, to differentiate between the shear and slip shares of the total volumetric flow. A detailed review about flows in tube with various geometric structures, for example a tube with constant circular cross-section, tubes with contraction and expansion (Arola et al. 1998), a tube with one cylinder or more cylinders (Götz et al. 2002e) and a tube with a U-bend is given in (Götz et al. 2003d).

The measurement of the time-averaged velocity offers, in a technological view, the possibility to study the influence of material characteristics (e. g. ratio of the fluid and the solid, type and concentration of additives, general formulation) and process-parameter (e. g. pretreatment of the sample, process and store temperature, convey distance) on the flow-behaviour and structure of dispersions.

Couette

Kose et al. (1985) and Kose (1994a, b) presented ultrafast MRI techniques to visualise steady and unsteady Taylor-Couette flows of water. In several papers (Chingas et al. 1992; Rofe et al. 1994; Mair and Callaghan 1997; Britton and Callaghan 1997; Britton et al. 1999; Mair et al. 1999) the velocity profiles of the Couette flow for homogeneous Newtonian and Non-Newtonian fluids was visualised by MRI and, thus, shear rate distributions could be derived. The aim of these investigations was to evaluate standard rheometric methods for one-phase fluids by means of MRI. Like in the case of the tube flow viscosity functions can be derived from the velocity profiles determined with MRI (Götz et al. 2001d).

Graham et al. (1991) and Abbott et al. (1991) used MRI to monitor the shear-induced diffusion and structure in concentrated density-matched suspensions undergoing Couette flow. MRI reveals that the PMMA (polymethyl-methacrylate) suspensions demix during the shear experiment. The fluid fraction increases at the rotating inner cylinder and decreases monotonously from the inner shaft to the outer cylinder. Götz et al. (2001d) used MRI to investigate the flow behaviour of PTFE pastes and other highly viscous fluids in a new Couette shear device, developed especially for pastes. The results prove that Couette shear experiments are generally not suitable for all pastes or concentrated suspensions. It cannot be guaranteed, without additional experiments, that the assumed constitutive law and the corresponding viscosity functions can be transferred to model the velocity profile in any three-dimensional problem.

Extrusion

Hayashi et al. (1988) observed advanced ceramics during slip-casting process. Altobelli et al. (1997) studied the fluid concentration and the velocity profiles of model suspensions undergoing extrusion, Rauwendaal (1990) the extrusion of filled polymers and Sinton et al. (1990) the mixing of different filled polymers (saturated suspensions) in a twin-screw extruder. McCarthy et al. (1992a, 1994) and Seymour et al. (1995) applied MRI for studying the velocity profiles during extrusion processing of a simple, one-phase model fluid (carboxymethyl cellulose solution) and Rombach et al. (1998) studied the flow of water through a single screw extruder. In order to determine the local proton density (i. e. the local fluid concentration) and the local ^{19}F-concentration (i. e. the local solid concentration) for the extrusion of PTFE-water pastes in a ram extruder ^{1}H-MRI and ^{19}F-MRI were combined (Götz et al. 2002c). Furthermore, displacement profiles can be derived from NMR images by means of correlation techniques without any preparation or marking of the pastes.

Other Test-Devices

Wang et al. (1998a, b) studied mixing profiles of fluids in scraped heat exchanger. Corbett et al. (1995) used MRI to determine concentration and velocity profiles of pure fluids and solid suspensions in different types of rotating geometries (Couette, screw extruder, straight-flight cylinder). The velocity distribution of the so-called Starling flow in a hollow-fiber bio-reactor was determined by Hammer et al. (1990). Nutritive solution flows through a microporous capillary. Around the capillary is the cell suspension. Nutrient are transported to the cells and reaction products back to the centre. Heath et al. (1990) found a good agreement between the numerical and experimental results for the transport processes in hollow-fibre reactors. Laukamper-Ostendorf et al. (1998) studied the flow in hemodialyzers containing hollow-fibres membranes. It is possible to determine the position of the capillaries and to observe the velocity field in and outside the capillaries. Heine et al. (2002) velocity distribution in falling liquid films. NMR velocimetry could also easily be used to study velocity and concentration distributions in other apparatus of process engineering like hydro-cyclones or stirred reactors.

Granular media consisting of particles with different properties tend to segregate during processes with relative movement like mixing in drum mixer, calcinating (e. g. lightweight aggregates), drying or processing in fluidised beds (e. g. Bridgwater 1976). Examples are foods or component of foods, pharmaceutical or agricultural products, grains, coals and sand. Segregation processes in rotating horizontal tubes or drum mixers have been studied by Hill et al. (1997a, b) with the help of MRI and additionally by Nakagawa et al. (1993, 1997) with flow experiments. Axial and radial segregation of binary mixtures with different particle diameters and in some cases different materials can be observed. The evolution of three-dimensional concentration-patterns are accessible with MRI flow experiments, which cannot be derived from optical surface measurements (Hill et al. 1997a, b). Nakagawa et al. (1997) showed that radial segregation precedes axial segregation. Kuperman et al. (1995) observed and differentiated convective and diffusive flow in vertically shaken containers using a tagging sequence. Above a critical acceleration of approx. 1.2 g convection exists, with a thin boundary layer at the wall.

Relevance for Process Engineering

MRI could provide information in order to optimise the design of the considered device with acceptable methodological and apparative efforts or the formulation of the disperse media, for example to avoid structural changes in suspensions (Götz et al. 2002f). Careful conveying/pumping without significant modification of the structure is relevant for many materials. Flow-induced structural change may for example cause a decreased tensile stress for hardened ceramic masses or concrete, a negative sensorial behaviour of foods or, in the case of energetic materials, an unpredictable burning behaviour (Götz et al. 2002a, b). MRI enables one to detect deposits or eddies. Both effects lengthen the residence time in the device which could affect adversely the quality of perishable materials, e. g. in the production of food, pharmaceutical or cosmetic products.

The insight into inner micro flow-processes and micro structure helps to characterise the flow behaviour of suspensions or emulsions in a more comprehensive way than with conventional rheometric methods alone. The studied suspensions or emulsions show different types of flow behaviour including the tendency to phase-separation. Therefore, the common concepts to model the flow behaviour of suspensions or emulsions (Hochstein 1997), especially the relative viscosity as a function of the solid volume concentration, which assumes a solid volume concentration homogeneous in the sample, are problematic. Industrially relevant materials have presumably to be simple from a rheological point of view in order to enable a reliable control of their processing. It might be necessary to avoid any time-dependent effects concerning the flow behaviour, for example by means of suitable pretreatments like sufficient kneading for the extrusion of ceramic masses (Götz 1994, 2002f).

The knowledge of the rheological behaviour of flowing materials involved in process engineering is important with regard to various aspects (Steffe 1992):

- It is required for the design of apparatus in process engineering like pumps, extruders, mixers, stirrers, heat exchangers, on-line viscometers, valves, tubes or storage vessels.
- The flow behaviour can be applied as process and quality control of initial, intermediate and final food and non-food products.
- It is necessary for the development and control of rheological constitutive equations, determination of the corresponding flow and material functions.

In many production processes the participating materials can only be characterised as inputs and outputs entering and leaving units appearing as a black-box. Models derived from these data are principally inappropriate to understand the physical-chemical effects, to realise required product properties and to control the corresponding production/storage processes. The design of apparatus and processes are based on various models and simulations which include generally thermodynamics, reaction kinetics and rheology (Ronson 2002). Due to the complexity of many natural and industrial processes the corresponding models, for example computational fluid dynamics models for simulating realistic processes (Harding et al. 1997; Rombach et al. 1998; Sousa et al. 1999), have to be validated by comparison with experimental data. A professional design of products, processes and apparatus requires tests with real industrial materials instead of relying on eventually insufficient, oversimplistic models (Schrader et al. 1992). Many process tomography methods enable one to verify models under industrial circumstances, without preparations (e. g. dilution of suspensions for optical techniques). NMR tomographic techniques, furthermore, have a large spatial extension and can be used for imaging in two and three dimensions.

Besides the objective to develop and optimise apparatus, processes and products the data obtained and derived from MRI flow experiments (velocity and concentration distributions, velocity spectra, flow and wall slip functions) can be applied for process and quality control (McCarthy and McCarthy 1996; Hills 1995). Zion et al. (1994, 1997) used one-dimensional magnetic resonance projections in order to detect pits in pickled olives and cherries passing on a conveyor belt (25 cm/s) through an NMR magnet. Marciani et al. (1998) developed a method to determine spatially resolved the viscosity of a model meal in the gastrointestinal tract using ultrafast MRI techniques like EPI. The aim was (i) to study the combination of the viscosity distribution inside the human gastric lumen, gastric emptying and motility measurements and (ii) to observe the dynamics of food processing in the stomach. The method is based on a correlation between the relaxation time T_2 and the corresponding dynamic viscosity η of a fluid (Bloembergen et al. 1947, 1948). Applications of the T_2/η-correlation are given in chapter 3.4.

Due to the great importance of the viscosity, especially for process and quality control, viscometric methods have been developed which allow an on-line determination of the viscosity (Cullen et al. 2000). There are principally two possibilities to derive information concerning the flow behaviour from NMR flow experiments:

1 A combination of velocity and eventually concentration profiles with the corresponding stress distribution in order to derive directly flow and wall slip functions after assuming constitutive laws for the flow and the wall slip (Götz 1994, Gibbs et al. 1997; Cheung et al. 1997).

2 Deriving flow and wall slip functions by fitting the velocity frequency distributions (Gibbs et al. 1997; Heinen et al. 2001):
    2.1 direct two-dimensional imaging of the tube cross-section and subsequent determination of the velocity frequency distribution,
    2.2 radial velocity profiles from one-dimensional projection images and subsequent determination of the velocity frequency distribution,
    2.3 velocity spectra (e. g. Seymour et al. 1995).

Heinen et al. (2001) used (2.1) in order to determine rheological flow parameters for a Newtonian and a power-law fluid. Principally it is possible to derive the flow functions (with given constitutive law) and information concerning the pore-radius distribution from the velocity frequency distribution and an additional single-point measurement of the shear stress (Seymour et al. 1995).

Another interesting application of MRI to characterise flow phenomena is the study of mastication and swallowing processes during eating and drinking. The sensorial perceptions during eating or drinking are obviously strongly influenced by the rheological behaviour of foods including texture, creaminess or fattiness and the mixing behaviour of various food systems or the demixing of single food-components due to the mastication process (Prinz 2002a). In order to elucidate the relevant rheological parameters it would be helpful to determine the temporal evolution of the velocity distribution or - even more general - of the deformation field during eating and drinking. Thus appropriate rheometers and the corresponding rheological experiments could be created which simulate adequately the characteristic flow-types during eating and drinking. Besides videofluoroscopy and ultrasonic imaging serial MRI has been tested. Problematic are the comparably low temporal resolution [Büttner et al. (2001): 6 images/s, Prinz (2002b): 2 images/s] and movement artefacts.

Ad (b) **Transport Processes in Solid Systems**. The flow through porous media or complex structures plays an important role in process engineering and nature. Examples are

- flow through filters and packed beds (Airey et al. 1998; Pope et al. 1996; Yao et al. 1995b, 1997),
- static mixer (Rombach et al. 1998),

- filters (e. g. Kaulisch 1995),
- packed beds (e. g. Seymour and Callaghan 1997; Götz et al. 2002e),
- flow past a bundle of tubes or cylinders or heat exchangers (Wang et al. 1998),
- adsorber,
- separating column (Tallarek et al. 1995; Park and Gibbs 1999),
- fluidised bed,
- trickle-bed reactor (Sederman et al. 2001b; van Buren et al. 2001),
- flow of ground water, and
- flow of water and oil in rocks (Guillot et al. 1989; Horsfield et al. 1990; Klemm et al. 1997).

The described processes differ with regard to the geometry (structure of the packing, geometry of the installations), the solid concentration (e. g. packing density, number of installations), the hydrodynamic characteristic numbers (e. g. Reynolds number) and the fluid properties (e. g. viscosity function). Many investigations are focused upon the flow behaviour in packed beds which have become more important in recent years (Seymour and Callaghan 1996, 1997; Kutsowsky et al. 1996; John et al. 2000; Götz et al. 2002e). The main motivation for the application of packed beds is the development of a continuous course of the corresponding reaction. The starting substances flow through the tube reactor filled with bulk solids. The reaction takes place at the surface of the filling material that consists of a catalyst or is coated with a catalyst.

An important prerequisite for a deeper understanding of the flow through porous media and a precise simulation of the corresponding processes is the detailed knowledge of the velocity field in the interior of the packing and the structure of the pore-system of the packed bed. Technically relevant quantities like the global pressure drop, the dispersive intermixing of the fluid (axial and radial dispersion coefficients), residence times distribution and - if the fluid contains particles/drops - the separating behaviour can be derived from the knowledge of the velocity distribution assuming constitutive laws for the flow and wall slip behaviour of the fluid. Further valuable information for the reliable design of a process are the fluid and solid hold-up, eventual stagnant volumina (for example due to yield stress of the fluid) in the apparatus dependent on the fluid flow behaviour. The existence of stagnant volumina is especially important for food products which tend towards spoilage. The flow of Newtonian fluids in packed beds has often been studied (e. g. Amin et al. 1996, Götz et al. 2002e). However, there are still knowledge deficits concerning non-Newtonian fluids (Müller et al. 1998; Heinen et al. 2001), although their filtration plays an important role in process engineering.

The structure of the porous system has a great influence on the flow pattern. Generally the pore system is characterised by integral measures like the mean porosity ϕ and a characteristic particle or pore diameter (Bird et al. 1960; Bear 1972; Löffler and Raasch 1991; Chhabra 1993). The knowledge of the mean porosity is, however, insufficient even for Newtonian fluids (Nagel and Buggisch 1996). For the development and testing of appropriate models and for the determination of the corresponding material- and system-parameters, spatially, temporally and - in some cases also - energy (chemical shift) resolved data are necessary. Various possibilities to derive transport properties in heterogeneous, complex materials (i) indirectly from spatially resolved MRI data (Packer et al. 1995; Pel 1995; Baldwin et al. 1996; Glantz 1997; Valckenborg 2001; chapter 3.1) or (ii) directly by means of different types of flow experiments have been developed [Sederman et al. (1997): local Reynolds number and free cross-section of the local constriction; Sederman et al. (1998): local Reynolds number and correlation number; Müller et al. (1996): mean volume-averaged velocity as a function of probe-volume radius; Rigby and Gladden (1999): T_1-relaxation mechanisms, specific surface, characteristic length representing the extension of the surface interaction enhancing the relaxation rate, tortuosity, fractal dimension; Barrie (2000): formation factor, wettability, pore size distribution, pore connectivity; Britton et al. (2001): correlation of flow, T_2-relaxation mechanisms and morphology of the solid matrix, Sederman et al. (2001a): histograms of pore radius, surface area, volume, coordination to other pores].

Seymour and Callaghan (1997) discuss various possibilities to use convective flowing substances instead of diffusing particles/molecules like in NMR diffusion experiments (chapter 3.3) for the characterisation of the structure of porous media. The phase of the spin-echo signal, which provides the mean velocity in the gradient-direction, depends on the coherent displacement due to the flow changes (e g. Holz 1986; Packer 1996a, b). The so-called NMR flow diffraction (Seymour and Callaghan 1996, 1997) uses a correlation between the spin-echo amplitude as a function of the gradient and the velocity. Thus more extensive regions can be studied within the same observation time compared to diffusion experiments (chapter 3.3) (Tillich et al. 2001).

For a precise prediction of the flow processes in porous media it is insufficient to use characteristic or integral values to characterise the pore-system. On the contrary highly spatially resolved MRI results describing the pore-system are for example required as a basis for detailed numerical simulations. Lebon et al. (1996) combined flow and diffusion experiments and found a good agreement with numerical simulations using the Stokes equation. Debus et al. (1998) simulated numerically the flow in packed beds of beads and found a good agreement for the calculated global pressure drop compared with known phenomenological solutions like Ergun (1952), Molerus (1977) and Anderson (1961). Additionally zones of compression and elongation can be detected. Irwin et al. (1999) combined flow experiments with the detection of water doped with gadolinium in porous model (glass beads) initially saturated with undoped water. This technique has already been used to detect dead zones for the extrusion of ceramic masses (Götz 1994). The detailed spatial and temporal data offer a valuable insight into the transport processes of solutes in porous media, for example of contaminants in ground water.

To summarise the findings, NMR flow experiments in disperse media enable one to determine the porosity and the velocity distribution - and thus the flow rate distribution - in the interior of porous media. Thus (i) the influence of the flow behaviour on the flow through porous media can be quantified, (ii) frequency distributions of the velocity, flow functions, residence time distributions and dispersion coefficients can be derived and (iii) rheological data can be correlated with geometric parameters.

As further development of NMR flow experiments it is imaginable to apply flow experiments to multi-component apparatus with convective transport processes in order to quantify hold-up, flow pattern, mixing behaviour, dispersion and residence time distributions integrally and substance-resolved. The possibilities to characterise the structure of porous media with the help of diffusion NMR experiments are presented in chapter 3.3.

3.3 Diffusive Transport Processes

The NMR applications in this chapter are concerned with diffusive transport processes in food and non-food products [e. g. building materials (Garrecht 1992), mortar (Gummerson et al. 1979), soils, rocks and sandstones, ceramics, detergent powders or catalysts] with the structure of disperse systems, porous media, polymeric materials or composites. The studies are focussed on

(a) the quantification of the molecular mobility of the diffusing substances or the molecules of the solid matrix and on the diffusive mass transport in homogeneous and disperse systems, and derived from this
(b) the characterisation of the pore-system or, generally, of the solid matrix probed by the diffusion behaviour of the corresponding solvents.

Diffusive flow processes in solid systems are mainly influenced by the pore-system architecture, the chemical composition of the solid surface and the resulting solid-fluid interactions. The combination of (a) and (b) allows one to analyse the transport phenomena of confined fluids and fluid-solid interactions. Both pieces of information are necessary for a reliable modelling of natural phenomena, production units or apparatus where diffusive processes are involved. Examples for diffusive mass transport processes in disperse systems are transport of contaminants in geological media, movement of water and solvents in biological tissues (Hills and Snaar 1992; Le Bihan 1996), fluid multi-phase systems (reactive or non-reactive), the hydration and dehydration of materials, fat bloom in chocolate confectionary, syneresis in dairy products and mustard, the foaming-up of polymers and the subsequent degassing where sorption and diffusion of aerating agent plays an important role, the desorption or removal of monomers, oligomers or additives (e. g. plasticisers, antioxidants) out of recently synthesised polymers, separation processes in membrane-filtration technologies, controlled release of drugs or fertilisers, heterogeneously catalysed chemical reactions in porous catalyst or catalyst carriers and thermal processing like drying, distillation, absorption and extraction.

Ad (a) **Molecular Mobility and Diffusion in Disperse/Solid Systems**. Diffusive transport processes play an important role in all solid systems which contain fluid or into which fluid can penetrate (e. g. Barrer 1951; Crank 1956; Comyn 1985; Vieth 1991). Many NMR diffusion experiments of foods have been concerned with the transport of water or aqueous solutions. Other liquid components like fat or oil and, furthermore, solutes and solids are also appropriate for diffusion measurements.

Molecular Mobility

NMR PFG techniques (Pulsed Field Gradient) allow one to determine self-diffusion coefficients D_S as a function of the effective diffusion time Δ and to calculate the mean distance travelled by the diffusing molecules during the diffusion time (Stejskal and Tanner 1965; Tanner and Stejskal 1968; Callaghan 1991; Kärger and Pfeifer 1992, 1994; Kimmich 1997). NMR PFG includes methods like PGSE (Pulsed Field Gradient Spin-Echo) and PGSTE (Pulsed Field Gradient Stimulated Echo, see below). The technique is applicable to pure fluids (liquids, gases) or fluids confined for example in porous media. Thus it is possible to determine self-diffusion coefficient as a function of temperature and pressure and to study the influence of dissolved or dispersed substances (e. g. salt, sugars, proteins) and their concentration on the self-diffusion of pure (e. g. Hertz 1986) or confined liquids. The effect of a heterogeneous distribution of the susceptibility in the sample can be compensated with the help of appropriate pulse sequences (e. g. Cotts et al. 1989).

In dilute solutions and gels with low material-specific solid concentration the self-diffusion coefficient D_S is independent of the diffusion time (e. g. Colquhoun and Goodfellow 1994; Hills 1998). D_S is reduced compared to pure water due to obstruction and hydration of the dissolved molecules like hydrocolloids (e. g. carrageenan, starch) or simply solutes like salts or sugars (Hertz 1986). This is in agreement with the Stokes-Einstein relation, where the Fickian diffusion coefficient D_F is given by

$$D_F = \frac{kT}{6\pi a}\frac{1}{\eta} \tag{3.3.1}$$

k	Boltzmann constant
T	absolute temperature
a	radius of a spherical particle
η	dynamic viscosity of the solvent

Eq. (3.3.1) describes the diffusion of a spherical particle with radius a in a solvent dynamic viscosity η. According to the proportionality between the Fickian diffusion coefficient D_F and the self-diffusion coefficient D_S (Eq. 3.3.2) an increased viscosity of the serum (as a consequence of dissolved substances) causes a reduction of D_F and hence also of D_S. The correlation between the viscosity and the diffusion coefficient D_S or D_F provides, furthermore, the possibility to determine the distribution of viscosities in disperse systems, for example in biological tissues, by spatially resolved diffusion experiments. Griffiths et al. (1995) used PGSE NMR to study the role of molecular architecture on the self-diffusion of mono-disperse polymer-molecules (polyethylene oxide) dissolved in D_2O. The self-diffusion coefficient D_S of the cyclic molecule is, in the studied regimes of temperature and concentration, higher than that of the linear molecule with the same molecular mass, due to the smaller hydrodynamic radius. Behr et al. (1998) determined self-diffusion coefficients D_S of free methanol and of methanol SiO_2 aerogels varying the pH value, the temperature (up to 80 °C) and the pressure (up to 10 MPa).

