

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

**Flow and Diffusion  
Measurements  
on Complex Fluids  
Using  
Dynamic NMR Microscopy**

A thesis presented in partial fulfilment  
of the requirements for the degree  
of Doctor of Philosophy in Physics  
at Massey University

Bertram Manz  
1996

# Abstract

This thesis deals with the measurement of fluid motion by NMR methods and the relationship of that motion both to the molecular organisation and to the fluid boundary conditions. The theory and technique of dynamic NMR microscopy are presented. A specially designed high gradient probe for Pulsed Gradient Spin Echo (PGSE) experiments is described.

First, the time evolution of electroosmotic flow in a capillary is measured. With increasing time after the application of an electrophoretic pulse a transition from plug flow to parabolic flow is found. The agreement of the measured flow profiles with theory is excellent.

Next, a two-dimensional velocity exchange experiment (VEXSY) is described. Experiments on unrestricted Brownian motion, laminar circular flow in a Couette cell and flow through microspheres are performed.

A major aspect of the thesis concerns molecular dynamics in semi-dilute polymer solutions close to a de-mixing transition. Therefore, a description of the Flory-Huggins model for the phase behaviour of polymer solutions is given along with a review of the literature on shear-induced effects in semi-dilute polymer solutions. PGSE experiments were performed in order to measure the temperature dependence of the self-diffusion coefficient of polystyrene in semi-dilute cyclohexane solutions near the de-mixing transition over a wide range of molar masses. The temperature dependence can be described by a Williams-Landel-Ferry (WLF) equation, characteristic of a glass transition. From the self-diffusion coefficients the values for the tube disengagement times were obtained.

NMR rheology experiments were performed on semi-dilute polystyrene/cyclohexane solutions near the de-mixing transition. The flow profiles exhibit power law behaviour, and from the power law index the entanglement formation times are extracted. A consistency of the values for the entanglement formation times and tube disengagement times was found.

As part of the study of polymer solutions at elevated temperatures, strong convective effects were observed. In order to carry out diffusion measurements these effects were suppressed using better thermal equilibration. However, the

convection process itself was subject to NMR investigation. Convective flow in a capillary was measured using PGSE NMR, VEXSY and dynamic NMR microscopy. The VEXSY experiment shows that the flow is stationary. The velocity propagator measured using dynamic NMR microscopy was used to calculate the echo attenuation function  $E(q)$ . It was found that the pronounced minima and maxima in the Stejskal–Tanner plots agree well with the measured  $E(q)$  values.

Flow profiles of lyotropic liquid crystals are presented. Using deuterium NMR spectroscopy it is shown that the shear-induced alignment of molecules can be measured using NMR microscopy.

# Acknowledgements

The following people have helped me with this work. It is a pleasure to thank them here.

Prof. Paul T. Callaghan, my first supervisor, for his constant support, enthusiasm and expertise.

Assoc. Prof. Rod K. Lambert, my second supervisor, for support and discussions.

The staff of the electronics workshop who built the shift register which enabled me to sleep at night while the experiments were running, and for helping me with many little problems.

The staff of the mechanical workshop for building a driving system for the Couette system and countless other items.

Grant Platt for building the dewars of the PGSE probe and for cutting and sealing my sample tubes.

Dr. Phil Back for designing and building the PGSE probe.

Dr. Bas Smeulders for supplying me with information about the Dobanol/Water system.

Dr. Joe Seymour who inspired me with his enthusiasm and gave me permission to use some of his data.

My fellow graduate students Andrew, Craig, Lucy and all other inhabitants of the NMR lab for being friends and colleagues.

The secretaries for their help with administration.

All members of the Physics department for maintaining a pleasant working environment.

The German Academic Exchange Service (DAAD) and the New Zealand Foundation for Research, Science and Technology for financial support.

Anna for putting up with me.