Multi-component fluid systems have wide biological, technical and theoretical interest (Wesselingh and Krishna 2000). Examples are stirred vessel, mixers, membrane processes, adsorption, chromatographic columns (Tallarek et al. 1995, 1999), heterogeneous catalysis, diffusion of two or more permeants through polymers, rocks, soils or cells. Diffusion phenomena are principally distinguished between inter-diffusion (for example due to a gradient of concentration, temperature or pressure) and self-diffusion (caused by the Brownian molecular motion) (e. g. Tyrell and Harris 1984). For a better understanding of diffusion processes with regard to the mixing- or reaction-behaviour multi-component diffusion in binary or higher mixtures can be studied by self-diffusion coefficients (NMR diffusion experiments, e. g. PGSTE) or by (ii) inter-diffusion measurements (e. g. 1D-MRI with selective excitation of one of the present species). A detailed description of NMR- and other measuring techniques to characterise self- and inter-diffusion phenomena is given by Bartusseck (2002). Concentration-dependent self-diffusion (i) or inter-diffusion coefficients (ii) (from the temporal evolution of concentration-profiles) can be derived by a combination of NMR diffusion experiments and MRI with selective excitation in order to determine the local concentrations of the present species. Stilbs et al. (1987) used PGSE experiments to determine a series of spectra by varying the duration of the gradient pulses and to characterise micro-emulsions. The great advantage of NMR techniques in order to study multi-component diffusion in complex systems is that complex labelling by stable or radioactive isotopes (Stilbs et al. 1987) or optical techniques like holographic interferometry (Wild and Stichlmair 2000), which can only be applied to transparent materials, can be avoided. Helbæk et al. (1996) determined self-diffusion coefficients D_S of methane or ethane mixtures with hydrocarbons over the whole concentration range at high pressures (30 to 50 MPa) and two temperatures (303.2 and 333.2 K) by PGSE NMR. Self-diffusion coefficients D_S increase with the temperature and the mole fraction of the lighter component and decrease with the pressure.

As shown above, the common objective of many NMR diffusion experiments is the characterisation of the diffusive mass transport in disperse systems. The Fickian diffusion or inter-diffusion coefficient D_F describing the diffusive mass transport can be determined (Kärger et al. 1998) from the self-diffusion coefficient according to Darken´s law (Darken 1948; Kuhn 1986)

$$D_F = D_S \frac{X}{a} \frac{da}{dX} \tag{3.3.2}$$

X	ratio of the masses of the diffusing substance and the solid material
a	activity

For water as diffusing substance holds

$$D_F = D_S \frac{w}{a_W} \frac{da_W}{dw} \tag{3.3.3}$$

w	ratio of masses of water and the solid material
a_W	water activity

Thus the self-diffusion coefficient D_S can be converted into translational diffusion coefficients which are required for the modelling of mass and heat transport phenomena. More advanced models have been supposed by Hartley and Crank (1949) and Mills and Hertz (1980).

Diffusion in Disperse/Solid Systems

A dependence of self-diffusion coefficient D(t) on t in diffusion experiments indicates that the diffusion is restricted due to physical barriers, for example network-systems in gels (e. g. Callaghan 1991; Kärger and Fleischer 1994; Knaus et al. 1996: hydrated collagen; Ohtsuka and Watanabe 1996: gellan gum; Watanabe and Fukuoka 2001: starch). NMR PFG methods allow, furthermore, the observation of diffusion in anisotropic structures or anisotropic diffusion. Examples are biological media (e. g. cells) and liquid crystal systems (Le Bihan 1995; Hsu et al. 1997). The possibilities of diffusion experiments to characterise the structure of disperse materials will be discussed in detail in the following chapter (b).

Ad (b) **Characterisation of the Pore-System/Solid Matrix**. In porous systems the diffusing particles can be used for probing the micro-structure with diffusion (e. g. Holz 1986; Kärger and Fleischer 1994; Velan and Chandrakumar 1996; Hills 1998). Characteristic lengths inside the solid matrix of a few micrometres are accessible. These spatial resolutions cannot be realised using MRI methods. Possible interactions of the diffusing molecules, in most cases fluid molecules, with the solid matrix might have a great effect on the resulting diffusive processes, for example if fluid molecules are dissolved in the solid matrix inducing a swelling of the solid matrix, changes of the mass density and of the mechanical properties, usually a deterioration with respect to engineering applications (Thomson et al. 1998). NMR diffusion experiments provide information concerning the degree of the fluid-saturation in pore-systems and the existence of fluid-layers adsorbed at the solid matrix (e. g. Appel et al. 1996b). It can, furthermore, be differentiated, if the mass transport principally takes place in the gas-, in the fluid-phase or through the solid material. This information is especially relevant for the design of drying processes. Possibilities and techniques of NMR PFG to characterise pore-systems are shown below.

A special version of PGSE-experiments, the so-called q-space microscopy, q-space imaging or diffusion diffraction experiments (e. g. Callaghan et al. 1991; Callaghan 1995; Packer 1996b;

Johnson 1996; Mitra 1997), has proven its capability to characterise the structure of connected porous systems. In these experiments the attenuation of the spin-echo amplitude $E_\Delta(\mathbf{q})$ as function of the wave vector **q**

$$\mathbf{q} = (2\pi)^{-1}\,\gamma\,\delta\,\mathbf{G} \qquad (3.3.4)$$

γ	gyromagnetic ratio, specific for the studied nucleus
δ	gradient-pulse duration
$\mathbf{G}$	gradient amplitude

is determined. For the spin-echo amplitude $E_\Delta(\mathbf{q})$ as function of **q** holds

$$E_\Delta(\mathbf{q}) = \int \overline{P}_S(\mathbf{R},\Delta)\exp(i2\pi\mathbf{q}\cdot\mathbf{R})d\mathbf{R} \qquad (3.3.5)$$

$\overline{P}_S(\mathbf{R},\Delta)$	average propagator
Δ	duration between two gradient pulses
$\mathbf{R}$	dynamic displacement with $\mathbf{r}' = \mathbf{r} + \mathbf{R}$
$\mathbf{r}$	position vector at $t = 0$
$\mathbf{r}'$	position vector at $t > 0$

The average propagator $\overline{P}_S(\mathbf{R},\Delta)$ contains information concerning the structure of the sample and the mass transport in it (Packer et al. 1996c; Tessier et al. 1998). The restricted diffusion can be characterised by the so-called correlation time τ, in which a species has travelled a characteristic length given by the geometry (e. g. boundaries) of the sample. For $\Delta < \tau$, this means for the self-diffusion, the propagator does not depend on the starting position **r** and is Gaussian

$$\overline{P}_S(\mathbf{R},\Delta) = (4\pi D_{Sf}t)^{-2/3}\exp(-\mathbf{R}^2 / 4D_{Sf}t) \qquad (3.3.6)$$

D_{Sf}	self-diffusion coefficient for free diffusion

For $\Delta > \tau$, this means for restricted diffusion, the diffusing particle looses the memory of its starting position after sufficient reflections at walls. For times $\Delta \longrightarrow \infty$ holds

$$\overline{P}_S(\mathbf{R},\infty) = \int \rho(\mathbf{r}+\mathbf{R})\rho(\mathbf{r})d\mathbf{r} \qquad (3.3.7)$$

$\rho(\mathbf{R})$	particle density

The average propagator is for times $\Delta \longrightarrow \infty$ the auto-correlation function of molecular particle-density of the mobile phase. PGSE NMR experiments allow one to derive various parameter describing the structure of solid matrices. Porous systems often have fractal properties (Mandelbrot 1977, 1982). Self-diffusion processes are sensitive to the dimensional character of the path, which the diffusing particle has taken induced by the micro-structure of the solid matrix. For the "normal", this means free diffusion, the mean square distance from the origin at $t > 0$ is

$$< r^2 >\sim D_{Sf}t \qquad (3.3.8)$$

For restricted diffusion in a porous system, however, it holds that (e. g. Gefen et al. 1983; Banavar et al. 1985)

$$< r^2 >\sim D_{Sf}t^{2/(2+\theta)} \qquad (3.3.9)$$

θ determines the effective dimensionality of the random walk within the structure. For Brownian motion θ is 0 (Callaghan 1991). Eq. (3.3.9) is valid for diffusion lengths smaller than the so-called correlation length of the porous system (Appel et al. 1996b; Kärger et al. 1998). Only for the corresponding times the diffusing particles probe details of the solid surface. For sufficiently long times the mean square distance $< r^2 >$ becomes linear as a function of time, like in the cases for free diffusion. This means that the diffusion way averages over several pores or solid particles of the matrix

$$< r^2 > \sim D_{Sr} t \tag{3.3.10}$$

D_{Sr} self-diffusion coefficient for restricted diffusion

The diffusion coefficient for long times D_{Sr} is also called effective diffusion coefficient D_{eff}. As the diffusing particles are used as probe, PGSE NMR experiments are also called Dynamic Imaging (e. g. Callaghan 1991; Hallmann et al. 1996). The time-dependence of the self-diffusion coefficient contains information about the structure of porous media (e. g. Latour et al. 1993, 1995; Griffiths et al. 1995; Appel et al. 1996b; Hallmann et al. 1996; Mitra 1997; Watson and Chang 1997, Price 1997, 1998; Kärger et al. 1998). NMR diffusion experiments provide, based on the time-dependence of the diffusion coefficient, (a) characteristic dimensions of the gel structure, for example the critical pore radius r_c, (b) the diffusion behaviour for short times, dependent on the pore-structure and the pore-fluid, D_{Sf} (that means diffusion inside the serum in free diffusion) and (c), if different from case (b), the diffusion behaviour for long times D_{Sr} (restricted diffusion), limited by the corresponding relaxation times. The diffusion coefficient in the long-time behaviour D_{Sr} is a measure for the macroscopic permeability of the pore structure, the diffusion coefficient in the short-time behaviour D_{Sf} characterises the viscosity of the serum (Stokes-Einstein relation, (Götz et al. 2004d)). The self-diffusion coefficient of the serum is generally smaller than that of water, for example due to solutes.

I_g is the signal, for example in a PGSE or PGTSE experiment, with applied gradient magnetic field **g**, I_0 is the corresponding signal without gradient. The ratio of the spin-echo amplitude with I_g and without applied gradient field I_0 (Stejskal 1965; Tanner 1970; Callaghan 1991) is given by

$$I_g / I_0 = \exp(-\gamma^2 \delta^2 g^2 (\Delta - \tfrac{1}{3}\delta) D_S) \tag{3.3.11}$$

Fig. 3.3.1 shows the ratio of the spin-echo amplitudes with and without gradient, I_g/I_0, (a) for a fluid with free diffusion, (b) an emulsion with mono-disperse drops (the signal of the matrix has been suppressed) and (c) a gel-network with free diffusion for short times and restricted diffusion for long times. Fig. 3.3.2 illustrates the method of how to derive the self-diffusion coefficients at free D_{Sf} (~ b: slope for short diffusion times Δ) and restricted D_{Sr} (~ slope d: for long times Δ) diffusion and of the critical pore radius r_c of the gel matrix (~ $[D_{Sf}\, t_0]^{0.5}$) with the help of the NMR diffusion experiments I_g/I_0. I_g is the signal, for example in a PGSE or PGTSE experiment, where the gradient-pulse is applied, I_0 is the corresponding signal without gradient. The intersection point of both straight lines, which are asymptotes for the short- and long-time diffusion behaviour (as a function of the diffusion time Δ), defines the critical time t_0. t_0 marks the cross-over from free to restricted diffusion. t_0 depends on the length-scales (characteristic lengths) of the pore-system and D_{Sf}. The critical pore radius r_c (assuming spherical cavities) is given by (e. g. Kärger and Fleischer 1994; Appel et al. 1995)

$$r_c = [5 \cdot D_{Sf} \cdot t_0]^{0.5} \tag{3.3.12}$$

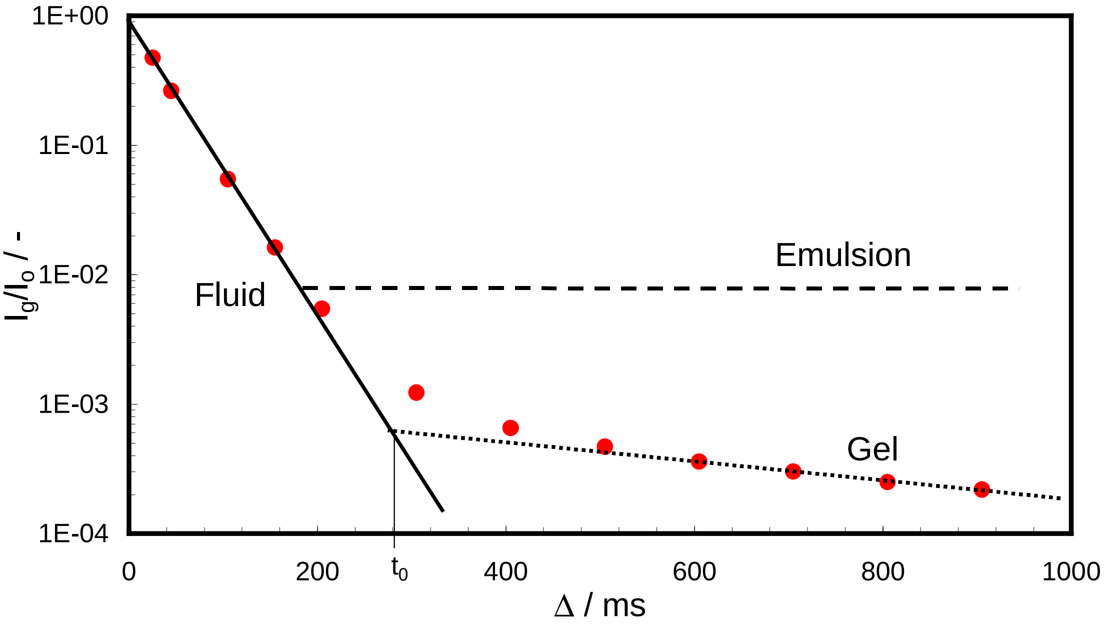


Fig. 3.3.1. Schematic presentation of the ratio of the spin-echo amplitudes with and without gradient, I_g/I_0, for a fluid with free diffusion, an emulsion with mono-disperse drops (the signal of the matrix has been suppressed) and a gel-network with free diffusion for short times and restricted diffusion for long times.

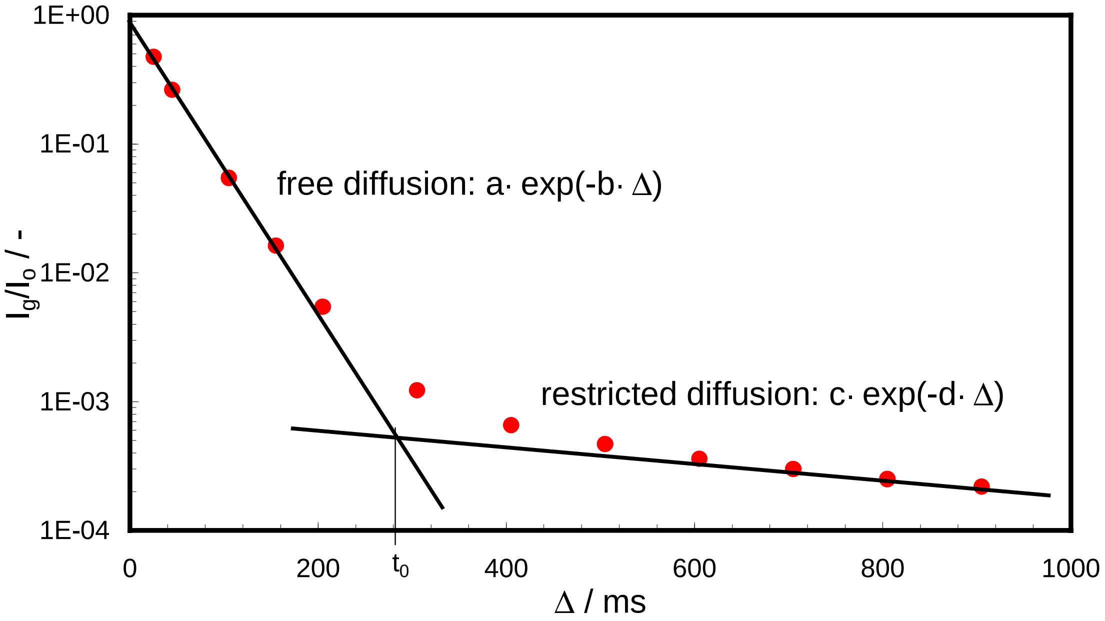


Fig. 3.3.2. Definition of free and restricted diffusion for a gel and method to derive the self-diffusion coefficients at free D_{Sf} (~ b) and restricted D_{Sr} (~ d) diffusion and of the critical pore radius r_c of the gel matrix from the results of the NMR diffusion experiments I_g/I_0.

The characteristic pore-size r_c might be relevant, for example, for the microbiological stability of food gels. The permeability which correlates with D_{Sr} is presumably relevant for the filtration behaviour of a porous media, especially for the washing of filter-cakes or the syneresis of gels. Besides the diffusion coefficients D_{Sf} and D_{Sr} and the critical pore-radius r_c, further parameters characterising the structure the pore-system can be derived from the dependence of the self-diffusion coefficient on the effective diffusion time:

- the tortuosity $T = D_{Sf}/D_{Sr}$ (Latour et al. 1993; Hürlimann et al. 1994; Kärger 1996; Kärger et al. 1998) or $T = [(1-\phi)D_{Sf}/D_{Sr}]^{0.5}$ with the mean porosity ϕ (Epstein 1989) (The tortuosity T characterises the distance travelled by a diffusing particle or fluid-element in a structured medium compared to the actual geometrical distance.),
- the surface-to-pore-volume ratio (specific surface) S/V with S pore surface area and V the pore volume (Kärger 1996; Swiet et al. 1996; Price 1997), derived from this (Eq. 3.4.11)
- the pore size distribution in combination with a T_1-experiment (Davies et al. 1991; Latour et al. 1995),
- characteristic lengths r_{ch} of the pore-system (Holz 1986; Kärger et al. 1988),
- the permeability of the pore-system (e. g. Sen et al. 1990; Watson and Chang 1997; Frosch et al. 2000).

The definition of the tortuosity by Epstein (1989) is less usual. Assuming spherical pores r_{ch} is 3V/S. The permeability of the pore-system can be calculated from the tortuosity and the surface-to-volume ratio with the help of models like Carman-Kozeny (1948, 1956; 1929) or Gupte (1970). The permeability is important for the oil production and the de-wetting/wetting or de-aeration/aeration of packed beds for example filter-cakes (Hürlimann et al. 1994; Latour et al. 1995, Friedmann and Windhab 1998; Frosch et al. 2000). Further quantities concerning microscopic and macroscopic properties of porous media (e. g. Watson and Chang 1997, Barrie 2000) which can be determined or derived from NMR experiments are presented in chapter 3.4.

The maximum diffusion time is mainly limited due to the T_2-relaxation for a 90°-180° sequence (PGSE) and due to the T_1-relaxation for a 90°-90°-90° sequence (PGSTE) (Tanner 1970). As $T_1 \geq T_2$, the 90°-90°-90° sequence allows longer diffusion times and longer diffusion lengths to be studied, especially in samples with short T_2-relaxation times. PGSE NMR is limited to dynamic displacements between approx. 10 nm and 100 μm (Callaghan 1991).

For Brownian diffusion the motion of single particles in a studied spin ensemble is incoherent and isotropic. In the case of an external driving force, for example a pressure gradient ∇p (Seymour and Callaghan 1997; chapter 3.2) or an electric field $\mathbf{E}$ for ions in a solution of electrolytes, a coherent anisotropic motion is superposed to the incoherent isotropic motion due to molecular diffusion. This induces a phase-shift of the spin-echo amplitude, additionally to the attenuation of the spin-echo amplitude caused by diffusion. The possibility to realise longer distances migrated by the studied particles than in diffusion experiments (limited by relaxation mechanisms, see above) is given by a combination of PFG NMR and in-situ electrophoresis, which is called Electrophoretic NMR (ENMR) (Holz et al. 1993; Holz 1994). ENMR allows one to study the electric transport due to additional applied electric fields in fluid-filled porous system and to derive information concerning the structure of the pore-system (Heil 1999; Holz et al. 2000). If the pore-system is in first approximation independent of the temperature, the observed distances can be increased by increasing the temperature.

Many disperse systems are not only heterogeneous at a microscopic scale, but also at meso-/macroscopic lengths. In some cases the heterogeneities are caused by sedimentation (e. g. sedimentary rocks), phase separation (creaming-up) including syneresis (e. g. dairy products, mustard, ceramic-gels), mechanical loading, swelling, the use of fillers/fibres (polymeric systems), production-imperfections or process-specific heterogeneities like different morphology of core and shell zones in many foams (e. g. Fig. 3.1.2). Hence it is desirable to infer structural data (e. g. tortuosity, S/V), which are spatially resolved by a combination of MRI and Dynamic Imaging methods (diffusion, flow and ENMR). This is especially helpful, if the characteristic lengths of the solid matrices are below the spatial resolution of conventional MRI techniques (Tillich 2002). As mentioned above (chapter 3.1) it is, furthermore possible to realise self-diffusion coefficient D_S-weighted images (Eq. 3.1.3). D_S-weighted MRI is generally less time-intensive as direct MRI of D_S. In the following chapter examples for the application of PFG NMR for the study of restricted diffusion are presented. These applications are classified with regard to the type of the solid systems, which is, however, not unambiguous for all samples.

Gels

PFG NMR allows to quantify the effect of the composition, of the pH-value, the ion-concentration (e. g. calcium), the concentration of sugars, the denaturation fraction of proteins and the impact of the processing or process conditions on the structure in gels (e. g. dairy products) (Götz et al. 2004d, Hinrichs et al. 2003). Five whey protein concentrate (WPC) gels were made of 15 w/w-% whey protein powder (Isolac: Bayerische Milchindustrie eG, Landshut, Germany) dispersed in distilled water and heated for 10 min at 85 °C in order to denaturate the whey proteins (Table 3.3.1) (Hinrichs et al. 2003). For the pure whey protein isolate solutions r_c is the smallest, for the protein solution with HCl the pore radius is the largest. The three parameters D_{Sf} , D_{Sr} and r_c do not seem to correlate with one another.

After the thermal treatment the five materials differ completely with regard to their optical appearance (transparent, milky, opaque, shiny), the firmness of the gel and the structure (fibrous, smooth) (Table 3.3.1). It is plausible to assume that the critical pore radius r_c , like the average drop radius of water in w/o-emulsions, is relevant for the microbiological stability of the gel. The diffusion coefficient of the serum D_{Sf} and, even to a higher extent, the permeability D_{Sr} presumably correlate with the texture, the sensorial (e. g. sandy) and syneresis-behaviour of the gel. It has to be confirmed by further experiments that the quantities mentioned above and other macroscopic quantities correlate with microscopic parameters derived from the NMR-diffusion tests (D_{Sf} , D_{Sr} and r_c). Thus, after an appropriate calibration, macroscopic quantities important for the production might be determined by means of NMR experiments.

Table 3.3.1: Qualitative macroscopic of the studied aqueous solutions of whey-protein isolate (15 % w/w)

Protein Solutions	**Properties**
aqueous solution of whey-protein isolate	no gel; yellowish, transparent
plus NaOH with pH = 9.5	soft; whitish, transparent, shiny
plus HCl with pH = 5.4	firm; fibrous, white
plus $CaCl_2$ (0.2 g/kg)	soft; smooth, white
plus $CaCl_2$ (2 g/kg)	firm; fibrous, white

It is, furthermore, possible to observe structural changes due to sol-gel transitions [induced by hydrocolloids like gelatine, carrageenan and starch (Götz et al. 2004d) or thermal denaturation Götz et al. 2004d)], their temporal evolution, dependence on denaturation temperature, denaturation duration, denaturation fraction or ageing-processes during storage like syneresis (e. g. Ohtsuka et al. 1994). Transport processes containing pore-matrices are not only relevant for the storage behaviour, but also for the possibilities to add further components (e. g. polymers: additives; foods: salts, sugars, aroma substances) and achieve an optimal compositional/structural homogeneity after appropriate mixing. The addition of components of an applied recipe is an important element of many production-processes in food- and non-food-technology.

Knauss et al. (1996) detected by a combination of PGSE NMR and T_2-relaxation two fractions of water in collagen II/water gels. One has a short T_2 and a high diffusion coefficient, and the other a long T_2 and an almost vanishing diffusion coefficient. The slowly diffusing, molecularly high mobile (due to long T_2) water fraction is retained in channels traversing a collagen fibre of approx. 2.3 μm. The second fraction represents water bound to collagen.

Kimmich et al. (1993) determined diffusion coefficient D_S of aqueous proteins systems as a function of protein concentration and temperature. D_S increases with increasing temperature and water-content. In the frozen state no dependence of D_S on the protein-concentration (myoglobin: $c_P < 70.2$ %) can be determined due to the still liquid hydration water. For room temperature the protein-concentration was varied from dilute solutions to wet powders which are only partly hydrated. D_S decreases about four magnitudes. The diffusion behaviour might be schematically described differentiating three regimes: In Range 1 (high water-content) free water dominates, whereby the diffusion of water is obstructed by macromolecules (Wang 1954). In Range 2 for reduced water-content the fraction of hydration water increases, the hydration shells are presumably in contact with one another. In Range 3 the connectivity between layers of hydration water is reduced. Analogous experiments have been performed in cellulose derivatives membranes and particles (Volkov et al. 1996), starch-sugar-water systems (Farhat et al. 1997) and casein dispersions and gels (Mariette et al. 2002).

Ohtsuka et al. (1994) studied potato starch gels as a function of storage time and starch concentration. D_{Sf} and D_{Sr} decrease with the starch concentration. For constant starch concentration D_{Sf} decreases with increasing storage time (up to 4 days). During retrogradation the amount of the dispersed starch-molecules decreases caused by an aggregation with the already existing network. The simultaneous recrystallisation reduces D_{Sr}, which is more significant for lower starch concentrations. The pore radius r_c is approx. independent of the concentration, but decreases with time. Ohtsuka and Watanabe (1996) investigated the effect of the concentration of K^+ and Ca^{2+} on the gelation of gellan gum. The correlation between D_{Sf}, D_{Sr} and r_c characterises different sol and gel states. Sufficiently high ion-concentrations, specific for the applied ion, induce aggregation of the helices of gellan molecules via junction zones forming a gel-network. The structure of K^+- and Ca^{2+}-induced gels are identical with respect to D_{Sf}, D_{Sr} and r_c, but the three network-structures develop for different ion concentration intervals. Watanabe et al. (1996) studied the formation of dextran-gels which can only be caused by K^+ and not by other ions. In dilute dextran-solutions with K^+ homogeneously distributed, not aggregated dextran coils hinder the diffusion of water. In the gel-state for higher dextran concentrations K^+ are involved in the formation of cross-links and the aggregation of chains. Thus the K^+-concentration in the increased pore-volume (r_c increases) decreases, combined with an increase of D_{Sf}. The permeability D_{Sr} decreases with the K^+-concentration.

Balcom et al. (1997) developed an MRI method to determine Fickian diffusion coefficients in gels by paramagnetic tracer ion diffusion. 1D experiments are performed on a sample which consist half of the gel, half of the solution of the paramagnetic tracer. The evaluation is based on the correlation between the longitudinal relaxation time T_1 and the concentration of the paramagnetic tracer C (Abragam 1961)

$$\frac{1}{T_1} = a + b \cdot C \tag{3.3.13}$$

a, b parameters

The derived evolution of the concentration of the paramagnetic tracer C allows one to determine Fickian diffusion coefficient by fitting it with known formula for the diffusive mass transport (e. g. Barrer 1951).

Emulsions

Emulsions are dispersions of two or more fluid phases which are hardly soluble in one another, mostly water and oil. At least one disperse phase is dispersed in the form of drops in a continuous phase, often stabilised by surface active agents. Water-in-oil (w/o) emulsions with water drops in a continuous oil phase and oil-in-water emulsions (o/w) are common emulsions (e. g. Lagaly et al. 1997; Teipel 1999). Many food emulsions are, however, not included in this traditional definition, for example if the disperse phase is partially not liquid (e. g. solid fat), contain crystallites (e. g. ice-cream) or gel-structures (Mooren et al. 1995). Emulsions are used as food, washing and cleaning agent and are applied in the cosmetic, pharmaceutical, photo, textile or plastic industry. Emulsification processes play an important role for the digestion of fat in the digestive tract and the transport of lipoid substances in blood circulation. Milk and mayonnaise are o/w-emulsions, whereas butter, margarine and related spreads are w/o-emulsions. Further examples are water-soluble varnishes, cremes and ointments (Karbstein 1994).

The droplet size distribution in food emulsions is correlated with the rheology, which is essential for the spreadability, mouth-feeling, melting behaviour, especially in the mouth, the shelf-life, the flavour of the product and the appearance of the product. Ingredients (emulgators and stabilisators, the composition of the fats) and the process parameters of the production (e. g. temperature for cooling, residence time in the cooler, type and intensity of the emulsification) have a great influence on the final droplet size distribution (Dinkelmeyer and Weisser 1997). Hence, droplet size distributions are often applied as quality and process control and for the optimisation of the production or the product-quality. Usually microscopic methods are used for the determination of droplet size distributions (Jokela et al. 1990). These methods are time-consuming and require a preparation of the samples.

In w/o-emulsions or o/w-emulsions the diffusion of water or fat molecules is restricted within the spherical water or fat droplets, respectively. This means the self-diffusion coefficient for restricted diffusion D_{Sr} vanishes and the ratio of the spin-echo amplitudes with and without gradient, I_g/I_0, keeps constant as a function of the diffusing time $\Delta > t_0$ (Fig. 3.3.1). A prerequisite is that the signal of the continuous phase has been suppressed by appropriate techniques. Based on the model of Packer and Rees (1972) who assumed a log-normal distribution of droplet sizes the mean droplet size diameter ($D_{3.3}$), the corresponding standard deviation and the diffusion coefficient of the fluid within the droplets can be determined by PFG NMR (Packer and Rees 1972; Callaghan et al. 1984; van den Enden et al. 1990; Mooren et al. 1995; Dinkelmeyer and Weisser 1997; Ambrosone et al. 2000). Usually products with small water droplets are preferable to those with a few larger droplets, since large water droplets can be infested by bacteria, degrade microbiologically and thus reduce the shelf-life of the corresponding product. This method is established in industry as quality and process control.

An analogous method has been developed to determine the droplet size distribution of oil droplets in o/w-emulsions such as mayonnaise, dressings and soft cheese (Callaghan et al. 1983). The NMR diffusion method does not require any preparation like dilution. Another advantage is that, due to the non-destructive character of NMR, experiments can be repeated to observe the storage behaviour of products (Söderman 1997). Spatially resolved PFG NMR, furthermore, enables one to detect and to observe the evolution of processes like creaming-up or coalescence. These processes change the flow behaviour and limit the shelf-life of emulsions. Highly concentrated emulsions have up to 99 % (v/v) dispersed phase (Söderman 1997). The droplets are separated from one another by films of about 10 nm which are not completely impermeable. In addition to the pore-size distribution the droplet-droplet distance and the permeability of the films (D_{Sr}) can be determined. Cornillon et al. (1997) determined by PGSE the pore-size in freeze-dried starch-gels which were saturated with octane after freeze-drying.

Using a combination of various ^{31}P NMR techniques it is possible to study the microscopic behaviour of a stearyl phosphate emulsifier in cosmetic o/w emulsions (Plass 2001; Plass et al. 2001). Emulsifier bound in the interfacial zone can be observed by High Resolution spectra (chapter 3.4). The amount of the excess emulsifier, which does not stabilise the emulsion, can be detected in the lipid phase as solid (solid state cross polarization magic angle spinning: CP-MAS). The emulsifier-concentration at the interface is constant above a critical global emulsifier-concentration. Both (i) the ratio T_2/T_1 in ^{31}P NMR (e. g. van de Ven 1995; Kimmich 1997), which is significantly smaller than one, and (ii) PGSE-diffusion experiments in ^{31}P NMR suggest an anisotropy of the molecular motion of the emulsifier, which decreases with increasing droplet size. The diffusion coefficients in emulsions are about four magnitudes smaller than that of emulsifier dissolved in deuterated tetrahydrofuran. They decrease with increasing diffusion time Δ indicating restricted diffusion.

Cell suspensions are a transition link between emulsions and suspension with solid particles. Cells are highly deformable whereby the deformability depends on their suspension medium and their metabolic state (Torres et al. 1998). Kuchel (2001) used PGSE to differentiate intra- and extra-cellular water fractions in red blood cell suspensions, to measure the permeability of the cell membrane to various solvents and to determine the mean cell dimensions and their deviations.

Polymers

Chemical environments, to which polymers are exposed to, usually have a strong impact on physical properties of polymers like the mechanical, optical and barrier behaviour (e. g. van Krevelen 1990; Piringer 1993). The sorption-, permeation- and migration-behaviour of many polymers show a strong dependence on the polarities of polymer and solvent (Piringer 1993). Fluid ingress into polymers can cause swelling (e. g. Gao and Mackley 1994), plasticisation and crystallisation (Overbergh et al. 1975), and in some cases also dissolving of the matrix or delamination in the case of composite-films (Crank 1956).

Some permeants induce, furthermore, chemical reactions causing degradation or hardening which will enhance (chain scission) or reduce (embrittlement due to cross-linking) the permeation rate, dependent on particular details of the phenomenon and its evolution (Campion 2000). Swelling and crystallisation induced behind the diffusion front of the permeant might lead to cracks in the polymeric material due to volume-changes. The plasticising effect of penetrant molecules is combined microscopically by an increase of the polymer segmental motion. If the polymer is in the glassy state, the plasticisation lowers the glass-transition temperature T_g (Sperling 1992). Macroscopically the plasticising effect can be described by a dependence of the translational diffusion coefficient on the solvent concentration (Webb and Hall 1990).

Diffusion plays an important role in polymeric materials used as foams (foaming-up and the subsequent degassing of aerating agents), for recently produced polymers (the desorption or removal of monomers or oligomers), as seal- and tube-materials (e. g. permeation and migration of fuels), as selective membrane (perm-selectivity) and as food packages. Plastic films have the disadvantage of transport phenomena between product and environment due to permeation and between product and package due to migration. Low-molecular substances migrate out of (i) the plastic into the food (e. g. O_2, monomers, plasticiser and solvents) and out of (ii) the food (CO_2 for carbonated beverages, aroma compounds, acids, vitamins) into and through the packaging. This aspect (i) is relevant with respect to food laws and eventually the toxicologic evaluation, (ii) reduces the quality and eventually the shelf-life of the product.

The solubility and permeability of a solvent/polymer combination are the principal criteria for the applicability of a polymeric material. A deterioration of the material behaviour by migrated substances, for example with regard to the mechanical stability, the impermeability or the dimensional stability, must be excluded. This requirement is especially important for plastic food packages or plastic bottles which have to be alkali-proof during the cleaning process when used as returnable containers.

The presently used methods to analyse the compatibility between polymers and diffusing substances are (i) the study of the swelling behaviour by measuring the length of a film made of the test-material (Wissinger et al. 1987, 1991), (ii) the determination of the amount of dissolved gas/fluid in the sample (Gorski et al. 1986), (iii) X-ray technique and (iv) radioactive tracer studies (Crank and Park 1968; Crank 1956). Disadvantages of the existing methods are:

- They are time-intensive.
- Integral data do not allow one to derive concentration distributions and thus to characterise the mass transport, the interactions and the swelling behaviour.
- Often specially prepared samples and not final products can be studied.

Advantages of NMR are:

- Besides the possibility to monitor the evolution of the solvent-concentration in the polymer non-destructively and non-invasively,
- Heterogeneities of the diffusion behaviour can be detected and quantified. Using other techniques, especially if these do not provide spatially resolved data, these effects are averaged and might be misinterpreted and cause higher apparent measuring errors.
- The diffusion process can completely be studied by means of NMR using one single sample, thus reducing systematic errors.
- NMR techniques allow one, furthermore, to study other diffusion phenomena including migration, desorption, self-diffusion of solvents in polymers, multi-component diffusion in polymers and dissolving of polymers by solvents (Weisenberger and Koenig 1989).

Serial MRI enables one to identify the three diffusion mechanisms proposed by Alfrey et al. (1966). Criterion for the classification is the ratio of the diffusion rate and the so-called rate of the mechanical relaxation (Crank 1956). The mechanical relaxation rate describes the temporal response of the polymer or polymer chains for achieving equilibrium, after the polymer has been exposed to an altered condition with regard to concentration, temperature or mechanical stress. The three classes are:

- *Case I-* or *Fickian diffusion*: The rate of diffusion is smaller than the rate of relaxation of the induced structural modification of the polymer. Case I systems are diffusion controlled. Case I-diffusion is valid for rubber-like elastomers above the glass-transition temperature. The distance diffused by a species and simultaneously the sorbed mass are proportional to $t^{0.5}$. Examples of this $t^{0.5}$-behaviour observed by different NMR techniques are vulcanised rubber/benzene, isooctan, acetone and cyclohexane (Webb and Hall 1990, 1991), polycarbonate (PC)/acetone and acetone/methanol (Ercken et al. 1995), polyhexamethylene adipamide (Nylon 6.6)/water as function of temperature and pressure (Mansfield et al. 1992). In all studied systems the solvent concentration decreases towards the centre and the solvent mobility (T_2) keeps constant.
- *Case II-* or *relaxation-controlled diffusion*: The rate of diffusion is higher than the rate of relaxation of the structural modification of the polymer (e. g. Frisch 1980; Thomas and Windle 1982; Kuipers and Beenackers 1990). Many glass-like polymers show Case II-behaviour. The Case II-diffusion is characterised by an advancing front with constant velocity, separating the sample into the initially glassy zone and, after sorption, the often swollen gel-zone with constant solvent-concentration. A Fickian concentration profile is in front of

the sharp front (Mills et al. 1986: Rutherford backscattering spectrometry). T_2 and thus the molecular mobility of the solvent and the polymer decrease towards the glassy zone (Weisenberger and Koenig 1990). The uptake of solvent is proportional to the time t. Examples for Case II-diffusion are PMMA/acetone, methanol (Weisenberger and Koenig 1990), PMMA/methanol (Weisenberger and Koenig 1989; Koenig 1992) and PVC/acetone (Perry et al. 1994).

- *Non-Fickian* or *anomalous diffusion*: The diffusion and the relaxation rate are comparable. The mass uptake lies between $t^{0.5}$ and t or changes from one to the other behaviour. Examples are porous polypropylene (PP)/polydimethylsiloxane (PSMS) (Appel et al. 1996b), acetone-preswollen (8 % w/w, -4 °C) PMMA/methanol (Lane et al. 1998).

Models describing the linear uptake of solvent usually assume that the swelling of viscoelastic polymers at the penetrating front is rate-limiting for the solvent transport in the polymer matrix (Thomas and Windle 1982). McDonald et al. (2001) found that alternatively, as long as the solvent-induced glass-transition takes place, the surface flux of solvent can limit the diffusion. Furthermore, a change between Fickian and Case II-diffusion can be induced. Especially for long times and large enough systems, the diffusion becomes Fickian. The experimental data can be confirmed by numerical simulations for polystyrene (PS)/toluene.

Tabak and Corti (1990) visualised by means of serial MRI of the spin density and T_1 the increase of the mobility of polymer chains (PMMA, PS) due to the swelling of a polymer matrix in contact with deuterated chloroform ($CDCl_3$) and carbon tetrachloride (CCl_4). The use of deuterated vapours guarantees that only the solid matrix contributes to the signal. T_1 as a measure of the average local correlation time characterises the mobility of the chains. It can be found that even in zones of constant spin density - exactly of the sufficiently mobile and thus detectable fraction of polymer-spins - the distribution of T_1 is not homogeneous. Obviously it takes more time for the polymer chains to achieve dynamical equilibrium than to "activate" mobile polymer chains. Hyde and Gladden (1998) performed two experiments in order to measure simultaneously the water and the polymer polyethylene oxide (PEO) concentration during swelling. The ingress of water into PEO was studied first using D_2O and serial MRI. H_2O was used for the second set of experiments using T_1-weighted serial MRI. T_1 of water in the gel varies approx. linearly with the local moisture content. T_1 of the polymer in the gel does not really depend on the moisture-content. Thus it is plausible to assume that the mobility of the polymer chain segments remains constant, after the polymer-molecules have been in contact with permeated water.

For several polymer/solvent combinations the amount of the migrated and permeated substances depends on the solvent-concentration (Crank 1956). This holds for example for fatty food products in contact with plastic packages. A review of recent MRI studies on diffusion is given by Harding et al. (1997). The ingress of isooctane (used a model-petrol) and olive oil into various polymers [high density polyethylene (HDPE), low density polyethylene (LDPE)] with different concentration of additives was studied by serial MRI. Additionally to the MRI, PGSE NMR was applied in order to determine the local self-diffusion coefficient. By a combination of the two techniques diffusion coefficients as a function of the solvent concentration can be derived. These data are required for numerical simulations of diffusion phenomena in plastic food packages. Seland et al. (2001) studied the diffusion in compact and porous polymer particles. The diffusion coefficients and derived from this the tortuosity depend in porous PE particles on the solvent and the filling degree of the solvent. Appel et al. (1995, 1996a) recorded the evolution of the uptake of silicone oil in the PS matrix of the two phase system PS/silicone oil by determining the critical pore-radius of silicone-oil droplets embedded in the PS/silicone oil. The diffusion of silicone oil into the polymer system is too slow to be detected directly by means of the self-diffusion coefficient. The diameter of oil droplets, however, can be determined by PFG NMR. The droplet size decreases with the temperature which is due to the solution of silicone oil in the PS matrix.

The diffusion of solvents into glassy polymers may cause a decrease of the glass-transition temperature combined with swelling and a transition from a glassy polymer into a rubber-like polymer with modified mechanical behaviour (e. g. van Krevelen 1990; Piringer 1993). On the other hand a mechanical treatment (elongation or shear deformation) might induce a structural anisotropy combined with changed, anisotropic mass transport properties [Reese et al. (1996): gelatine]. The barrier properties can be changed both during and after the mechanical loading. The prehistory/pretreatment of the polymer materials may influence the barrier properties of polymers, for example by orientation of fillers, fibres or crystallites or by changing the level of crystallinity in semi-crystalline thermoplastics caused by the fabrication. Examples are the extrusion and eventually the subsequent orientation applied for OPP (oriented polypropylene) films or the blow moulding of PET (polyethylene terephthalate) bottles (Thomson et al. 1998; Campion 2000). Fillers with a permeability smaller than the polymer or, additionally in elastomers, an increased cross-link density also reduce the integral permeability of the polymeric material.

Abbott et al. (1998) observed the ingress of carbon tetrachloride, toluene and cyclohexane into extruded PP (Case II-diffusion) by means of Stray Field Imaging (STRAFI) and MRI. The absorption rate through intact moulded surfaces is approx. 40 times smaller than the rate through the cut ends. Rapid cooling at the surface during the extrusion causes the polymer molecules to keep a significant orientation along the flow direction. The core cools down slower in combination with a smaller degree of molecular orientation. The skin layer has a thickness of about 15 µm (Sawyer and Grubb 1987). If the surface layer is removed, the normal (perpendicular to the original flow direction) diffusion is as high as the transversal (parallel to the original flow direction) diffusion. MRI shows that the fabrication and the corresponding process conditions might induce inhomogeneous anisotropic barrier properties of extruded polymer products. This could be applied to produce inexpensive coatings with reduced permeability.

If the sorption/diffusion behaviour of a polymer-system/solvent for which the solvent-uptake has a deleterious effect on the technical characteristics of the product, the time of the failure can be reliably estimated (Webb and Hall 1990). The lifetime of the product for a multicomponent solvent diffusion can, however, not be predicted based on the knowledge of the unicomponent data due to mutual interactions of the penetrants and the polymer material and the solvents. Examples are (i) foods, especially when containing fats (Piringer 1993) or cyclic mono-terpenes like limonene (Götz 1999), in contact with plastic packages causing delamination of composite-foils or (ii) fuel-lines or tank materials reducing their barrier properties in the presence of methanol (Twardon et al. 1999).