# Contents

<b>Abstract</b>	<b>i</b>
<b>Acknowledgements</b>	<b>iii</b>
<b>Table of Contents</b>	<b>v</b>
<b>List of Figures</b>	<b>xi</b>
<b>List of Tables</b>	<b>xv</b>
<b>1 Introduction</b>	<b>1</b>
1.1 Introduction . . . . .	1
1.2 Organisation of the Thesis . . . . .	2
<b>2 Introduction to NMR and Imaging</b>	<b>5</b>
2.1 NMR Theory . . . . .	6
2.1.1 The Quantum Mechanical Description . . . . .	6
2.1.1.1 Quantum Mechanical States and Operators . . . . .	6
2.1.1.2 Angular Momentum Operators . . . . .	7
2.1.1.3 Nuclear Spins in a Magnetic Field . . . . .	7
2.1.1.4 The Ensemble Average . . . . .	8
2.1.1.5 Time Evolution . . . . .	9
2.1.2 The Semi-Classical Picture . . . . .	10
2.1.2.1 The Rotating Frame . . . . .	10
2.1.2.2 Excitation . . . . .	11
2.1.2.3 Relaxation . . . . .	13
2.1.2.4 Free Induction Decay . . . . .	14
2.2 Nuclear Interactions . . . . .	15
2.2.1 Magnetic Field Inhomogeneity . . . . .	15
2.2.2 Chemical Shift . . . . .	15
2.2.3 Dipolar Coupling . . . . .	16

2.2.4	Quadrupolar Coupling . . . . .	17
2.3	Spin Manipulations . . . . .	17
2.3.1	The Spin Echo . . . . .	17
2.3.2	The Stimulated Echo . . . . .	21
2.3.3	The Quadrupole Echo . . . . .	21
2.3.4	Two-Dimensional Spectroscopy . . . . .	22
2.3.5	Signal Averaging and Phase Cycling . . . . .	23
2.3.6	The Effect of Magnetic Field Gradients . . . . .	25
2.4	Introduction to NMR Imaging . . . . .	25
2.4.1	$k$ -Space Imaging . . . . .	25
2.4.2	Selective Excitation . . . . .	26
2.4.2.1	Hard Pulses and Soft Pulses . . . . .	27
2.4.2.2	Slice Selection . . . . .	28
2.4.3	Fourier Imaging in Two Dimensions . . . . .	28
2.4.4	Measuring Self-Diffusion: The Pulsed Gradient Spin Echo . . . . .	30
2.4.5	Dynamic NMR Imaging . . . . .	32
2.4.5.1	Introduction to $q$ -Space . . . . .	32
2.4.5.2	The Dynamic Spin Echo . . . . .	32
2.5	Hardware and Software . . . . .	34
2.5.1	The Bruker AMX300 Spectrometer . . . . .	34
2.5.2	The FX60 Spectrometer . . . . .	35
2.5.3	The High-Gradient Probe . . . . .	35
2.5.3.1	The Gradient Coils . . . . .	36
2.5.3.2	Gradient Calibration . . . . .	37
2.5.3.3	Gradient Eddy Currents . . . . .	38
2.5.3.4	Temperature Control . . . . .	38
2.5.3.5	r.f. Stage . . . . .	39
2.5.4	Data Processing . . . . .	40
<b>3</b>	<b>Imaging of Electroosmotic Flow</b> . . . . .	<b>43</b>
3.1	Introduction . . . . .	43
3.1.1	Electrophoresis and NMR . . . . .	43
3.1.2	Electroosmosis . . . . .	45
3.2	Theory . . . . .	45
3.3	Experimental Section . . . . .	49
3.4	Results . . . . .	51
3.5	Discussion . . . . .	55