This complex of problems includes also the ingress of solvent A into a polymer previously saturated or partially saturated with solvent B. In order to distinguish different species diffusing in polymeric materials, mixtures with mutually deuterated components, selective-excitation, selective-suppression, relaxation times scalar coupling or STRAFI have been used.

Webb and Hall (1990) observed that the diffusion rate of isooctane in vulcanised rubber (VR) preswollen with cyclohexane exceeds the diffusion rates of both unicomponent solvents. In contrast, for an acetone/water mixture in VR the water-uptake is not enhanced by acetone and that of acetone significantly reduced (Webb and Hall 1991). The reason for the extremely low diffusion rate of water in VR are interactions with hydrophilic sites within the VR. Strong interactions between water and acetone reduce the uptake of acetone compared to the unicomponent diffusion in VR. In an acetone/benzene mixture the two components diffuse with the same rate in VR, acetone faster and benzene slower than in single-component diffusion. A model of the influence of so-called hydrophilic impurities on permeation processes in polymers is given by Muniandy and Thomas (1984).

Grinsted and Koenig (1992) studied the multicomponent diffusion of acetone/methanol mixtures, with one component deuterated for each series of experiments, into polycarbonate (PC) rods using serial MRI. Above a critical concentration of acetone two separate diffusion fronts are observed, with acetone diffusing faster than methanol. Acetone decreases the glass-transition temperature T_g from 149 °C to -9 °C thus inducing Fickian instead of the originally expected Case II-diffusion. Translational diffusion coefficients D_F (Eq. 3.3.2) are derived from the evolution of the concentration distributions by fitting them with known theoretical formula (e. g. Crank 1956). Simultaneously the applicability of the used modelling can be tested. The translational diffusion coefficient increases with increasing acetone concentration, presumably due to the increased molecular mobility caused by acetone in the polymer. The molecular mobility is characterised and monitored by T_2 (Lane and Donald 1997).

Lane and McDonald (1997) characterised the diffusion of methanol/acetone vapour-mixtures into PMMA. By using completely deuterated vapour-mixtures changes of the polymer chain dynamics due to the solvents can be visualised. The solvent velocity front increases linearly with an increasing acetone fraction in the methanol/acetone mixture. In order to quantify eventual synergistic or antagonistic effects in a mixture of solvents on the individual ingress rate into a polymer below its glass-transition temperature T_g, further experiments are performed (Lane et al. 1998): (i) the ingress of liquid methanol/acetone mixtures, with one component deuterated, into pure PMMA and (ii) the ingress of methanol into PMMA preswollen with acetone of different concentrations. The experiments (i) show that the velocity of the front of the two components are identical. The objective of (ii) is to quantify an eventual reduction of the barrier behaviour due to residual solvents, for example monomers left from the synthesis. (ii) shows that the rate of methanol uptake is increased in acetone-preswollen PMMA. There is a transition from Case II- to Fickian diffusion above a critical acetone concentration. The presumption that T_g in the acetone-preswollen PMMA (8.5 % w/w) is lower than that in pure PMMA can be confirmed by Differential Scanning Calorimetry (DSC): $T_g(8.5\ \%) = 70.6$ °C and $T_g(0\ \%) = 109.9$ °C.

Mixtures of methanol and toluene are often used as model fuels to study the permeation of fuels or constituents of fuels through polymeric tubes and tanks. The evolution of the two-component desorption of a methanol/toluene mixture out of a plane sheet of industrially applied polymeric fuel-line material (thickness: 6.2 mm, orientated parallel to the $\mathbf{B}_0$-axis) saturated by the mixture at $t = 0$ is recorded by serial MRI with selective excitation of methanol and toluene. In Fig. 3.3.3 the schematic set-up for the desorption test of a pre-saturated polymeric material is illustrated. The sample was placed into an NMR test tube. On the left side of Fig. 3.3.3 is the open end, on the right side the closed end. Fig. 3.3.4 shows one-dimensional concentration profiles of methanol and toluene, respectively, through the centre of the sheet. The desorption fronts migrating into the material demonstrate that the diffusion of methanol and toluene is obviously non-Fickian. Further studies are, however, required to quantify the swelling/deswelling and to discriminate volume-changes from the ingress of the desorption front into the interior of the polymeric material. Different desorption behaviour of toluene and methanol can, however, be observed. The concentration of toluene in the interior is approx. constant and has slightly developed maxima at the transition to the desorption front. The methanol profiles reveal, besides the apparent existence of a desorption front, a Fickian-like behaviour. The concentration profiles are not symmetric due to closed lower end of the NMR test tube.

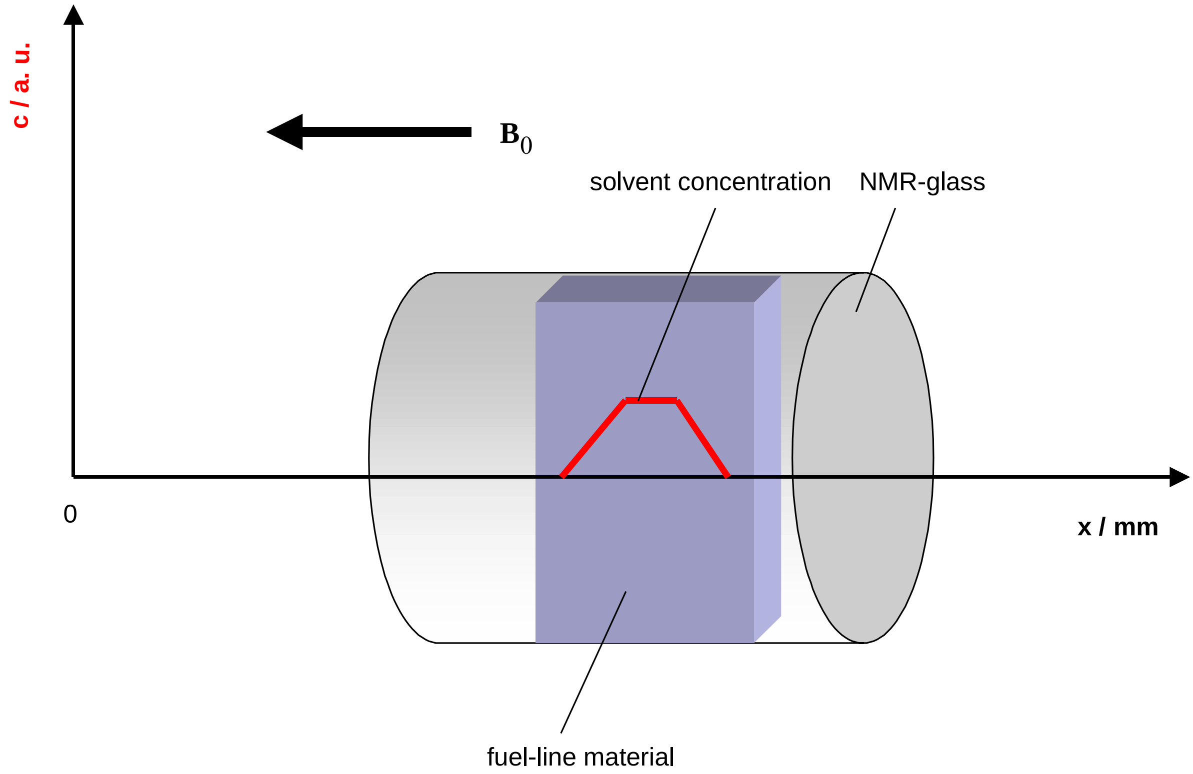
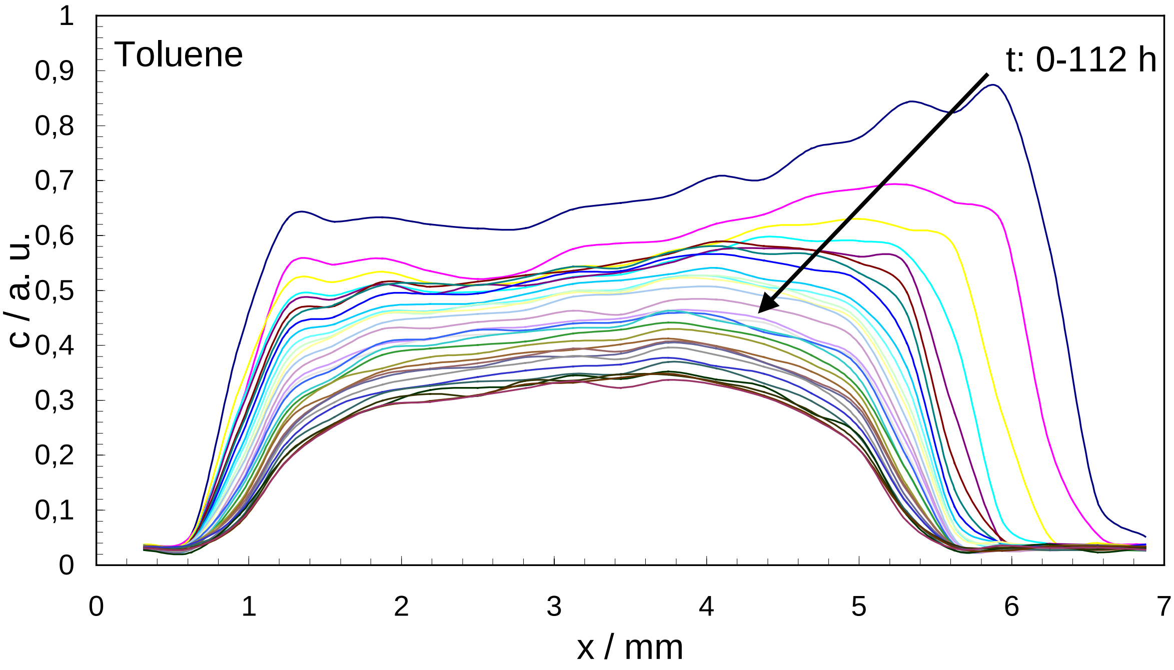


Fig. 3.3.3. Schematic experimental set-up for the desorption test of a pre-saturated polymeric material. The drawing is not true to scale, in favour of a better understanding, especially the dimensions of the fuel-line material and the test-tube.



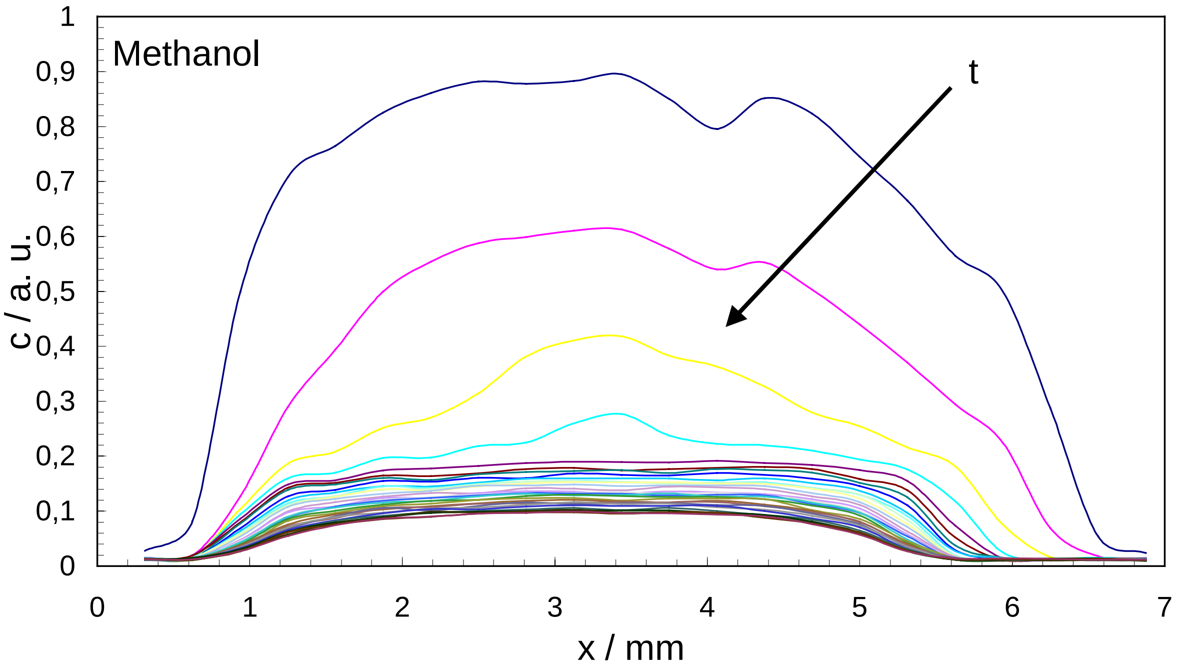


Fig. 3.3.4. Serial MRI (interval between two images: 4 h) with selective excitation of concentration profiles of toluene and methanol for the desorption out of plane slice of fuel-line material, thickness: 6.2 mm (Götz et al. 1997). The tube material is saturated (t = 0) with a mixture of toluene/methanol 1:1 (w/w). Concentration profiles. Measuring sequence: Spin Echo 1D with the sequence-parameters: FOV = 10 mm; number of pixels N = 32; spatial resolution: 0.31 mm; TE = 1 ms; TR = 1000 ms; averages: 2, total measuring time of a single experiment: 34 min.

Porous Foods and Starting Products, Biological Materials

When drying capillary-porous material by a convective stream of air or, generally, gas, three characteristic time-phases can usually be distinguished (e. g. Krischer and Kast 1978). During the experiment the air temperature ϑ_∞, the air velocity w, the air humidity Y_∞ and the air pressure p are kept constant. The drying rate in phase 1 is, in contrast to phase 2 and 3, independent of the properties of the material to be dried. The drying process of non-hygroscopic capillary-porous materials is completed at the end of phase 2. Hygroscopic capillary-porous materials, however, contain even after phase 3 the so-called hygroscopic equilibrium moisture. Analogous to the classification of diffusion mechanisms in polymer materials (Alfrey et al. 1966) Schlünder (1976) supposed four principal mechanisms for the drying process. The relevant parameter is the moisture conductivity κ in the product which is (1) infinite, (2) vanishing, (3) proportional to the moisture X or (4) proportional to X and infinite above a material-specific moisture X_o.

Due to the complexity of the processes in phase 2 and 3, including the water transport in the fluid- and gas-phase, the hygroscopic bonding of water to the solid material and the heat transport through eventually incompletely dried zones of the sample with varying moisture content, it is still not possible to predict the evolution of a material with sufficient accuracy (Gnielinski 1998). As many industrial products show a drying behaviour which is composed of the four mechanisms, methods to record the integral drying kinetics like weighing do not allow a complete or even comprehensive characterisation of the drying process. The design of drying processes is, therefore, still based on empirical knowledge and additional practical experiments.

Regier et al. (2002) studied the microwave vacuum drying of fruits by MRI of the spin density and the self-diffusion coefficient. The aim of the study is a deeper understanding of the correlation between electromagnetism, heat and mass transfer. Based on this knowledge the local and integral power input might be reduced and simultaneously the process and the product-quality be optimised. The translational diffusion coefficient describing the moisture transport through the food matrix can be derived from the self-diffusion coefficient measured by PGSE NMR. The diffusion coefficient and the real and imaginary parts of the electrical permittivity ε' and ε'' are dependent on the temperature and the moisture content (Regier and Schubert 2001). Usually regions with higher moisture content absorb more energy due to higher dielectric loss. The fruit-samples show an inhomogeneous moisture-distribution after the microwave drying (Regier et al. 2001). The applied power/time programme has a strong impact on the moisture profiles obtained. In some cases the water concentration in the centre is significantly smaller than in the surrounding zones. Heterogeneities in the moisture content are problematic, since zones with local high moisture and high water activity can cause spoilage and decrease the micro-biological stability of the product.

PGSE NMR experiments enable one to record the evolution of the structural changes during the microwave vacuum drying of fruits (Badalato et al. 2001). The self-diffusion coefficients decrease with decreasing moisture. That means the moisture transport is controlled by the fluid phase and not the gas phase. The tortuosity T is approx. 4 and decreases slightly as a function of the moisture. The critical pore radius r_{ch} decreases during the drying process which corresponds to the macroscopically visible shrinkage of the fruit samples. The surface-to-pore-volume ratio S/V increases with decreasing moisture, presumably due to the shrinkage of the pores and cells having a larger surface and/or a smaller volume. The self-diffusion coefficients at the surface of dried fruit samples are higher than that of free water. This indicates that the moisture transport above a critical temperature is not only in the fluid-, but also in the gas-phase (Maklakov et al. 1993; Anisimov et al. 1998; Regier 2002). Maklakov et al. (1993) suggested for a partially saturated porous medium that liquid is present in the free pore volume as vapour, but also in a stable aerosol phase.

Nott et al. (1999) combined MRI of the spin density and the temperature T. For the determination of T the local phase was mapped using the correlation between the water proton chemical shift and the temperature (Hall and Talagala 1985). Another possibility to determine temperature distributions provides the so-called pseudo self-diffusion coefficients D_S^* which are considerably more sensitive to temperature variations than T_1 and even D_S (Le Bihan et al. 1989; Sun et al. 1994). Thus it is possible to observe the evolution of temperature profiles in the interior of materials during thermal treatments after preceding calibration.

Hopkinson et al. (1997) studied the ingress of liquid water and water vapour into pellets of amylose with serial MRI and PGSE NMR. A Fickian behaviour was found for the vapour and a Case II-diffusion behaviour for the water. Anisimov et al. (1998) and Novikov et al. (1998) showed how PGSE experiments can be extended to biological media containing sub-cellular compartments and cell-to-cell mass transport. Membrane permeabilities, the extension of compartments, diffusion coefficients and relaxation times inside these compartments are obtained by simulations of the restricted diffusion and the magnetisation transfer on the basis of Fickian law (Tanner 1979; Hills and Snaar 1992; Novikov et al. 1998).

With the help of diffusion experiments it is, furthermore, possible to characterise the pore-system in materials with anisotropic structure. In wheat grain endosperm tissue the position, orientation and inner dimensions of capillaries, which are randomly orientated in the tissue, can be determined (Callaghan et al. 1979). In cheese samples thin layers at the protein matrix with restricted diffusion are detected (Callaghan et al. 1983). The diffusion of water is confined to surfaces inside the protein matrix. Fat exists in cheese in the form of droplets. The droplet-size of fat globules in cheddar cheese which was also determined by PFG NMR is comparable with the size-distribution measured with electron microscopy (e. g. Kimber et al. 1974). Reviews concerning the application of restricted diffusion to food-based material like gels and tissues are given by Hills (1998).

Biofilms allow, in contrast to suspensions, the retention of microorganisms in a reactor, thus realising high biomass concentrations and short residence times (Karel et al. 1985). Biofilms can evolve spontaneously or they are cultivated for industrial processes like wastewater treatment (Characklis and Marshall 1989) or the production of fine-chemicals or beverages (Lommi 1990). For the modelling of mass transport processes concerning biofilms accurate diffusion coefficients are required. In contrast to other techniques irregularly shaped and inhomogeneous biofilms can reliably be tested with regard to their diffusive properties using PFG NMR (Beuling et al. 1998).

Non-Food Porous Media

Salt water ice can be characterised, additionally to MRI (chapter 3.1), by PFG NMR. Menzel et al. (2000) observed in salt water ice anisotropic self-diffusion and different critical lengths in all three dimensions by means of PGSTE. The samples were frozen in tubes (i) placed horizontally at constant temperature or (ii) placed vertically in a temperature gradient parallel to the tube thus introducing a preferred direction. Callaghan et al. (1998) obtained similar results for sea ice extracted in the Antarctica, using PGSE by means of Earth´s field NMR in the Antarctica.

Kärger and Pfeifer (1992, 1994) studied diffusion processes in microporous zeolites deriving information on the intracrystalline (short-time behaviour), the long-range self-diffusion (long-time behaviour) and the intermediate range. For the industrial application of microporous systems as adsorbents and catalysts multicomponent diffusion plays an important role. The difference of the diffusivities in zeolites for the single components in the mixture are usually smaller than that in unicomponent diffusion. The anisotropy of diffusion was studied by changing the direction of the magnetic field gradients. The ratio of the diffusion coefficients D_z and D_{xy} for the diffusion of methane in a ZSM-5-type zeolite crystallites, which are oriented parallel to the z-direction of the magnetic field $\mathbf{B}_o$, is about 0.2. A detailed description of characterising anisotropic diffusion and thus anisotropic structure by means of the diffusion tensor (or diffusion spectrum) is given by Callaghan (1991). Diffusion tensor imaging is at present principally used to characterise tissues (Basser et al. 1994a, b; Le Bihan et al. 2001). Thus information concerning the microstructure of tissues and their physiologic state are obtained which are not accessible by means of scalar quantities like relaxation times or apparent diffusion coefficients. There are no applications to polymeric materials in the literature known to the author. Problems are caused presumably by the required long echo times.

Hallmann et al. (1996) used PFG NMR of cyclohexane and PDMS (polydimethylsiloxane) to probe the inner structure of silica beads used as adsorbent particles in HPLC columns. Using cyclohexane two fractions with different mobility can be detected in the porous beads (690 m^2/g determined with N_2-sorption). One fraction diffuses through the pore-system, the diffusion coefficient decreases with increasing loading (about two orders of magnitude). The other fraction is retained in zones of about 700 nm in diameter. For the study of non-porous silica PDMS was used. The reduced translational mobility D_F of PDMS combined with comparably long T_2 times (due to the high internal flexibility of the PDMS molecules) enables one to detect displacements in the order of 100 nm in the silica as a consequence of the reduced attenuation by the diffusion.

Sandstones have been studied with the help of PFG NMR for example by Fordham et al. (1994) (S/V, relaxivity), Hürlimann et al. (1994) (S/V, relaxivity), Packer and Tessier (1996) (propagator), Packer et al. (1998) (propagator for water/oil flow), Frosch et al. (2000) (S/V, tortuosity, permeability) and Stallmach et al. (2001) (S/V, D(t) for water/hexadecane flow). Frosch et al. (2000) determined, furthermore, T_1 as a function of the cation concentration for three different electrolytes. An increase of the cation concentration causes a reduction of active sites in the porous medium at which water molecules can relax. As a consequence the relaxivity ρ_1 (chapter 3.4) decreases.