<b>4</b>	<b>Velocity Exchange Spectroscopy</b>	<b>57</b>
4.1	Introduction . . . . .	57
4.2	Theoretical Considerations . . . . .	58
4.3	Experimental . . . . .	60
4.3.1	Unrestricted Brownian Motion . . . . .	60
4.3.2	Laminar Newtonian Flow in a Couette Cell . . . . .	61
4.3.2.1	Calculation of the VEXSY Spectra . . . . .	61
4.3.2.2	Measurement of the VEXSY Spectra . . . . .	64
4.3.3	Flow Through Micropores . . . . .	68
4.4	Conclusions . . . . .	70
<b>5</b>	<b>Polymer Physics</b>	<b>73</b>
5.1	Introduction . . . . .	73
5.1.1	Definition of a Polymer . . . . .	73
5.1.2	Molecular Weights and Polydispersity . . . . .	73
5.1.3	Polystyrene . . . . .	74
5.2	Dynamics of Polymer Chains in Solution . . . . .	74
5.2.1	Random Coils in Dilute Solutions . . . . .	75
5.2.2	Thermodynamics of Polymer Solutions . . . . .	76
5.2.3	Osmotic Pressure and the Flory Temperature . . . . .	78
5.2.4	Phase Equilibria . . . . .	78
5.2.5	Concentration Regimes . . . . .	81
5.2.6	The Reptation Model . . . . .	83
5.3	Rheology of Polymer Solutions . . . . .	87
5.3.1	Introduction and Definitions . . . . .	87
5.3.2	Dependence of Non-Newtonian Viscosity on Shear Rate . . . . .	88
5.3.3	The Glass Transition . . . . .	91
5.4	Flow-Induced Structures in Polymer Solutions . . . . .	92
5.4.1	Shear-Induced Phase Transitions . . . . .	92
5.4.2	Enhanced Concentration Fluctuations . . . . .	93
5.4.3	Shear-Induced Ordering . . . . .	94
5.5	Rheo-NMR . . . . .	94
5.6	Rheometers . . . . .	95
<b>6</b>	<b>Diffusion Measurements</b>	<b>97</b>
6.1	Polystyrene in Cyclohexane . . . . .	97
6.2	Experimental Section . . . . .	98
6.2.1	Sample Preparation . . . . .	98
6.2.2	Measurement of the Self-Diffusion Coefficient . . . . .	99

6.3	Results . . . . .	101
6.3.1	The Temperature Dependence of $D_s$ at Different Molar Masses	101
6.3.2	The Temperature Dependence of $D_s$ at Different Concentrations . . . . .	102
6.4	Discussion . . . . .	104
6.4.1	Reptation Times . . . . .	104
6.4.2	Concentration Fluctuations . . . . .	106
6.4.2.1	Some Calculations . . . . .	108
6.4.2.2	Comparison With the Experimental Values . . . . .	110
6.4.3	Glass Transition . . . . .	111
6.5	Conclusions . . . . .	113
<b>7</b>	<b>Flow Measurements on Polymer Solutions</b>	<b>115</b>
7.1	Instrumentation . . . . .	115
7.1.1	The Couette Cell . . . . .	115
7.1.2	Data Analysis . . . . .	117
7.2	Experimental . . . . .	117
7.2.1	Sample Preparation . . . . .	117
7.2.2	Flow Measurements . . . . .	118
7.3	Results . . . . .	121
7.4	Discussion . . . . .	122
7.4.1	Shear-Induced Phase Transitions . . . . .	122
7.4.2	Entanglement Formation Times . . . . .	123
7.4.3	Glass Transition . . . . .	125
7.5	Conclusions . . . . .	126
<b>8</b>	<b>Convection in a Capillary</b>	<b>129</b>
8.1	Introduction . . . . .	129
8.2	Experimental . . . . .	131
8.2.1	The PGSE Experiment . . . . .	132
8.2.2	The Flow Imaging Experiment . . . . .	133
8.2.3	The VEXSY Experiment . . . . .	135
8.3	Conclusions . . . . .	137
<b>9</b>	<b>Shear-Induced Order in Liquid Crystals</b>	<b>139</b>
9.1	Lyotropic Systems . . . . .	139
9.1.1	Introduction . . . . .	139
9.1.2	Rheology on Lyotropic Systems in the Lamellar Phase . . . . .	141
9.1.3	NMR on Lyotropic Systems in the Lamellar Phase . . . . .	142