Besides MRI (chapter 3.1), flow experiments (chapter 3.2) and NMR diffusion experiments (chapter 3.3) also spectroscopic methods (chapter 3.4) provide structural characteristics of disperse media as shown in the next chapter.

3.4 Spectroscopic Material Characterisation

Foods are often heterogeneous mixtures of materials with complicated properties. Water and fat are constituents of many foods and non-food products. Redistribution (hydration, dehydration) and structural changes including phase-transitions are induced by many processing operations or occur during storage. Water, especially, acts as a transportation medium, reacting agent, intermolecular link and textural medium. In food process technology the type of water-binding and the mobility of water molecules are relevant with regard to the yield, the sensory evaluation, the stability (in physical and microbiological terms), the texture, the flow behaviour and the appropriate processing (Liebenspacher 1991). The integral moisture-content, the states of water present in the sample and their mobility (e. g. free, retained or adsorbed) play an important role both for natural processes and technical applications, e. g. drying, heating, freezing, heating technology, solid-fluid separation, adsorption and desorption processes, mixing and demixing (e. g. syneresis in foods or ceramic masses), agglomeration and deagglomeration, diffusive mass transport and flow properties. The applications of NMR in this chapter deal with NMR spectroscopic methods (Belton 1994a) applied in process engineering and especially in food technology in order

(a) to characterise (identification, authentication) the food composition, the chemical structure, the physical state (solid/liquid, crystalline/amorphous) or molecular dynamics of materials applied in food analysis, product characterisation and quantification of structural changes caused by processing (e. g. Belton 1994b; Wilson 1994; Bovey and Mireau 1996; Cornillon 1998),

(b) to derive correlations between NMR parameters and macroscopic quality factors of products in initial, intermediate and final states which can be applied as tools for process and quality control including on-line process NMR spectroscopy.

NMR spectroscopic methods enable one to obtain (i) molecular/microscopic properties of samples like the molecular mass (Götz et al. 2001a) and (ii) macroscopic properties like the viscosity (Götz et al. 2001a, 2003b) or the permeability (Watson and Chang 1997). The quantities can be determined volumetrically averaged or spatially resolved. Two basic types of NMR instruments exist, with low and high resolution. Usually low-resolution NMR (LR-NMR) devices have resonance frequencies smaller than 100 MHz for the hydrogen isotope ^{1}H. LR-NMR is used to study bulk properties of pure samples or mixtures by means of the so-called T_1-, T_2- or $T_{1\rho}$-relaxation times, self-diffusion coefficients (chapter 3.3) or sequences based on these quantities. The significantly lower price is an important advantage of LR-NMR compared with High Resolution methods. The great disadvantage of LR-NMR is the lower resolution of the applicable measuring sequences and the thereby restricted possibilities of structural analysis. High Resolution NMR enables more detailed structural, kinetic and equilibrium studies of individual substances or even molecular groups in the pure state or in mixtures (Horman 1984).

High Resolution NMR spectrometers are, for example, seldom applied in process engineering inclusive of food technology due to essentially higher acquisition costs compared to LR-NMR and the need of highly skilled operators. While High Resolution NMR is mainly used in research and development, LR-NMR is, furthermore, applied in food technology and in other fields of process engineering both for quality and process control. As explained in the preface, in the following chapter only actual or potential industrial applications of NMR spectroscopy are presented.

Ad (a) **Material Characterisation**.

Composition

The application of appropriate NMR techniques provides information concerning the composition of food systems, especially the concentration of individual components, interactions between individual ingredients and effects of different preparation or production processes like thermal or pressure treatment, foaming, pumping, extrusion, ultrasonic, acidification by acids or cultures, addition of sugars, hydrocolloids, protein and lipid components, mineral nutrients or vitamins.

The measurement of the moisture content of food products in initial, intermediate and final states has been one of the first applications of NMR techniques (e. g. Shaw and Elsken 1950; Karmas 1980; Weisser 1980; Korn 1983; Schmidt 1990, 1991; Schmidt and Lai 1991; Gambhir 1992; Isengard 1995). Problems, however, cause the unambiguous characterisation of different physical states of water or other components present in heterogeneous systems, derived from spectroscopic data (e. g. Zimmerman and Brittin 1957; Woessner 1966, 1977; Belton 1990, 1994b, 1995, 1997; Belton and Ratcliffe 1985; Belton et al. 1988; Hills et al. 1990; Schmidt 1990; Hills 1992a, b; Colquhoun and Goodfellow 1994), due to chemical (Carver and Richards 1972; Berliner and Reuben 1980), diffusion (Brownstein and Tarr 1979; Belton and Hills 1987) or spin quantum exchange (Edzes and Samulski 1978) processes. The relaxation in aqueous systems has been studied by ^{1}H, ^{2}H (e. g. Hallenga and Koenig 1976; Kumosinski et al. 1991), ^{13}C NMR (Cassin et al. 1998) and ^{17}O (Swift and Connick 1962; Halle et al. 1981a, b; Belton and Wright 1986; Halle et al. 1999) NMR. The main relaxation mechanisms are dipolar for ^{1}H and quadrupolar for ^{2}H and ^{17}O. ^{1}H NMR is applied in the majority of the relaxation experiments because of the wide spreading of spectrometers which only allow ^{1}H NMR and because foods can be analysed without preparation. ^{2}H and ^{17}O NMR, however, provide many fundamental data on water relaxation in heterogeneous media. Reviews of NMR relaxation mechanisms in complex systems are given for example by Packer (1977), Nusser (1990), Colquhoun and Goodfellow (1994), van de Ven (1995), Cavanagh et al. (1996), Gregory (1998), Ruan and Chen (1998), Belloque and Ramos (1999) and Nölting (1999).

T_1 and T_2 are measures of the interaction of a spin with its surroundings and the mobility of a spin, respectively. As such, it is principally possible to distinguish between free water that does not interact with the solid particles or dissolved molecules and immobilised water, e. g. crystallisation-, hydration-water or other chemically or physically bound water. Assuming models for eventual chemical, diffusion or spin quantum exchange processes the relaxation times and fractions of the corresponding water-types can principally be derived from the relaxation data.

Heterogeneous food or non-food systems usually exhibit single-phase behaviour for low concentrations of solute concentrations like dilute protein or polysaccharide aqueous solutions. For higher solid concentrations (substance-specific for the present type of solute) multi-phase relaxation behaviour is often observed, especially for transverse (T_2) relaxation

$$I(t) = a + d_1 \cdot \exp(-(t / 2T_{2,1})^2) + \sum_i d_i \cdot \exp(-t / T_{2,i}) \qquad (3.4.1)$$

with $\sum_i d_i = 1$

a	zero drift
d_1 , $T_{2,1}$	fraction and average T_2 time of spins in the solid state
d_i , $T_{2,i}$	fractions and average T_2 times of spins in fluid states for $i > 1$

$T_{2,1} < T_{2,2} < T_{2,3} < \ldots$

Another approach to describe the evolution of the magnetisation I(t) is not to assume discrete relaxation times (Eq. 3.4.1), but a continuous T_2-distribution. The corresponding frequency distribution of T_2 can be determined for example with the CONTIN algorithm (Provencher 1982). The continuum model provides additional information about the homogeneity of the morphology in the sample due to the half-widths of the observed phases.

The temporal evolution for the T_1-relaxation is given by

$$I(t) = a + \sum_i d_i \cdot [1 - 2 \cdot \exp(-t / T_{1,i})] \qquad \text{(inversion recovery)} \qquad (3.4.2a)$$

or

$$I(t) = a + \sum_i d_i \cdot [1 - \exp(-t / T_{1,i})] \qquad \text{(saturation recovery)} \qquad (3.4.2b)$$

depending on the applied NMR sequence (e. g. Abragam 1961; Farrar and Becker 1971). The ratios of the present phases are defined as in the case of T_2-experiments.

The interpretation of ^{1}H relaxation time data has not been clarified to its full extent. Usually up to four different groups of spins can be distinguished in protein and polysaccharide solutions (Nusser 1990; Colquhoun and Goodfellow 1994). Two of them are correlated with the water and two with the dissolved macromolecules. Hydroxyl- or amino-protons in solutes can exchange with water protons, other protons are not able to exchange. Hikichi (1993) detected in κ-carrageenan-gels three water phases with different molecular mobility combining ^{1}H, ^{23}Na, ^{87}Rb and ^{133}Cs NMR after adding the corresponding cations. The relaxation results indicate free bulk water, water molecules strongly interacting with κ-carrageenan and water molecules weakly "bound" to the gel network. Using ^{1}H MAS NMR it is possible to observe three water types in red blood cell suspensions: extracellular free water, intracellular free water and intracellular water immobilised by Fe-ions (Humpfer 1997).

For systems with ^{1}H-free solids and ^{1}H-containing fluids like water the interpretation of T_2-experiments with regard to the mobility of water-phases is straightforward. The preparation of samples with homogeneous moisture, especially at low moisture contents, is problematic. The so-called CPF-technology (Concentrated Powder Form) based on the spraying of liquid by means of a supercritical gas, in most cases carbon oxide, in a static mixer enables the production of extremely homogeneous products consisting of powder and liquid up to very high loadings (Steiner et al. 2000). CPF is implemented in the spice industry and in the production of animal feed.

Appropriate examples are T_1- and T_2-relaxation experiments with SiO_2/water mixtures produced with the CPF-technology (Götz et al. 2002d). The aim of this study is to develop a method for the characterisation of solid/liquid systems with regard to their loading capacity of the liquid. That means a critical liquid content has to be determined up to which the loaded product is homogeneous, free flowing, without undesirable agglomerates and without free liquid in the bulk. The analysis of the T_1-relaxation times shows the occurrence of an additional phase at higher moisture contents F values. The T_2-relaxation times provide more detailed differentiation of the mobility of the phases. The results of the NMR measurements show on the microscopic scale the same order of magnitude of the critical moisture content F of about 0.70 for T_1 and T_2 like the results of an optical control and a filter method on the macroscopic scale. The differentiation by T_2 in five regimes, furthermore, correlates with the results of the optical control. The number of the layers of absorbed water molecules (estimated with the immobile fraction of T_2-experiments) lies between 0.5 and 7 within the studied moisture range (F = 0.04-0.80).

For one-phase relaxation the observable T_2-relaxation times T_{2obs} can be used as characteristic T_2-relaxation time. For very slow exchange, that means if the characteristic times for the exchange processes are small compared to the mean residence time (life time) in the corresponding phase-volume, the observed fractions and average T_2-relaxation times are identical with the actual fractions and T_2-relaxation times, respectively (Zimmerman and Brittin 1957; Woessner 1963). Mean relaxation times T_{jm} (j = 1 or 2) in multiple phase systems can be derived for the so-called very slow exchange (mathematical average only)

$$T_{jm} = \sum_i d_i T_{j,i} \tag{3.4.3}$$

or for the very fast exchange (experimentally observable average)

$$\frac{1}{T_{jm}} = \sum_i \frac{d_i}{T_{j,i}} \tag{3.4.4}$$

If exchange processes are present and τ_b is the mean residence time in the "bound" environment τ_b, the observed mean relation times are approx. given by (e. g. Kiihne and Bryant 2000)

$$\frac{1}{T_{jm}} = \frac{d_{j,f}}{T_{j,f}} + \frac{d_{j,b}}{T_{j,b} + \tau_b} \tag{3.4.5}$$

$d_{j,f}$, $T_{j,f}$	fraction and average T_j time of spins in the free state
$d_{j,b}$, $T_{j,b}$	fraction and average T_j time of spins in the "bound" state

For protein solutions with low protein concentrations of bovine serum albumin (BSA) Kiihne and Bryant (2000) found that 21-29 water molecules are bound to the protein molecules for times long compared to the so-called rotation correlation time τ_{rot} of the complex (5-100 ns). If the mobility of water molecules within the "bound" phase is taken into consideration, the amount of bound water is increased by a factor of 1.5. Hills et al. (1989a) studied the effect of the protein concentration on the T_2 of BSA-solutions. The dependence of the mean T_2-relaxation time on the 90°-180° pulse spacing in a CPMG (CarrPurcellMeiboomGil) sequence (Farrar and Becker 1971) points to chemical exchange processes between water and NH and OH groups of BSA.

A selection of empirical and theoretically established models of the correlation between the concentration of dissolved (macro-)molecules and the observed or the average T_2-relaxation time of solutions, respectively, is given in Table 3.4.1. Thus conclusions concerning the influence of the type of macromolecules and their concentrations on the existence of multiple water phases ($T_{2,i}$) and their fractions on the total water content can be drawn.

NMR is not appropriate for trace analysis due to the low sensitivity with regard to concentrations compared to alternative measuring techniques. This is, however, not problematic for NMR and especially for LR-NMR, as in most cases mainly major components are analysed (e. g. Barker and Stronks 1990; Barker 1991). Hence LR-NMR is widely used as a rapid tool for the determination of moisture contents (Schmidt 1991) and for the analysis of oils and fats (Waddington 1986), for example in foods (e. g. chocolate, cocoa or milk powder), seeds, nuts, olives, wax, paraffin or sulphur. The existing experimental techniques can be classified into (i) ratio measurements, (ii) absolute measurements and (iii) the analysis of the complete relaxation decay (Colquhoun and Goodfellow 1994). Ratio measurements (i) are applied to determine for example the solid fat content (SFC) (so-called direct method) and melting curves of fat-containing systems and to observe their melting and crystallisation behaviour, respectively (Brosio et al. 1980). The influence of fat composition and polymorphic states can be quantified with the help of melting curves. This information is especially important in the margarine and chocolate industry (Leung et al. 1985; Gribnau 1992). The signal amplitude needs to be measured only at two characteristic times.

Table 3.4.1: Selection of empirical and theoretically established models of the correlation between the concentration of dissolved (macro-)molecules and the average T_2 of solutions. T_{2obs}: observed average T_2-relaxation time; f: free; b: "bound"/immobilised; P: protein; W: water; k_e: exchange rate; n_H: protein hydration = mass of immobilised water/protein mass = m_{wb}/m_P; τ_b: life time H_2O-molecule in the immobilised phase; protein concentration $c_P = m_P/m_W$ = mass of protein/mass of water; p_f: fraction of free water; p_b: fraction of immobilised water

Model	**Systems**	**Ref.**
$\frac{1}{T_{2obs}} = \frac{p_f}{T_{2f}} + \frac{p_h}{T_{2h}} + \frac{p_e}{T_{2e} + \frac{1}{k_e}}$ f protons of free molecules h protons H_2O-molecules interacting with proteins or hydrating other H_2O-molecules e exchangeable protons of proteins (-OH, -NH_2, -SH) or hydrocarbonates	milk proteins, skim milk, phosphocaseinates	Mariette et al. (1993); Le Dean et al. (2001)
$\frac{1}{T_{2obs}} = \frac{1}{T_{2f}} + p_{PR}\left(\frac{1}{T_{2b}} - \frac{1}{T_{2f}}\right)$ p_{PR} molar fraction of the protein	human, horse and hen proteins	Halle et al. (1981a)
$\frac{1}{T_{2obs}} = \frac{1}{T_{2f}} + \frac{hP_{CH}}{T_{2b} + \tau_b}$ h number of exchangeable H_2O-molecules per dissolved macromolecule P_{CH} molar fraction of the carbohydrate	κ-carrageenan	Hikichi (1993)
$\frac{1}{T_{2obs}} = \frac{1}{T_{2f}} + \frac{c_P n_H}{1 - c_P n_H} \frac{1}{T_{2b} + \tau_b}$	whey proteins	Lambelet et al. (1989)
$\frac{1}{T_{2obs}} = \frac{1}{T_{2f}} + n_H c_P \left(\frac{1}{T_{2b}} - \frac{1}{T_{2f}}\right)^*$ $\exp(2B_o c_P + 2B_{0.5} c_P^{0.5} + 0.667 B_{1.5} c_P^{1.5} + 1.5 B_2 c_P^2 + \ldots)$ B_i i=0, 0.5, 1,5, 2 virial coefficients	caseins	Mora-Gutierrez et al. (1996)
$\frac{1}{T_{2obs}} = \frac{p_f}{T_{2f}} + \frac{p_b}{T_{2b}}$	whey proteins	Padua et al. (1991)
$\frac{1}{T_{2obs}} = \frac{1}{T_{2f}} + n_H c_P \left(\frac{1}{T_{2b}} - \frac{1}{T_{2f}}\right)$	caseins	Pessen and Kumosinski (1985)
$\frac{1}{T_{2obs}} = \frac{1}{T_{2f}} + \frac{\sigma\lambda}{T_{2b}}$ σ specific surface of the gel matrix λ thickness of the water layer with enhanced relaxation	skim milk	Tellier et al. (1993)
$\frac{1}{T_{2obs}} = \frac{1}{T_{2f}} + \left(\frac{1}{T_{2b}} - \frac{1}{T_{2f}}\right) c_b$ c_b mass of the bound water / mass of the clay	hectorite clay	Woessner (1980)
$\frac{1}{T_{2obs}} = \frac{1}{T_{2f}} + \frac{p_b}{1 - p_b} \frac{1}{T_{2b} + \tau_b}$	agar gels	Woessner and Snowden (1970)

Absolute measurements (ii) are used in order to determine the mass concentration of a component, often water or fat. The required concentration in a sample can be derived from the knowledge of its weight and the signal at a material-specific time. A prerequisite is a calibration with an independent method to determine the mass concentration. For the so-called indirect method of the SFC-determination, which is applicable for all products (e. g. chocolate and fillings) containing fat, but also other solids, the SFC is calculated using an external standard (soybean oil) at the same temperature. The direct method of the SFC-determination provides usually better reproducibility than the indirect one. With appropriate modifications of the NMR sequence or in combination with chemometrics (see below) a simultaneous determination of water, oil and protein contents, for example in oilseeds, is possible (Gambhir 1992; ISO 10632-1993; ISO 10565-1995; Sobottka and Grätsch 1999; Pedersen et al. 2000; van Duynhoven 2002).

Rapid measurements of T_1 and T_2 allow one to record on-line the freeze-drying of potato tissues (Monteiro Marques et al. 1991). T_1/T_2 increased abruptly, when the frozen core is completely eliminated. It is, furthermore, possible to trace approx. the evolution of alcohol and sugar concentration during fermentation by means of T_1 and T_2 (Tellier et al. 1989). Further applications of relaxometry are the determination of content of spin-finish on textile fibres (used as lubrication of the fibre surface, cohesion of filaments and static protection of the fibre bundle), the total hydrogen content (used as criterion for product quality) in hydrocarbons like fuels and the fluorine content (used as criterion for product quality) in tooth-pastes by means of ^{19}F NMR (Bruker 1999). Empirical correlations between mean T_1 or T_2 and concentration of constituents have been deduced for various systems like the sugar content in fruits (Cho et al. 1993), the amount of free fatty acids and total polar materials (Sun and Moreira 1996) or the sugar content in osmotic dehydrated apples (Cornillon 1998, 2000). Thus time- and cost-intensive wet chemistry methods can be substituted by experimentally simpler and faster NMR techniques.

In food-technology High Resolution NMR is principally used for the structure determination of complex natural products and quantitative analysis of ingredients (e. g. lipids, sugars, amino acids). A detailed list of constituents and products quantitatively determined by NMR is given by Watanabe et al. (1995) and, especially for monomers and additives used in food packaging plastics, by Gilbert et al. (2000). Another High Resolution NMR technique is the so-called selective natural isotope fractionation (SNIF) NMR which allows one to analyse the authentication of foods and food constituents based on the ratio of deuterium ^{2}H and hydrogen ^{1}H or ^{13}C and ^{12}C (Colquhoun 1998). The isotope ratios for molecules and even special groups within molecules synthesised by a plant-type are influenced by biochemical, geographical and climatic parameters. Thus the origin of a wine-type or the addition of sugar to a wine can be checked (Martin and Martin 1990). Corresponding tests have been developed in order to decide if foods or food components are natural, semi-synthetic or synthetic. Hernandez and Rutledge (1994) used LR-NMR to analyse the geographical origin and the impact of the roasting process for cocoa masses. Thus LR-NMR provides the possibility to adapt the process conditions of roasting for different beans.

Additionally to the application as a tool for the determination of structures in chemistry, NMR spectroscopy is applied to study physiological and metabolic processes and technical-chemical reactions using for example ^{1}H, ^{2}H, ^{13}C, ^{17}O, ^{19}F or ^{31}P NMR (Roberts 1987; Fischman and Tompkins 1992; Alves et al. 1996; Hayman and Dufuor 2001; Ramos et al. 2002). Examples for technical reactions are the study of hydration and pozzolanic reactions in concrete and concrete components (Zanni et al. 1996a: ^{29}Si NMR; 1996b: ^{29}Si NMR, ^{1}H NMR, ^{43}Ca NMR; Saadatmanesh and Ehsani 1997: ^{1}H NMR), the hardening of slag- and ash-based construction materials (Nestle et al. 2000). Reviews on the application of high resolution NMR are given for foods by Horman (1984), Colquhoun and Goodfellow (1994), Gidley et al. (1995), Cornillon (1998), for polymers McBrierty and Packer (1993), Bovey and Mireau (1996) and Blümich and Blümler (1998).

Volume-Selective Spectroscopic Methods

Two principal techniques are available for obtaining volume-selective structural information:

- localised NMR spectroscopy and
- NMR spectroscopic imaging.

For localised NMR spectroscopy spatial localisation is achieved by the use of surface coil excitation or by volume selection applying magnetic field gradients (Doddrell et al. 1992). By varying the position of the selected volume it is possible to achieve spatial information on the observed phenomena. The volumina in tissues are in the order of 1-64 ml (in many cases 8 ml) for ^{1}H and 125 ml for ^{31}P (Frahm et al. 1989). Spectroscopic imaging methods provide in one experiment a spectroscopic dimension in addition to basic imaging data. They require, however, generally long total measuring times (Doddrell et al. 1992). Both localised NMR spectroscopy and NMR spectroscopic imaging enable one to observe the progress of chemical/physical reactions or - generally spoken - of structural changes in materials (e. g. Tallarek et al. 1999).