9.2	Experimental Section . . . . .	143
9.2.1	Sample Preparation . . . . .	143
9.2.1.1	Dobanol/Water . . . . .	143
9.2.1.2	Aerosol OT/Water . . . . .	143
9.2.2	Measurement of Flow Profiles . . . . .	143
9.2.3	Measurement of Order Parameters . . . . .	145
9.3	Results . . . . .	146
9.3.1	Flow Profiles . . . . .	146
9.3.1.1	Dobanol/Water . . . . .	146
9.3.1.2	AOT/Water . . . . .	147
9.3.2	Deuterium NMR Spectra . . . . .	148
9.4	Discussion . . . . .	149
9.5	Conclusions . . . . .	150
<b>10</b>	<b>Conclusion</b>	<b>153</b>
10.1	Summary . . . . .	153
10.2	Outlook on Future Work . . . . .	154
	<b>Bibliography</b>	<b>157</b>
<b>A</b>	<b>The PGSE Probe</b>	<b>167</b>
<b>B</b>	<b>The Pulse Sequences</b>	<b>179</b>
B.1	Pulse Sequence to Send Trigger Pulses to External Shift Register . . . . .	179
B.2	Dynamic Spin Echo Soft Soft . . . . .	179
B.3	Pulsed Gradient Spin Echo . . . . .	181
B.4	Pulsed Gradient Spin Echo With Ramped Gradient Pulses . . . . .	183
B.5	Dynamic Stimulated Echo with Electroosmosis Trigger Pulse . . . . .	184
B.6	VEXSU . . . . .	186
B.7	VEXSU with Carr–Purcell Train . . . . .	188
<b>C</b>	<b>The AU Programs</b>	<b>191</b>
C.1	Program to Send Trigger Pulses to External Shift Register . . . . .	191
C.2	AU Program for a Set of Experiments with Different Temperatures . . . . .	192
C.3	AU Program for a Set of Experiments with Different Motor Speeds . . . . .	192



# List of Figures

2.1	Decomposition of an Oscillating Field . . . . .	12
2.2	The Free Induction Decay . . . . .	15
2.3	The NMR Spectrum . . . . .	16
2.4	The Quadrupolar Interaction . . . . .	18
2.5	Spin Echo Pulse Sequence . . . . .	18
2.6	Formation of a Spin Echo . . . . .	20
2.7	Stimulated Echo Pulse Sequence . . . . .	21
2.8	Quadrupole Echo Pulse Sequence . . . . .	22
2.9	Two-Dimensional Spectroscopy . . . . .	22
2.10	Phase Cycling . . . . .	24
2.11	Slice Selection . . . . .	27
2.12	The Spin Warp Pulse Sequence . . . . .	29
2.13	The Pulsed Gradient Spin Echo . . . . .	31
2.14	The Dynamic Spin Echo Pulse Sequence . . . . .	33
2.15	Circuit Diagram to Show the Connection of Primary and Secondary Coils . . . . .	36
2.16	Calibration of the High Gradient Probe . . . . .	37
2.17	“Switch-off” Test of the High Gradient Probe . . . . .	39
2.18	Temperature Calibration of the High Gradient Probe . . . . .	40
2.19	Circuit Diagram of the r.f. Stage . . . . .	40
2.20	Photos of the High Gradient Probe . . . . .	42
3.1	Poiseuille Flow in a Capillary . . . . .	46
3.2	Pulse Cycle of the Electric Field Gradient . . . . .	49
3.3	The Electroosmotic Cell . . . . .	50
3.4	The Pulse Sequence for the Electroosmosis Experiments . . . . .	51
3.5	Velocity Images of the Electroosmotic Cell . . . . .	53
3.6	Velocity Profiles of the Electroosmotic Cell . . . . .	54
4.1	The Basic VEXSY Pulse Sequence . . . . .	59

4.2	Two Types of Displacements that Cannot Be Distinguished . . . . .	60
4.3	VEXS <sub>Y</sub> Spectrum of Diffusion . . . . .	61
4.4	Motion in the Complex Plane . . . . .	62
4.5	The VEXS <sub>Y</sub> Pulse Sequence Using a CPMG Train . . . . .	65
4.6	VEXS <sub>Y</sub> Spectra of Laminar Couette Flow . . . . .	67
4.7	Flow Through a Porous Medium . . . . .	68
4.8	VEXS <sub>Y</sub> Spectra of Flow Through a Porous Medium . . . . .	71
5.1	Polystyrene . . . . .	74
5.2	Random Coils . . . . .	76
5.3	Polymers in Solution . . . . .	77
5.4	Diagrams of the Free Energy . . . . .	79
5.5	Phase Diagrams . . . . .	81
5.6	Cloud Point Curves . . . . .	82
5.7	$c^*$ vs. $M_w$ . . . . .	84
5.8	The Reptation Model . . . . .	85
5.9	A Velocity Profile of Fluid Flowing Along a Boundary . . . . .	87
5.10	Shear Stress vs. Shear Rate Diagram . . . . .	88
5.11	Viscosity vs. Shear Rate Diagram . . . . .	89
5.12	Viscosity And Power Law Exponent vs. Shear Rate . . . . .	90
5.13	Cone and Plate Rheometer and Couette Rheometer . . . . .	96
6.1	Cyclohexane . . . . .	97
6.2	Stejskal-Tanner Plots . . . . .	102
6.3	$D_s$ vs. $T$ at Different Molar Masses . . . . .	103
6.4	$T_p$ , $T_c$ and $\Phi_c$ vs. $M_w^{-1/2}$ . . . . .	104
6.5	$\log D_s$ vs. $\log M_w$ at Different Temperatures . . . . .	105
6.6	$D_s$ vs. $T$ at Different Concentrations . . . . .	106
6.7	$\log D_s$ vs. $\log \Phi$ at Different Temperatures . . . . .	107
6.8	$\tau_d$ vs. $M_w$ at Different Temperatures . . . . .	108
6.9	Concentration Fluctuations . . . . .	109
6.10	$D_s$ vs. $T$ at Different Molar Masses With Fitted Curves . . . . .	111
6.11	$T_g$ , $T_p$ and $T_c$ vs. $M_w$ . . . . .	113
7.1	The Couette Cell Used For the Experiments in This Thesis . . . . .	116
7.2	The Pulse Sequence <i>motorstep</i> . . . . .	116
7.3	NMR Image of the Couette Cell . . . . .	118
7.4	Resolution Enhancement Using Double Slice Selection . . . . .	119
7.5	Dynamic Spin Echo With Double Slice Selection . . . . .	120

7.6	Velocity Profiles in the Couette Cell at Different Temperatures . . .	122
7.7	$n$ vs. $T$ . . . . .	123
7.8	$\log \dot{\gamma}$ vs. $\log r$ . . . . .	124
7.9	$\tau_{\eta}$ vs. $M_w$ . . . . .	125
7.10	$a_T$ vs. $T$ with WLF Fit . . . . .	126
8.1	Convection . . . . .	129
8.2	Bénard Cells . . . . .	130
8.3	PGSE Experiment of a Polymer Solution Undergoing Convectioal Flow . . . . .	133
8.4	Velocity Image of a Convectioal Cell . . . . .	134
8.5	Three Different Types of Motion . . . . .	135
8.6	The Fourier Transform of the Velocity Propagator . . . . .	136
8.7	VEXSY Images of a Polymer Solution Undergoing Convectioal Flow	137
9.1	Nematic and Smectic Liquid Crystals . . . . .	140
9.2	The Lamellar Phase of a Lipid/Water System . . . . .	141
9.3	Velocity Profiles of Dobanol/Water in the Couette Cell . . . . .	144
9.4	Velocity Profiles of AOT/Water in the Couette Cell . . . . .	145
9.5	$\dot{\gamma}$ vs. $r$ for Dobanol/Water in the Couette Cell . . . . .	147
9.6	$\tau$ and $\eta$ vs. $\dot{\gamma}$ for Dobanol/Water . . . . .	148
9.7	$\dot{\gamma}$ vs. $r$ for AOT/Water in the Couette Cell . . . . .	149
9.8	Deuterium NMR Spectra of Sheared Dobanol/D <sub>2</sub> O . . . . .	150
9.9	Deuterium NMR Spectra of Sheared AOT/D <sub>2</sub> O . . . . .	151



# List of Tables

2.1	Gradient Coil Specifications . . . . .	36
5.1	Specifications of the PS samples . . . . .	75
6.1	Physico-chemical Parameters of Cyclohexane . . . . .	98
6.2	Parameters for the PGSE Experiments at Different $M_w$ . . . . .	100
6.3	Parameters for the PGSE Experiments at Different Concentrations	101
6.4	Parameters for the WLF Fit . . . . .	112
7.1	Parameters for the Flow Imaging Experiments . . . . .	121
9.1	Parameters for the Flow Imaging Experiments . . . . .	145