Simoneau et al. (1992, 1993) demonstrated the potential of localised NMR spectroscopy to study the evolution of crystallisation of fats in o/w-emulsions or of the melting processes in chocolate with regard to solid/liquid ratios, the polymorphism of the present fats and the kinetics of crystallisation or melting. Other applications of spectroscopy imaging are the study of biochemical processes in humans and animals, principally in the brain and the design of tablets and the release and evaluation of drugs (Decorps et al. 1992). Spatially resolved spectroscopy allows one to detect the distribution of metabolites in specific tissues (Fischman and Tompkins 1992). Reviews concerning applications and technical details of volume-selective spectroscopic methods are given by Doddrell et al. (1992), Watanabe et al. (1995), von Kienlin and Pohmann (1998) and Klose et al. (1999).

Usually the measuring volume is in the interior of NMR devices which enable, therefore, only the study of samples with limited extensions. These difficulties can be overcome by portable NMR devices with NMR-surface techniques, e. g. surface coils, which allow one to realise T_1-, T_2- and D_S-experiments. Portable NMR devices have various advantages (Blümich et al. 1998; Guthausen 1998; Guthausen et al. 1998; Haken and Blümich 2000; Wolter 2001): (i) Surface-near volume regions of arbitrarily large samples can be studied by moving the coil at the object-surface. (ii) Ferromagnetic components of the sample like steel in steel-braced radials do not inevitably disturb the measurements. (iii) The orientation between the sample and the symmetry-axis of the surface coil can easily be varied by rotation of the coil in order to detect anisotropic structures in samples on a microscopic/molecular level. Applications are the oil exploration (Kleinberg 1996b), the moisture-measurements in concrete (Matzkanin 1989), cross-link density, ageing and composition of polymeric materials (e. g. Guthausen 1999) and the characterisation of porous materials (Wolter 2001).

By rotating the device and thus the direction of $\mathbf{B}_0$ relative to the sample, structural orientations in the materials, for example in biological tissue, can be detected by means of T_2-experiments (Blümich et al. 1998; Haken and Blümich 2000: pork tendon). Various NMR techniques and sequences have been developed to characterise and quantify anisotropic orientations in polymeric materials induced by flow-induced deformations. A detailed review is given by McBrierty and Packer (1993). For example $T_{1\rho}$-experiments enable one to differentiate crystalline and amorphous spectra varying the sample orientation in $\mathbf{B}_0$ and to derive the corresponding contributions (Kasuboski 1988). Additionally to the crystalline and amorphous (or liquidlike) zones an interfacial/interzonal region can be observed (Sperling 1992). The three regions have, for example, for PE with a molecular mass of 250,000 Da 75, 10 and 15 %, respectively (^{13}C NMR).

Structural Changes Including Phase Transitions and Denaturation

Denaturation. Many foods and food components are thermally treated like for example pasteurisation, sterilisation, rectification, distillation, drying, freezing, freeze-drying and freeze-concentrating (Harz 1987). The variation of the temperature or the pressure generally causes changing NMR parameters like relaxation times, spectra or diffusion coefficients. For simple fluids like water T_1, T_2 and D_S for example increase with the temperature, whereas their behaviour as a function of the pressure is more complex (e. g. Lüdemann 1992; Ballard and Jonas 1997). In the following possibilities of spectroscopic NMR techniques for the detection of (i) different compositions of raw materials and of (ii) structural changes caused by various types of mechanical, thermal, chemical or other processes are presented.

NMR is a modern method for the detection of structural changes of proteins. High Resolution NMR is an independent method besides X-ray analysis for the characterisation of protein-structures including thermal and pressure denaturation and pH phenomena (e. g. Jonas and Jonas 1994; Cavanagh et al. 1996; Ballard and Jonas 1997; Hancock and Hsu 1996; Nölting 1999). Investigations concerning the heat treatment of proteins from milk and eggs by means of LR-NMR (T_1, T_2, self-diffusion coefficient D_S) have been performed by Trumbetas et al. (1979), Goldsmith and Toledo (1985), Lambelet et al. (1988, 1989, 1991, 1992, 1995), Hills et al. (1989b), Roefs et al. (1989), Barfod (1991), Padua et al. (1991) and Le Dean et al. (2001). In these studies the process temperature, the pH-value and the concentrations of protein, lactose and calcium chloride are varied. The protein samples are studied after and not during the thermal treatment. The NMR experiments are performed after a thermal treatment, at a temperature below the denaturation temperature in order to prevent further changes during the measurement. Reversible (increase of T_2: higher mobility of the protein molecules at higher temperature) and irreversible transformations (decrease of T_2: aggregation above the denaturation temperature) due to the thermal treatment can thereby not be differentiated. This procedure does not provide information concerning the kinetics of the denaturation, unless a series of tests with different samples is performed. This is a great disadvantage for natural substances due to their compositional variety. In aqueous protein systems generally four phases can be distinguished with T_2-experiments. These phases are denoted as "immobile", "moderate mobile", "mobile" and "very mobile", with increasing T_2-relaxation times (Eq. 3.4.1-2).

There are (i) proteins whose T_2-relaxation times of the phases with higher mobility ("mobile", "very mobile") are increased due to the thermal denaturation and (ii) proteins with T_2-relaxation times reduced after the thermal denaturation, whereby only two phases have been detected (Lambelet 1991). The dependence between T_1 or T_2 and the temperature after a fixed treatment duration and the T_2/T_1 ratio indicate structural changes, for example sol-gel transitions. In order to demonstrate the possibilities of LR-NMR to observe structural changes the average relaxation times T_{2m} of a whey protein isolate solution ($c = 10$ %) are shown as a function of the temperature (Fig. 3.4.1). The sample was heated from $T = 10$ °C stepwise to 70 °C, cooled down to -20 °C and subsequently heated up to 10 °C. The heat treatment for constant temperature was continued, until equilibrium can be observed with respect to T_2-relaxation. Between 50 °C and 60 °C a significant decrease of T_{2m} could be observed. This is obvious due to the thermal denaturation and the combined reduction of the molecular mobility of the whey proteins. The results of the chilling curve are in good agreement with the experiments of Lambelet et al. (1988).

The effect of thermal (freezing and heating) and pressure treatment concerning the maximum value of the temperature and the pressure, respectively, and the duration of the treatment on the structure cod can be monitored by T_2-relaxation (Lambelet et al. 1995). The measurements are performed at 20 °C. The studied treatments cause the appearance of an additional phase of higher mobility, presumably due to the exudation of serum. Thus T_2-relaxation might be appropriate to detect a possible structural deterioration of products due to thermal, pressure or generally mechanical treatment, for example the freezing damage of frozen foods (Dinkelmeyer 1999).

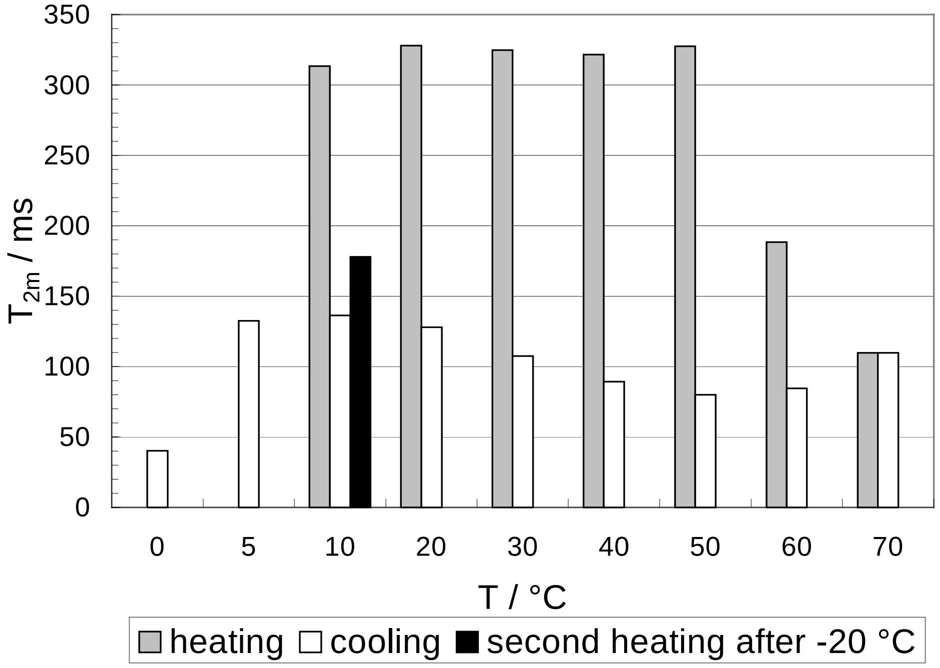


Fig. 3.4.1. Average relaxation times T_{2m} for a thermal treatment of a whey protein isolate solution 15 % (w/w) in bidistilled water (Isolac: Milei GmbH, Rosenheim, Germany): Heating from the temperature T = 10 up to 70 °C, cooling down to -20 °C and afterwards a second heating up to 10 °C.

Another possibility to observe denaturation phenomena by means of LR-NMR is to perform on-line NMR-measurements during the thermal treatment and determine the average time T_{2m}, the relaxation times of the single phases $T_{2,i}$ and the corresponding fractions d_i (Götz et al. 2004b). The advantage of this method is that several measurements can be performed with the same sample without interrupting the thermal treatment and continuing with another sample as in the literature cited above. Higher accuracies of measurements can, furthermore, be achieved by the use of one single sample instead of several samples for a series.

For the T_2-experiments a combination of FID (Farrar and Becker 1971) (with a scanning time distance of $5 \cdot 10^{-4}$ ms) and a subsequent CPMG (Farrar and Becker 1971) sequence with a duration (90°-180°) of 0.2 ms and 19600 pulses was applied. Thus the influence of field inhomogeneities and diffusion and chemical exchange on the relaxation can be minimised (Hills et al. 1990). Comparably long total measuring times (~8 s) can be achieved in spite of the high scanning rate. The T_2-experiments do not only provide the average T_{2m}-times, but also by means of a multi-component fit the relaxation times of the present phases with the corresponding relaxation times. This offers the possibility to determine the reaction orders and rate constant of the participating reactions.

Aqueous solution of ovalbumin, conalbumin, β-lactoglobulin and β-lactoglobulin mixed with ovalbumin were heat-treated at constant temperatures (5, 20, 60, 65, 70 and 75 °C) for 98 min in an LR-NMR spectrometer (20 MHz) (Götz et al. 2004b). The denaturation temperatures are for ovalbumin and conalbumin below 60 and 65 °C, respectively. The average relaxation times T_{2m} of the mixture β-lactoglobulin/ovalbumin are unexpectedly smaller than the relaxation times T_{2m} of the single components at the same temperatures. It is plausible to assume that both proteins β-lactoglobulin and ovalbumin interact with one another and that the protein mixture corresponds after the denaturation more to a "copolymer" than to a "blend". If the relaxation experiments provide different results after varying the temperature, the pressure or other parameters for the same set of variables, for example $T = 10$ °C in Fig. 3.4.1 (T_{2m} for a thermal treatment of a whey protein isolate solution), reversible and irreversible structural changes due to, for example, freezing damage or heat treatment can be identified and quantified.

To summarise the findings, the protein-denaturation is applied for the formation of structures in food-products and, thus, for the defined modification of relevant product-properties. Furthermore, it might be possible to use the knowledge concerning the denaturation behaviour for the determination of appropriate time-intervals for adding further food ingredients (e. g. hydrocolloids) during the production process. With respect to the denaturation fraction and relevant macroscopic properties (e. g. viscosity) this guarantees an optimal mixing quality within an acceptable mixing time (Götz et al. 2004d).

Freezing Behaviour - Glass-Transition. Freezing-curves are part of state diagrams and describe the dependence of the concentration of the freeze-concentrated solution or the ice-fraction on the temperature (Leung and Steinberg 1979; Goff 1994; Roos 1995). Freezing-curves allow one (i) to study the structure of frozen food and non-food materials (Hills and Le Floc´h 1994a, b), (ii) to establish appropriate processing and storing conditions for frozen foods and (iii) to quantify the influence of the formulation and the pre-processing of components on the freezing behaviour (Dinkelmeyer and Weisser 1998). LR-NMR has the following advantages for the determination of freezing-curves, compared to other measuring methods (e. g. calorimetric methods, rheology, microscopy, dilatometry):

- The measurements can be performed at constant temperature in a steady state.
- Freezing-curves can completely be obtained by using one single sample. A prerequisite is the knowledge of the formulation.
- Even with commercial NMR devices a wide temperature range (up to -60 °C) can be studied.
- The determination of the freezing curve can totally be automated by beginning at the deepest temperature and rising the temperature stepwise, until the sample has completely thawed and all spins are detectable.

The fraction of the frozen water is relevant for the mouth-feeling and the spoonability of frozen foods, for example of ice-cream, which are generally characterised by means of penetration- and draining-tests. Quantitative correlations between the mouth-feeling, the spoonability and the freezing-curve still have to be established. Various hydrocolloids (see below) are applied in order to reduce the fraction of water which can be frozen out, to produce uniform crystallites with narrow size distribution and to avoid crystal ripening during storage (Franks 1985). The effect of hydrocolloids is presumably due to the increased viscosity of the solution for viscosity increasing hydrocolloids, the network for gelling hydrocolloids or the hindered ice growth rate because of hydrocolloids at the interfaces.

Although freezing is less invasive and modifying to the original product-properties than other thermal treatments, freezing damages might be caused by (i) volume-increase due to the density anomaly of water combined with mechanical stresses, (ii) crystallisation and recrystallisation, (iii) freezer burn due to moisture loss as a result of imperfect, not tight packages or (iv) chemical/enzymatic reactions (Franks 1985; Heiss and Eichner 1995). Crystallites induce damages in structured materials like gels. Chemical reactions might be favoured by increasing concentrations, for example of reactants, or altered pH-values as a consequence of the freezing process.

Another important element of phase diagrams are the so-called glass-transition curves besides solubility- and freezing-curves (Donth 1981; Goff 1994; Ross 1995; Ruan et al. 1998; Ruan et al. 1999a). Glass-transitions affect many macroscopic properties of foods (e. g. flow behaviour, stiffness, crispness, caking behaviour, release of flavours and lipids) or of non-food products like polymers (e. g. deformation behaviour, solubility/permeation/migration behaviour). Both glass-transitions and freezing damages are combined with dramatic changes of physical properties like spectra, T_1, T_2 or the corresponding fractions of spins (Harz et al. 1989; Rössler 1990a, b; Rössler et al. 1993, 1994; Dinkelmeyer and Weisser 1997; Cornillon 1998; Kou et al. 2000; Koxholt 2000). Van den Dries et al. (2000) found in concentrated glucose systems above the glass-transition temperature a further transition which is referred to as the so-called collapse temperature.

Bogillo et al. (1997) studied the influence of coating of TiO_2 particles with Al_2O_3 and SiO_2 on the film thickness of fluid molecules influenced by the solid surface by varying the temperature up to bulk freezing. Dependent on the coating material the fluid film increases up to 20 nm and is thicker for water (presumably due to interactions between polar sites) than for deuterochloroform. Relevant for the thickness of the fluid layer is the distribution of charges at the solid surface which can be modified by appropriate coatings.

Mechanical Processing. In addition to the previously mentioned possibility to monitor structural changes due to thermal treatment, chemical or biological reactions, potential modifications caused by mechanical processing can be monitored by NMR techniques. Ablett et al. (1991) designed a probehead which allows NMR experiments during the compression of samples. The frequency distribution of T_2 of chamois leather and cooked beef is shifted by increasing compression to smaller times due to the expression of water with high mobility.

Schmidt et al. (1997) found that ultrasonic dispersion and subsequent homogenisation by ball milling does not change the chemical structure of organic matter in geochemical samples as far as such modifications can be observed by solid-state ^{13}C NMR. MRI and spectroscopy of sheared materials with a yield stress depending on the history of deformation like oxide-ceramics (Felder 1990; Götz 1994) show that (i) the evolution of agglomerates and (ii) the increase of the shear stress in shear flow is correlated with (iii) the immobilisation of water for increasing energy input (Götz et al. 2002f).

Water-Holding Capacity (WHC) Including Sol-Gel Transitions and Syneresis. In food process technology the bonding-type of water and the mobility of water molecules are relevant with regard to the yield, sensory evaluation, stability (in physical terms), texture, flow behaviour and processing. There are many measuring methods available to characterise the WHC of a mixture (e. g. Kinsella 1984; Kinsella and Fox 1987; Kneifel et al. 1991; Kulicke et al. 1996; Windhab 1987). Many techniques, which were originally developed in practice, provide quick and easy indications concerning the studied material. Most of the available methods usually provide differing results which are not absolute values and are, therefore, generally not comparable or transferable to technological processes. The reasons for the described difficulties are due to (i) the different measuring principles and experimental conditions which the methods are based on and (ii) often they destroy the structure when applying the measuring procedure. Presumably only a combination of physical/chemical methods enables relevant conclusions concerning the correlation between the production of a sample (pretreatment, history), the related structural changes and the WHC. A precise characterisation of the WHC for food-constituents like proteins and hydrocolloids, however, is required for a reliable design of products and production processes.

For different materials the relationship between the WHC and other macroscopic (rheology, particle-size distribution, micro-structure, flow behaviour, firmness, syneresis and sensorial behaviour) and microscopic properties (fine-stranded- or particulate gel structure) is not identical, which causes major problems for a practicable definition of the WHC. Rennet acid-gels, for example, have a coarser network structure with thicker protein strings than products without rennet. Thus rennet acid-gels are firmer, have, however, a lower WHC than pure acid gels (Schkoda 1998).

The appropriate definition of water-types (e. g. free, retained in capillaries, physically or chemically bound) depends, furthermore, on the applied measuring technique. This will be demonstrated for rheology and NMR (Fig. 3.4.2). The fraction of bound water is defined in rheology as water which is bound physically or chemically at solid-surfaces or retained in the interior of solid-particles. With regard to NMR water is bound, if it interacts with solid material or if the water molecules are in sufficiently small cavities. It is not of any importance, if fluid molecules are inside or outside of solid-particles. It is free water. Another difficulty is that disperse media usually have different micro-structures during (i) rheological experiments (in the flowing state) and (ii) NMR experiments where the samples are in most cases at rest. Exceptions are Rheo-NMR (see below) and NMR flow experiments (chapter 3.2). It is, therefore, not surprising that dependent on the measuring technique and the evaluation method different material data are derived (Kinsella and Fox 1987; Kneifel et al. 1991). A great disadvantage of various techniques for the determination of the water-holding capacity WHC is the principle-inherent modification/destruction of the gel matrix due to necessary preparations or system-immanent modifications (e. g. centrifugation).

In order to differentiate *free water*, which can be removed through capillaries in the gel-matrix of not stirred products or out of the pore-system of stirred samples, from *water*, which is *retained* in micelles or agglomerates, the set-up presented in Fig. 3.4.3 was developed. The sample is filled into an NMR-glass which is closed at the bottom with a PTFE-thread. T_2-experiments are performed firstly at the original sample and secondly at the sample, after it has been washed with heavy water (D_2O). Between sample and thread is a filter-membrane with 0.01 μm pore-size. The mobile free water in the sample is substituted by D_2O, which cannot be detected by ^1H NMR. For the evaluation it is assumed that exchange processes between water and OH-, NH- or SH-groups of constituents in the product can be neglected. Thus, with the help of the wash-out test, immobilised water, retained free water and mobile free water can be distinguished and conclusions concerning the inner structure of the matrix can be drawn. The fraction of water, more precisely serum, that contributes to phase-separation phenomena like syneresis possibly correlates with the phase-distribution and the amount of the water which can be washed out. If the water content of a sample is known, it is possible to derive a definition of the WHC with regard to physically and chemically bound water plus water retained in pores of the sample with the help of the fraction p_r of washable water/serum determined by the wash-out test.

$$\mathrm{WHC}_{\mathrm{NMR}} = \frac{m_{\mathrm{Wnw}}}{m_S} = \frac{m_{\mathrm{Wnw}}}{m_W}\frac{m_W}{m_S} = p_r F \tag{3.4.6}$$

m_{Wnw}	mass of non-washable water
m_W	total mass of water
m_S	dry mass
p_r	m_{Wnw}/m_W, averaged over all phases
F	water content of a gel (w/w per dry mass)

It is remarkable that not only water/serum of the phase with the highest mobility, but also of phases with reduced mobility (smaller T_2) is washed out. This means that the molecular mobility characterised by T_2 and the washability quantified by WHC_{NMR} (Eq. 3.4.6) are different, but complementary practice-relevant characteristic features of disperse media.

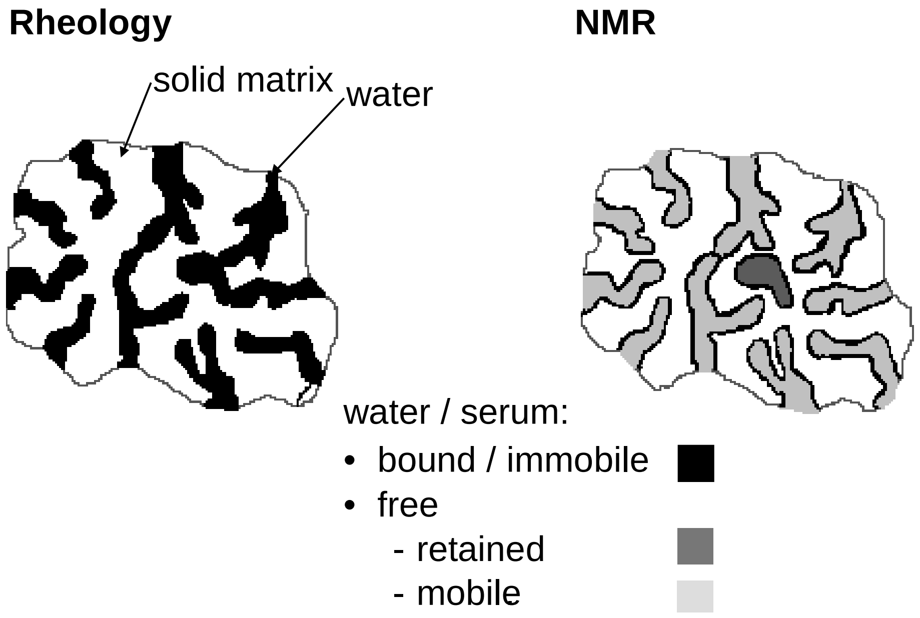


Fig. 3.4.2. Water-types in porous media characterised by means of rheology and NMR

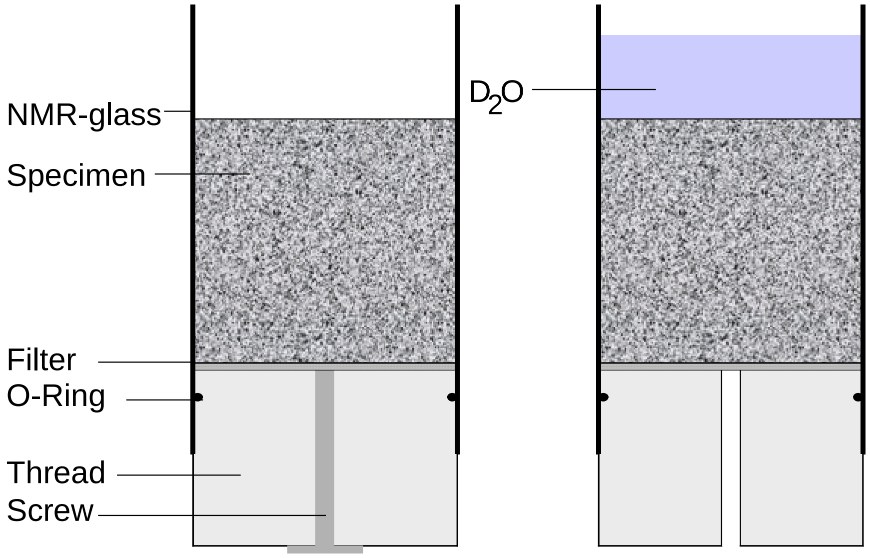


Fig. 3.4.3. Schematic set-up of the NMR wash-out test (Hinrichs et al. 2003)

The wash-out test was used to study the influence of the recipe and processing on the temporal evolution of the WHC of yoghurts (Table 3.4.2) and the amount of serum removable by washing with D_2O (Hinrichs et al. 2003). It is possible to ferment the samples in NMR-glasses or to cut out samples of already completely fermented yoghurt. It can be seen that, dependent on the recipe and processing, the distribution of the ratio of the phases is different, before and after the washing-out. While for the yoghurt of the pasteurised milk (P) and of the pasteurised milk with carrageenan (PC) the mobile phase represents the major fraction, the distribution is for the other samples (R, RC and M, Table 3.4.2) approx. homogeneous, before and after the washing-out. The samples also show differences between the yoghurts in the water content p_r after washing out the capillary water. The high standard derivations in Fig. 3.4.4 point to an inhomogeneous structure of the product (Hinrichs et al. 2003).

Table 3.4.2: Recipes and processing of the yoghurt samples. Fermentation temperature: 43 °C, final pH = 4.5; storing temperature: 10 °C (Hinrichs et al. 2003)

Yoghurt	Milk Pretreatment	Heat Treatment	Hydrocolloid	Fermentation
P	pasteurised, homogenised denaturation fraction: 99 %	30 min, 90 °C	-	Lactobacillus delbrückii ssp. bulgaricus, Streptococcus salivarius ssp. thermophilus
PC	pasteurised, homogenised denaturation fraction: 99 %	30 min, 90 °C	κ-carrageenan (0.2 %)	Lactobacillus delbrückii ssp. bulgaricus, Streptococcus salivarius ssp. thermophilus
R	raw milk, native	30 min, 65 °C	-	Lactobacillus delbrückii ssp. bulgaricus, Streptococcus salivarius ssp. thermophilus
RC	raw milk, native	30 min, 65 °C	κ-carrageenan (0.2 %)	Lactobacillus delbrückii ssp. bulgaricus, Streptococcus salivarius ssp. thermophilus
M (merchandise)	unknown	unknown	unknown	unknown

Table 3.4.3: Ratio of the mass of non-washable serum and of the total mass of serum p_r and WHC according to Eq. (3.4.6) of the studied yoghurt, measured one day after the production or directly after the purchase (M) (triple determination) (Hinrichs et al. 2002).

Yoghurt	P	PC	R	RC	M
p_r / %	27.2	10.3	19.6	21.1	19.2
WHC	1.62	0.60	1.17	1.23	unknown

Table 3.4.3 shows the ratio of the mass of non-washable serum and of the total mass of serum p_r and WHC according to Eq. (3.4.6) of the studied yoghurt, measured one day after the production or directly after the purchase (M). Both p_r and WHC differ approx. about a factor three at one day after the production or directly after the purchase (M). In Fig. 3.4.4 the temporal evolution of p_r of the studied yoghurt samples is presented as a function of the storage duration (Hinrichs et al. 2002). The straight horizontal line marks p_r (Eq. 3.4.6) of the mer-

chandise directly after the purchase. Remarkable is that p_r (and thus WHC) of PC is smaller than that of P directly after the production (1 day) and higher than that of P after 8 days. That means obviously that the formation of the gel-network of κ-carrageenan and caseins requires more than 1 day. Only after the network has developed sufficiently, can serum be significantly adsorbed or retained. Whereas p_r of the yoghurt of the pasteurised milk (P) keeps almost constant after 8 days, p_r of PC decreases after 8 days. p_r of the yoghurt of the native raw milk (R) and of the native raw milk with carrageenan (RC) are similar 1 day after the production (within the standard deviations). After 8 days p_r of R is higher than that of RC. Afterwards the samples of R were spoiled by mould and the series had to be stopped.

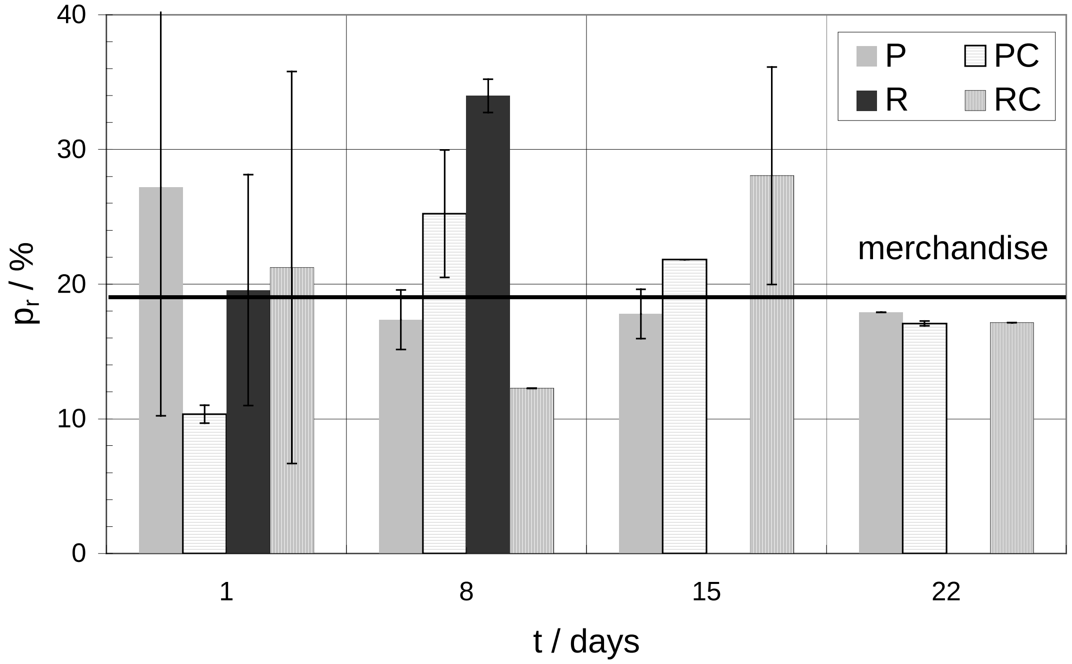


Fig. 3.4.4. p_r of the studied yoghurt samples (Table 3.4.2) during storing. The straight horizontal line marks p_r (Eq. 3.4.6) of the merchandise directly after the purchase (Hinrichs et al. 2002).

The washing-out reveals the fraction of a serum-phase contained in closed pores, which are presumably not capable of syneresis, or in open capillaries, which might contribute to syneresis. PC, for example, has the smallest value of p_r (≈ 10 %, Table 3.4.3) and contains, therefore, the highest portion of serum in capillaries. The serum retained in pores is approximate distributed among small, middle and big pores (increasing T_2). The results may be a hint to evaluating the structure of the gel matrix with regard to technically required standards and to identify those phases which should be modified by processing or additives in order to prevent, for example, syneresis.

Hydrocolloids. Hydrocolloids are used in food technology (e. g. jellied products, desserts and puddings, yoghurt, cocoa, ice-cream, marmalade, sausages, convenience food), but also in non-food products like ceramics, sewage sludge, paper or concrete as thickeners, gelling agents or stabilisers (physical stability). It is, furthermore, to incorporate water into foods in order to improve the yield and to design low-fat products like fat-reduced margarine. The majority of the functional properties of proteins in food systems are attributed to interactions with water and other food constituents (Kneifel et al. 1991). Miscibility, complex coacervation or incompatibility can occur which eventually lead to syneresis or sandy mouth-feeling (e. g. Edmond 1968; Syrbe 1998; Syrbe et al. 1998). Many hydrocolloids exhibit hysteresis of their T_1 and T_2 or rheological parameters for cyclic variations of the temperature (e. g. Suggett 1975; Lewis et al. 1987; Hinrichs et al. 2003).

Gelatine and polysaccharides like carrageenan and starch form polymer networks based on intermolecular H-bridges (Suggett 1975; Lagaly et al. 1997; Belitz et al. 2001). Polymer networks are usually thermoreversible due to the H-bridges which break up at sufficiently high temperatures. The critical material-specific concentration for gelling, which depends on the pH, the ion composition and concentration and the temperature, is generally low compared to aggregated dispersions of globular proteins (5-10 %). In contrast to polymer networks protein-gels are often based on intermolecular hydrophobic bindings of molecule-groups which are exposed by unfolding of protein-molecules or molecule-groups. The hydrophobic bonds are responsible for the thermoirreversible temperature-behaviour of protein-gels which do not melt, when heated. In some cases, however, they plastify and shrink (Guenet 1992; Belitz et al. 2001). Various spectroscopic NMR studies of solutions containing hydrocolloids (e. g. starch, carrageenan or gelatine) are presented below, together with relevant experimental parameters.

Gelatine mainly extracted from collagen of mammals is used because of its gelling properties in food technology, pharmaceutical and cosmetics industry (Falbe and Regitz 1998). The influence of temperature and gelatine concentration on the structure of gelatine-solutions was studied with the help of T_1 (Labuza and Busk 1979) and T_2 (Lambelet et al. 1988). Hills (1992a, b) modelled the water relaxation in biopolymer systems based on the proton exchange cross-relaxation. The mean T_2-relaxation times in gelatine-water systems increases dramatically at the temperature-induced sol-gel transition. This increase is, according to this model, caused by the increased relaxation times of exchangeable protein ^{1}H-proton spins and not by changing fractions or relaxation times of "structural water" postulated by Djabourov (1986). Traoré et al. (2000) studied chemical and diffusive exchange processes in water/gelatine systems by variation of the pulse spacing (90°-180°) in a CPMG sequence.

The combined application of ^{1}H and ^{23}Na NMR (T_1- and T_2-relaxation) enables one to differentiate three water-phases in aqueous gelatine gels as a function of the total water content (Vackier and Rutledge 1996; Vackier et al. 1999). The pH of the gels was adjusted with NaOH. The interpretation of the data is analogous to relaxation experiments with solid-fluid systems containing non-organic solid particles where dependent on the solid materials up to four phases have been detected (e. g. Götz et al. 2002d). The ^{23}Na relaxation times show at the same critical moisture contents (about 15 %) like the ^{1}H relaxation times a significant increase. This is probable due to their solvation in a multi-layer of water molecules appearing about 15 %.

Starch which serves as reserve-carbohydrates in many plants is mainly derived from maize, waxy maize, potato, manioc and wheat (Barsby et al. 2001; Belitz et al. 2001). Material properties relevant for structure or flow behaviour of starch-types are determined by the shape, the size, the particle-size distribution, the composition and the level of the moisture-dependent crystallinity of the starch granules (Noel et al. 1993; Buleon et al. 1998; Belitz et al. 2001). Further properties of starch relevant for food technology are the swelling as a function of temperature and moisture (Lechert and Hennig 1976; Lechert and Kuhn 1976; Hennig and Lechert 1976; Lechert et al. 1980: ^{1}H T_1, T_2, ^{2}H spectra; Lechert 1994: ^{1}H T_1, T_2, ^{2}H T_1, T_2,), the plastisication (used in starch terminology to describe the increase of viscosity) and eventually subsequent gelatinisation (Tang et al. 2001: ^{1}H T_2, ^{2}H spectra), the degree of polymerisation, glass transitions as a function of the moisture (Kou et al. 2000: T_1, T_2, spectra), the retrogradation (extensively irreversible transition from a dissolved or highly swollen state into a insoluble, not swollen micro-crystalline state) (Farhat 2000, Farhat et al. 2000: T_1, T_2, temperature, moisture), conformations of dissolved starch-molecules like multiple-(double)-helices or egg-box (Suggett 1975; Neszmélyi and Holló 1990: helicity), the fraction of crystallinity in starch (Blanshard et al. 1990: CP-MAS; Gidley et al. 1995: ^{13}C NMR), the ratio of amylose/amylopectin (Dunn and Krueger 1999) and the water content (Gamyunov et al. 1975: T_2; Leung and

Steinberg 1976: T_1, T_2; Labuza and Busk 1979: T_1; Yakubu et al. 1991: ^{2}H spectra; Kou et al. 2000: T_2) and the storage behaviour (Ruan et al. 1996: MRI, T_2). The mobility of the less mobile water phases decreases and the mobility of the more mobile water phases increases in starch-based foods during storage.

Carrageenan is extracted from red algae (Chondrus crispus and Gigartina stellata). Various carrageenan types can be differentiated with regard to the position and number of sulfate groups in carrageenan molecules. The industrially most relevant types are κ-, ι- and λ-carrageenan. After a heat treatment at 70 °C for 20 min the carrageenan molecules are present in the solution in a disordered coil-form. When reducing the temperature the conformation of κ- and ι-carrageenan changes to ordered helical structure (e. g. double helices) and aggregates of helices which have been shown to be coupled to gelation (e. g. Lewis et al. 1987). This transition is favoured by the availability of K^+-ions for κ- and Ca^{2+}-ions for ι-carrageenan. λ-carrageenan, however, is only viscosity increasing. Various parameters like concentration, temperature, carrageenan-type (κ, ι: Suggett 1975: T_1, T_2; Welti 1977: ^{1}H spectra; Labuza and Busk 1979: T_1), molecular weight of carrageenan (κ: Knutsen and Grasdalen 1992: ^{1}H spectra), composition of carrageenan molecules [for example containing κ- and ι-units (van de Velde 2001: ^{1}H and ^{13}C spectra)], ionic type and content (Lewis et al. 1987), salt composition (Borgstrom et al. 1998: influence on the nematic/isotropic phase transition; spectra) have a strong impact on macroscopic (e. g. texture, flow behaviour, sensorial behaviour, sol-gel transition temperature) and microscopic properties (e. g. T_1, T_2, spectra). The volume fraction of the nematic phase [liquid-crystal behaviour (Falbe and Regitz 1998)] correlates with the helical amount in gelling carrageenans (Borgstrom et al. 1998). Thus it is possible to observe coil-to-helix transitions by recording the evolution of the fraction of the nematic phase.

Gelling and only viscosity-increasing carrageenan types can be differentiated by the temperature-dependence of the relaxation times of the present phases $T_{2,i}$ and their fractions d_i (Eq. 3.4.1). For κ-, ι-, λ- and a hybrid κ/ι-carrageenan four phases can be detected in the temperature range from 10 to 70 °C by means of T_2-relaxation (Hinrichs et al. 2003). The mobility of the phases increases from phase 1 ("immobile") to phase 4 ("very mobile"). If the carrageenan is able to form a gel, like κ-carrageenan, ι-carrageenan or the used hybrid-type κ/ι a hysteresis-behaviour can be observed in the phases 2 to 4. Phase 1, which represents the solid and immobilised phase, does not seem to be involved in the gelling process. λ-carrageenan which is only viscosity-increasing shows no hysteresis in its temperature-profile (Hinrichs et al. 2003). The behaviour of mean relaxation times T_{2m} for the solutions is analogous to their voluminosity, that means the amount of “bound”/immobilised water. The voluminosity in gels, however, is in contrast to solutions at present not determinable by means of rheology. Sol-gel transitions can, furthermore, be detected by means of $T_{2,i}$ and d_i (Hinrichs et al. 2003), which provides a more detailed insight into the occurring micro-structural changes than the mean T_{2m}-times alone (Suggett 1975).

For various polysaccharides including cellulose ^{13}C CP-MAS spectra of hydrated samples have smaller half-widths than spectra of dry powders revealing an ordering effect with increasing hydration (Horii 1989). Baar et al. (1994) used ^{1}H and ^{13}C spectra to study the structure of carbomethyl-cellulose with regard to the positions of hydroxyl groups in the molecule. Pectins were studied varying the temperature and the concentration (Leung and Steinberg 1976: ^{1}H T_1, T_2; Williams et al. 1998: ^{2}H spectra).

Ad (b): The motivation to derive correlations between NMR parameters and macroscopic properties of materials is that these correlations are ideal to determine industrially relevant quantities (material properties, process conditions, controlled conditions) by partly methodologically or apparatively more comfortable NMR methods. NMR techniques enable non-destructive measurements which are often less time-consuming compared with other methods and which provide the possibility to on-line measurements (see below). This is a necessary prerequisite for an effective process and quality control.

The composition of many food and non-food systems, however, complicates the analysis of the structure, the elucidation of structurally relevant parameters and the development of correlations between microscopic and macroscopic or, especially for food systems, between the physical and microbiological data (Hills 1999). Dependent on the type of materials and the corresponding applications, nevertheless, various empirical and, in few cases, even theoretical relationships exist between characteristic industrially relevant quantities and NMR results. In the following chapter examples pertinent to the processing of disperse media are given.

Correlation between flow behaviour and T_1- or T_2-relaxation times

For pure fluids (e. g. water, glycerine, ethyl alcohol, acetic acid) Bloembergen et al. (1947, 1948) found for simple Newtonian fluids theoretically and experimentally a correlation between the NMR relaxation times T_1 and T_2, respectively, and the dynamic viscosity η, which is valid independently of temperature and pressure. Harz (1987) showed that this correlation also holds for aqueous solutions like aqueous sugar solutions, fruit juices, beer and wine. Further studies on silicone oil/glass sphere suspensions and beer mashes demonstrated that the T_2-η correlation which was originally exclusively derived for Newtonian fluids can also be applied to suspensions (Götz et al. 2000b, 2003b). In contrast to aqueous sugar solutions there is not a simple potential dependence in suspensions between the viscosity and the corresponding relaxation times. The correlation between characteristic viscosities such as the zero-shear-rate viscosity η_0 or the viscosity at high shear rates κ η_∞ can, nevertheless, be used to determine viscosities by means of the corresponding T_1- or T_2-relaxation times. In other words the viscosities η are a function of the relaxation times T_1 and T_2: $\eta = \eta(T_1, T_2)$. For the modified four-parameter Carreau model, for example, holds (Carreau et al. 1996, 1997)

$$\eta(\kappa) = \frac{\eta_0 - \eta_\infty}{\left[1 + \left(\frac{\kappa}{\kappa_1}\right)^a\right]^{0.5}} + \eta_\infty \tag{3.4.7}$$

κ	shear rate
η_0	zero-shear-rate viscosity
η_∞	viscosity at high shear rates
a, κ_1	parameters

Only finely ground malt can be tested in conventional rheometers, as due to scale effects (Becker and Bürger 1975) with respect to the maximum particle size suspensions containing particles with diameters in the order of the characteristic dimensions of the rheometer do not fulfil the prerequisites of continuum mechanics. Continuum mechanics is, however, one of the main prerequisites of conventional rheometry.

For silicone oils with different molecular weights it is possible to determine the viscosity and the molecular mass by using a correlation with the corresponding T_2 NMR-relaxation times (Götz et al. 2001a). Similar correlations between T_1 or T_2 and η have been found for cis-polyisoprene solutions (Charlesby and Bridges 1981), solutions and suspensions of carbohydrates and sugars of corn (Mora-Gutierrez and Baianu 1989), for milk during acidification with yoghurt culture with and without stabilisers (storage and loss moduli G' and G'': Barfod 1991), for binary mixtures of methanol and tetrahydrofuran (Gill et al. 1993), for paper pulps (Draheim and Ragauskas 1997), for industrial sauces containing starch with different cooking time

(G′ and G′′: Thebaudin et al. 1998), for extra-heavy crude oils (Fisher et al. 1999) and for model cheese samples (compression and stress relaxation measurements: Budiman et al. 2000).

Besides scale effects homogeneity is another prerequisite for simple rheological constitutive laws. This is a crucial aspect in process engineering, as many products are multi-phase systems. Phenomena causing heterogeneity like phase separation (e. g. creaming), sedimentation, tearing apart (e. g. fats, ointments) are usually difficult to detect and quantify in conventional rheometry. Flow experiments (chapter 3.2) combined with spatially resolved spectroscopy (chapter 3.4) or eventually MRI (chapter 3.1) will allow to observe heterogeneity causing flow-induced effects and wall slip. Appropriate spectroscopic methods enable to characterise flow-induced time-effects caused by the energy input or due to special preparation techniques like agglomeration, desagglomeration or crushing (Götz et al. 2002f).

Rheo-NMR

Nakatani et al. (1990) proposed the so-called Rheo-NMR to record the microscopic structural changes (e. g. shear-induced phase-transitions) in polymer melts and solutions as a function of the shear rate, the time (energy input) and the temperature both in transient and steady-state flow. Conventional rheometer designs (e. g. cone/plate, plate/plate, Couette) are integrated into standard NMR probeheads. The usage of isotopic labelling enables one to differentiate the "mechanical" behaviour of chain ends from internal segments of the sheared molecules. Applications to polymeric systems (including polymer melts, rigid rod and random coil polymers in solution, liquid crystals and food systems) in shear and extensional flow are given by Siebert et al. (1997), Manz and Callaghan (1997), Callaghan and Gil (1999, 2000), Callaghan (1999) and Callaghan and Fischer (2001). Callaghan and Gil (2001) studied carrageenan sol and gels which can be distinguished by means of flow experiments. If a flowing sol is cooled down slowly beneath the sol-gel temperature, which holds for materials at rest, only partial gelation can be observed. The sol state (65 °C), the gel state (30 °C) and the shear-induced sol state (30 °C) exhibit clearly distinguishable spectra. (i) polymer sites with reduced segmental mobility (junction zones) caused by intermolecular interactions and (ii) molecules or molecule-groups, which are not or less influenced by these interactions and thus reveal higher T_2, can be observed by means of T_2-distributions. Shearing causes a reduction of junction zones (i).

Rheo-NMR probeheads enable, as shown above, one to monitor flow-induced structural changes in complex fluids undergoing well-defined flow-types and thus mechanical treatments (stress, deformation, deformation-velocity tensor and derivatives). They could, furthermore, be used to guarantee homogeneity as mixing devices with known shear rate distributions during arbitrary NMR experiments (Götz et al. 2004a). This is very interesting for materials like beer mashes or aqueous starch suspensions which require mixing during thermal treatment. Without mixing, these systems tend to sediment and eventually stick to the walls of the apparatus. As a consequence the corresponding processes achieve a minor efficiency and quality. The same holds for ceramic masses which require sufficient mechanical energy input by shearing or kneading (Götz et al. 2002f) or ultra-sonification (Götz et al. 1999) in order to obtain and maintain structural homogeneity for time periods sufficient for a reliable handling during processing. Comparable materials are problematic to study by non-localised NMR spectroscopy without continuous mixing. Thus Rheo-NMR probeheads enable one to characterise online reacting, eventually phase-separating disperse systems, to identify occurring processes and to derive relevant kinetic parameters.

Porous Media

Besides self-diffusion coefficients determined by PFG NMR, relaxation times are another independent approach to characterise the structure of solid materials and to study the dynamics of hydration and dehydration of water or other fluids in porous systems. The NMR relaxation times of fluids in partially or completely saturated porous media are generally reduced compared to the free, bulk fluid due to interactions between liquid molecules and the liquid-solid interface (e. g. Rigby and Gladden 1999). Examples are cement pastes, soils, porous silica particles and foods. In many cases a simple two-site model is used to interpret the observed enhanced relaxation rates in porous media (e. g. Brown and Fatt 1956; Zimmerman and Brittin 1957; Brownstein and Tarr 1979; Kleinberg et al. 1994; Watson and Chang 1997; Barrie 2000).

$$\frac{1}{T_1} = \frac{1-f}{T_{1f}} + \frac{f}{T_{1s}} \tag{3.4.8}$$

f	fraction of the fluid in contact with the solid
T_{1f}	T_1-relaxation time of the free or bulk fluid
T_{1s}	T_1-relaxation time of the surface fluid with enhanced relaxation rate

If a homogeneous water layer is assumed at the solid surface (pore surface area S and pore volume V) with the thickness h, the Eq. (3.4.8) can be rearranged as (e. g. Tellier et al. 1993, Table 3.4.1)

$$\frac{1}{T_1} = \frac{1}{T_{1f}} + \frac{h \cdot S}{V}\left(\frac{1}{T_{1s}} - \frac{1}{T_{1f}}\right) \tag{3.4.9}$$

The thickness h is a characteristic length representing the extension of the surface interaction responsible for the enhanced relaxation. Eq. (3.4.9) may be rewritten in order to define the so-called surface relaxivity ρ_1 which describes the enhancement of T_1 at the surface (Brownstein and Tarr 1979; Kleinberg et al. 1994; Barrie 2000)

$$\frac{1}{T_1} = \frac{1}{T_{1f}} + \rho_1 \frac{S}{V} \tag{3.4.10}$$

ρ_1	relaxivity

A detailed derivation of Eq. (3.4.10) is given by Watson and Chang (1997). Analogous expressions exist for T_2-relaxation (Swift and Connick 1962; Kleinberg et al. 1994; Jehng et al. 1996; Kleinberg 1996a; Barrie 2000).

The wettability is a measure of the tendency of a fluid to adhere to a solid surface. For simple solid systems the contact angle between a liquid and the solid phase characterises the wettability of a specific solid surface by the liquid (e. g. Löffler and Raasch 1991). The surfaces in many real porous media are both geometrically and chemically heterogeneous so that the determination and interpretation of the contact angle is problematic. A practicable approach based on T_1-relaxation is the assumption of rapid exchange of liquid molecules between (i) the zone at the solid surface, more precisely the zone with interactions between the liquid and the solid material, and (ii) the molecules in the bulk fluid according to Eq. (3.4.8). The change of T_1 (in the porous medium) compared to T_{1f} in the bulk phase can be used to derive the fraction f of the fluid interacting with the solid. In order to characterise the density of reactive surface sites in a fluid saturated porous system (potassium feldspar) the influence of ion concentrations from different salts on T_1 was measured (Frosch et al. 2000). In the studied pH range mineral surfaces are considered as negatively charged. The added cations interact with active sites on the solid surface, thus reducing the probability of a water molecule to relax at active sites at the surface. Macroscopically this means that the relaxivity ρ_1 decreases. The size and charge of the cations seem to have a strong influence on T_1 for high cation concentrations, which is not completely clarified.

Fluid molecules near solid walls are exposed to relaxation mechanisms different from those in the bulk fluid. Various models have been developed to derive pore-size distributions from relaxation measurements. Due to the actual complex interactions and the corresponding relaxation mechanisms, formalisms generally valid for all porous media have not been developed yet (e. g. Smith et al. 1994). In spite of these ambiguities, relaxation measurements enable one to characterise individual pore-systems. Gallegos et al. (1987) found, based on a two-site model, that the mean relaxation time T_1 is related to the pore radius by

$$\frac{1}{T_1} = \frac{1}{T_{1f}} + \frac{\beta}{r_p} \tag{3.4.11}$$

r_p hydraulic pore radius with $r_p = 2V/S$

β parameter depending on fluid-solid interactions at the wall, for example van der Waals or hydrogen bonding

For pores with diameters smaller than 3 nm a third term arising from purely geometrical effects have to be added in Eq. (3.4.11) (Watson and Chang 1997). Assuming these correlations it is possible to derive the pore-size distribution from the frequency distribution of T_1. This method works also in hydrogels (Chui et al. 1995). Another possibility to determine mean pore-sizes are chemical shift measurements of gases, for example ^{129}Xe, as a function of the loading (Ripmeester and Ratcliffe 1990; Jameson et al. 1992). The method works for pore sizes in the order of 1 nm. Advantages of the relaxation and chemical shift studies are that the samples do not need to be dried or the pore fluid has to be exchanged. The knowledge of the chemical composition of the fluid is, however, necessary for the interpretation of relaxation and chemical shift measurements.

The dependence of T_1 on the resonance frequency ω_0 ($\sim|\mathbf{B}_0|$) can be determined for porous media saturated with fluids by means of field-cycling T_1-relaxation time measurements (e. g. Stapf and Kimmich 1995; Zavada and Kimmich 1998, 1999). The measurements are performed at temperatures above and below the freezing phase transition of the studied fluid. While the bulk fluid is frozen, a non-frozen fluid-layer exists at the solid surface due to the different and often incommensurable crystal structures of the fluid-adsorbate and the structure of the matrix surface. Thus the fluid-molecules in the adsorbed layer are, even in the frozen state of the bulk-fluid, surprisingly mobile due to translational diffusion mechanisms along the surface. As a consequence pores or irregularities in the solid surface can be characterised by spin-lattice relaxation dispersion $T_1 = T_1(\omega_0)$. This method is applicable to porous media whose structures do not significantly alter in the temperature regime above and below the freezing phase transition of the fluid.

Hills et al. (1998) determined the size distribution of pores in freeze-dried starch gels by T_2-relaxometry. Acetone was infused into the pore-system. The aim of the study was to obtain information concerning the size-distribution of crystallites in frozen gels which is important for the optimisation of freezing- and freeze-drying processes and for the improvement of the product-quality. In order to determine the pore-size distribution of porous solid systems like rocks water is used to saturate the pore-system (Hills et al. 1996d). Acetone does not - in contrast to water - cause a collapse of food matrices.

Besides the possibility to calculate the permeability of a porous medium from the tortuosity and the surface-to-volume ratio (Hürlimann et al. 1994; Latour et al. 1995, Frosch et al. 2000) with the help of models like Carman-Kozeny (1948, 1956; 1929) or Gupte (1970) it is possible to derive permeabilities by correlating results of T_1-, T_2- and self-diffusion experiments D_S and the porosity ϕ (Timur 1969: sandstone with ϕ; Banavar and Schwartz 1987: sandstone with T_1, ϕ; Friedmann and Windhab 1998; Friedmann 1999: glass spheres, kieselguhr and cellulose with T_1, T_2, D_S, ϕ; van der Zwaag et al. 2001: sandstone, chalk with T_2). Thompson et al. (1989) found a correlation between the permeability and $T_{1\rho}$ by means of ^{2}H NMR in sandstones and carbonates.

Kleinberg (1996a) showed that capillary pressure curves, which are important to characterise the wetting- and de-wetting behaviour of capillary-porous media, can be derived from NMR T_2-distributions. This provides the possibility to characterise on-line the quality of subsurface geological formations using borehole NMR apparatus.

Water Activity

In food technology the microbial stability and thus the shelf-life are important properties of initial, intermediate or final materials. The so-called water activity a_W proved to be a better critical parameter in the control of microbial spoilage and chemical (both enzymic and non-enzymic) reactions for many food systems than the moisture content (Hills et al. 1996c; Ruan and Chen 1998). Detailed reviews concerning the prerequisites and the limitations of the a_W concept including extensions based on polymer science are given by Levine and Slade (1991), Hills (1996), Hills et al. (1996b), Kessler (1996), Ruan and Chen (1998) and Kalichevsky-Dong (2000).

Ruan et al. (1999b) studied various dough systems at moisture contents F of 12 to 45 % with T_2-experiments. The amount and state of water play an important role in the preparation and properties of wheat flour doughs and the final products (flow behaviour, texture, shelf-life) (Götz et al. 2003a). Depending on the moisture content, up to five phases of water can be detected in dough with a continuum model assuming continuous frequency distribution of T_2-relaxation times. The contributing regions of the five phases partly overlap. A discrete model, assuming a sum with a finite number of exponential functions, however, provides three phases. The relaxation times T_2 and the corresponding fractions change significantly for both models at moisture contents of 23 and 35 %. These critical moistures correlate with results from sorption isotherm studies (Daniels 1975): (i) $F = 0\text{-}6.5$ % or water activity $a_W = 0\text{-}0.2$: first monolayer, (ii) $F = 6.5\text{-}14$ %, $a_W = 0.2\text{-}0.7$: further monolayers, (iii) $F = 14\text{-}23$ %, $a_W = 0.7\text{-}0.95$: capillary condensation, (iv) $F > 23$ %, $a_W = 0.95\text{-}1$: free water.

Critical values of the water activity for the water sorption have also been observed in paper and cardboard (used as packaging materials for foods) in combination with T_1-, T_2-, moisture content and self-diffusion measurements (Weisser and Liebenspacher 1991; Liebenspacher 1991). Experimentally (Curme et al. 1990: casein model systems) and semi-empirically linear relationships (Hills 1998: packed beds of silica particles) between the reciprocal value of the observed mean relaxation time T_{2m} and the water activity a_W have been found for higher values of the water activity. The germination time of Aspergillus niger conidia, however, shows a better correlation with the self-diffusion coefficient D_S compared to a_W, the moisture content, T_1 and T_2 (Kou et al. 1999).

Baking and Storing (Staling)

Low field ^{1}H NMR (T_2-relaxation) in combination with chemometric data analysis were applied to characterise the water binding-types in dough (during the baking and storing) and to study the kinetics of the baking process from dough to bread inside the NMR magnet (Engelsen et al. 2001). Characteristic temperatures, for example at approx. 55 °C for the gelatinisation of starch, have been identified. Chinachoti (1998) studied the ageing of bread and starch gels with ^{1}H NMR and ^{2}H NMR. Changes of the mobility of water during the storage might be influenced by a decrease of freezable water (observable by DSC), a migration of water between gluten and starch and an immobilisation of water, for example induced by a crystallisation of starch, leading to water of crystallisation and smaller T_2.

Further Correlations

Storage-dependent structural changes of intact shell eggs are detectable by T_2-experiments using LR-NMR (Schwägele et al. 2001). Eggs were stored at various temperatures and relative humidities or predetermined temperature/time conditions. T_2-experiments of intact eggs, which have been inoculated with a pool of bacteria, show that microbially induced changes can be observed by exclusive use of NMR for sufficiently high bacterial counts (> 10^8 c.f.u./g egg content) (Kröckel et al. 2001).

The spoilage of foods with water activities $a_w > 0.9$ can be quantified by NMR (Schenz et al 1993). The method has been tested for bacillus circulans and bacillus megaterium. The amplitude of a FID as a function of the time after inoculation with various types of bacilli decreases with increasing spoilage. Problematic is presumably the detection level which might depend on the studied food product.

The swelling and deswelling of materials correlates with different spectroscopic data. The macroscopic swelling correlates with the chemical shift of the absorbed solvent in cross-linked polymers (O´Connor et al. 1996, 1997) and in coals with the corresponding T_1 and T_2 (Hou et al. 1996).

The evolution of the solution-rate and the time-length of the complete reconstitution of milk powders can be determined by means of LR-NMR (Davenel et al. 1997). This method allows, furthermore, to quantify the impact of the composition (proteins, polysaccharides, salts, etc.) and of the processing on the reconstitutability of spray-dried powders.

The pattern of temperature-T_2 curves provides a classification of powders with regard to their caking behaviour (Chung et al. 2000). The kinetics of the drug release in proteineous matrices is correlated with the evolution of T_1 and T_2 during the hydration (Katzhendler et al. 2000). Thus the efficiency of varying formulations can be characterised by NMR relaxation measurements. The sensory texture of cooked potatoes correlates with uniaxial compression tests and even better with T_2-relaxation times (Thybo et al. 2000).

Chemometric Techniques

Usually the results in an NMR experiment in the time domain (e. g. FID or CPMG) are Fourier transformed into the frequency domain in order to obtain a spectrum (frequency distribution). Quantitative information concerning the composition of the sample can be derived by fitting the corresponding spectrum with a sum of Gaussian and/or Lorentzian functions. Problems arise for overlapping resonances, usually especially at low magnetic fields B_0 (Nordon et al. 2001). Chemometrics, which includes the application of statistical, analytical and numerical methods to analytical measuring techniques, allow, in many cases, one to enhance the extracted information from experimental data (Brereton 1987; Martin and Martin 1990; Adams 1995; Massart et al. 1997; Rutledge and Barros 1998; Lai et al. 2000). Applications of chemometrics techniques to NMR data are the discrimination between apple varieties for juices (Belton et al. 1998a), the simultaneous determination of the dry matter and the fat content in different cheese-types (Vackier et al. 1998), the determination of the total content of styrene in copolymers (Sardashti et al. 2001) and the simultaneous determination of the oil and water content in intact fish samples (Jepsen et al. 1999) or cheese (Chaland et al. 2000).

McCarthy and McCarthy (1996) and Hills (1995) proposed NMR and MRI (chapter 3.2) for process control in food research and production based on correlations between NMR parameters and quality factors of food products. The development of rapid measuring methods for process and quality control represents a major challenge for food control including analytics and food technology (e. g. Windhab and Bolliger 1996). NMR spectroscopy and especially LR-NMR offer interesting options for food characterisation regarding different material properties. In combination with fast automated evaluation-procedures NMR and MRI measurements in real time offer the possibility for an effective quality and process control of dynamic processes including enzymic and non-enzymic chemical reactions. Process NMR spectroscopy will not be applied for trace analysis. Time-consuming tests, however, can partly be substituted.

In order to optimise processes, process conditions and devices the corresponding reactions are monitored with continuous-flow NMR, additionally in combination with chromatographic or other measuring methods (Nordon et al. 2001). Two modi of process NMR spectroscopy are realised: continuous-flow and stop-flow as in the common tube NMR spectroscopy. The continuous-flow requires usually premagnetisation in order to guarantee a complete polarisation when the sample enters the measuring volume. The sensor can be integrated into a pipe, belts or chutes.

High Resolution continuous-flow NMR experiments have been performed by Fischer et al. (2000). The sample is pumped through a glass cell with a tube-loop through the measuring volume with 60-120 µl and transport time from apparatus (e. g. agitator vessel, thin-film evaporator) to the magnet within 1 min. The reaction order, the rate constant and the equilibrium constant of the participating reactions can be derived.

Roy and Marino (1999) realised a process control based on LR-NMR. For polymers various structural-morphological parameters can be derived with an accuracy sufficient for process control of industrial polymerisation reactions. Multivariate calibrations allow one to determine or estimate the degree of crystallinity, viscosity, total hydrogen content in hydrocarbons, fluorine content, additive content, mass density, cross-link density, tacticity, degree of polymerisation, melt index and molecular mass. Draheim and Ragauskas (1997) showed that LR-NMR can be used as process control for the pulp and paper industry. Firstly, T_{2m} correlates with the viscosity and, secondly, the FID (Free Induction Decay) signal with the solid content of the pulps.

On-line process NMR spectroscopy has also been applied in bio- or food-technology to characterise the energetic status of cells (Alves et al. 1996: ^{31}P NMR), to monitor the fermentation of yoghurts (Hinrichs et al. 2004: ^{1}H LR-NMR, recipes, pretreatment, culture), the mashing of beer (Götz et al. 2003b, 2004a: ^{1}H LR-NMR, raw fruit, malt, particle size of the malt after milling) and the cooking of various rice-types (Götz et al. 2004c: ^{1}H LR-NMR, rice-species, shelling and polishing process). The production processes are realised in the measuring volume of the NMR device. The obtained data may be used (i) to record and understand dynamic processes including enzymic and non-enzymic chemical reactions during the production processing and (ii) to form the basis for an effective quality and process control of production units.

3.5 Relevance of NMR for Process Engineering

To summarise the findings, NMR enables one to study many products and processes in engineering science which are often inaccessible by other measuring techniques. Reviews on spectroscopic and tomographic methods applied in process engineering are given by Beck et al. (1994), Wilson (1994), Plaskowski et al. (1995), Williams and Beck (1995), Windhab and Bolliger (1996), Cullen et al. (2000) and Nordon et al. (2001). The advantages of NMR-applications in engineering are:

- Numerous measuring quantities and contrast giving parameters (chapter 2.2) are available in MRI, for example in contrast to X-ray tomography.
- None or only minor preparation (e. g. dilution of suspensions for optical techniques) is necessary.
- Tracers generally do not have to be added. Detectable spins themselves can act as tracers.
- NMR measurements are non-destructive and non-invasive.
- Processes can be studied completely by means of NMR using one single sample, thus reducing systematic measuring errors resulting from compositional or experimental variations.
- Using other techniques without spatial resolution, effects are averaged, for example in systems with a tendency to phase-separating, and might be misinterpreted and added eventually to measuring errors.
- Temperature-determinations and -control can be realised.
- NMR is applicable to materials in different physical states, e. g. states of aggregation, and in difficult process conditions [pressure up to 900 MPa (Zahl et al. 1994; Ballard and Jonas 1997), temperature up to 2500 °C (Müller 2002)].
- There are no restrictions concerning the structure of the sample, for example with regard to the viscosity or elasticity.
- An on-line determination of practice-relevant quantities (viscosity, water-holding capacity, denaturation fraction) is possible in order to control the assumed or required process conditions with regard to the temperature, concentration and velocity distributions.
- The use of electromagnetic (e. g. micro-waves, laser, IR) and ultrasonic waves is possible in the interior of the measuring volume.
- Scale effects influence NMR measurements less than other measuring techniques (Becker and Bürger 1975).
- Demixing can be prevented (e. g. by ultra-sonification or Rheo-NMR probehead).
- Evaporation and hence a concentrating of the solid content or a physical/chemical structural modification can be hindered.
- The measuring times of specific NMR sequences are comparatively short.

Critical issues or restrictions concerning the samples of NMR are:

- Ferromagnetic materials cannot or only in special cases be studied. Paramagnetic or electrically conductive components of the sample are problematic, as they cause a reduction of relaxation times or eddy currents.
- Trace analysis, that means the detection and quantitative determination of low concentrations, is generally not possible due to the comparably low sensitivity.
- The acquisition and maintenance costs of NMR devices are, apart from LR-NMR instruments, comparably high. For many applications highly-skilled operators are required.

The potential of NMR for engineering was demonstrated by means of selected natural and technical examples. Four topics offer promising applications of NMR: (a) imaging for the analysis of structure and structural changes of disperse media, (b) convective and (c) diffusive transport processes and (d) spectroscopic material characterisation. Besides the established role of NMR in chemistry, biochemistry and biology as *chemical structural analysis* or for the *detection and quantitative monitoring of physical, chemical and enzymatic reactions*, the relevance of NMR for engineering is based on the following possibilities and applications of non-invasive and non-destructive spectroscopic and tomographic NMR sequences with eventual temporal, spatial and chemical resolution:

- The *composition* and *inner structure* of static and dynamic systems and processes are accessible for quantitative characterisation.
- *Process and quality control* can be realised without preparation or disturbing the corresponding product or process.
- *Micro-models* and *physically established, phenomenological constitutive laws* may be derived from the microscopic data. These models are required for the professional design of industrial processing units and products.
- By means of the microscopic non-destructive and non-invasive access the development and *validation of models*, boundary and initial conditions and the critical *verification of predictions* for technical solutions is possible.

Chapter 4

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