

Physical Properties of Macromolecules

Table of Contents (22)---pdf files for all chapters were updated on 02/15/2007

Preface (7)

Glass Transitions in Amorphous Polymers

Basic Concepts (57)

Diffusion in Amorphous Polymers Near the Glass Transition Temperature (11)

Lattice Theories for Polymer/Small-Molecule Mixtures and the Conformational Entropy

Description of the Glass Transition Temperature (67)

DC Electric Field Effects on Phase Transition in Pure Materials and Binary Mixtures (33)

Order Parameters for Glasses; Pressure and Compositional Dependence of T_g (19)

Macromolecule-Metal Complexes: Ligand Field Stabilization and T_g Enhancement (61)

Semicrystalline Polymers and Melting Transitions

Basic Concepts and Molecular Optical Anisotropy in Semicrystalline Polymers (40)

Crystallization Kinetics via Spherulitic Growth (48)

Experimental Analysis of Semicrystalline Polymers (8)

Mechanical Properties of Linear and Crosslinked Polymers

Mechanical Properties of Viscoelastic Materials: Basic Concepts (80)

Problems, Solutions to Problems, and the Appendix: Linear Viscoelasticity (27)

Finite Strain Theory of Viscoelastic Materials (9)

Distribution of Linear Viscoelastic Relaxation Times (9)

Nonlinear Stress Relaxation in Macromolecule-Metal Complexes (16)

Molecular Weight Distributions in Linear Polymers (64)

Gaussian Statistics of Linear Chain Molecules and Crosslinked Elastomers (59)

Classical and Statistical Thermodynamics of Rubberlike Materials (35)

Statistical Thermodynamics of Stress-Optical Relations for Rubberlike Materials

Thermo-Reversible Gelation in Macromolecule-Metal Complexes that Contain Visible-Photon-

Emitting Lanthanides (17)

Solid State Dynamics of Polymeric Materials

Molecular Dynamics via Magnetic Resonance (i.e., NMR), Viscoelastic, and Dielectric Relaxation Phenomena (51)

Magnetic Spin Diffusion at the NanoScale in Multiphase Polymers and Molecular Complexes (39)

Totals: 779 pages, 51 tables, 79 figures/graphs, 141 problems, 56 solutions

(1) Glass Transitions in Amorphous Polymers: Basic Concepts

Glass transitions in amorphous materials are described primarily from a thermodynamic viewpoint, but the kinetic nature of T_g is mentioned, also. The pressure dependence of first- and second-order phase transitions is compared via the Clapeyron and Ehrenfest equations, respectively. Compositional dependence of T_g in single-phase mixtures is addressed from volume and entropy continuity. The connection between fractional free volume and T_g is introduced. Then, physical variables that affect T_g are discussed in terms of their influence on free volume. Effects of molecular weight, particle size, film thickness, and surface free energy on the glass transition are also considered.

57 pages, 1 table, 1 graph, 33 problems, 26 solutions

Volume-temperature & enthalpy-temperature relations in the vicinity of 1st-order & 2nd-order phase transitions; discontinuous thermophysical properties at T_m and T_g

The "equilibrium" glassy state

Physical aging, densification, and volume & enthalpy relaxation

Temperature-pressure differential phase equilibrium relations for 1st-order processes; the Clapeyron equation

Temperature-pressure differential phase "equilibrium" relations for 2nd-order processes; the Ehrenfest equations

Volume continuity

Entropy continuity

Compositional dependence of T_g via entropy continuity

Compositional dependence of T_g via volume continuity

Linear least squares analysis of the Gordon-Taylor equation and other T_g -composition relations for binary mixtures

Generalized linear least squares analysis for a 2nd-order polynomial with one independent variable

The linear vs. non-linear least squares dilemma

Free volume concepts

Temperature dependence of fractional free volume

Compositional dependence of fractional free volume and the plasticizer efficiency parameter

Fractional free volume analysis of multicomponent mixtures; compositional dependence of the glass transition temperature

Molecular weight dependence of fractional free volume

Experimental design to test the molecular weight dependence of fractional free volume & T_g

Pressure dependence of fractional free volume

Effect of mechanical strain on fractional free volume

Effect of particle size or film thickness on the glass transition temperature, *ACS Division of Polymer Chemistry discussion list*

Effect of the glass transition on surface tension, *ACS Division of Polymer Chemistry discussion list*

Effect of chemical structure on the magnitude of T_g
Problems

(2) Diffusion in Amorphous Polymers near the Glass Transition Temperature

Advanced concepts in fractional free volume are discussed in connection with a primitive lattice model to evaluate hard-sphere diffusion coefficients via entropy maximization with constraints. This Lagrange multiplier diffusion model is extended to include solvent size in polymer solutions, as well as the effect of temperature on diffusivities above and below T_g via the discontinuity in thermal expansion coefficients.

11 pages

Free volume theory of Cohen & Turnbull for diffusion in liquids and glasses

Free volume theory of Vrentas & Duda for solvent diffusion in polymers above the glass transition temperature

Influence of the glass transition on diffusion in amorphous polymers

References for diffusion in polymers near T_g

(3) Lattice Theories for Polymer/Small-Molecule Mixtures and the Conformational Entropy Description of the Glass Transition Temperature

Several lattice theories are presented to analyze thermodynamic properties of polymer solutions, plasticized polymer-diluent blends, and phase-separated binary mixtures. Comparisons between binodal and spinodal points on temperature-composition phase diagrams are discussed. The entropy of mixing on the Flory-Huggins and Guggenheim lattices is compared. These statistical analyses provide the background required to appreciate the Gibbs-DiMarzio conformational entropy description of the glass transition in binary systems, where the mixture's entropy vanishes at T_g upon cooling. Structural characteristics of additives that increase and decrease a polymer's T_g are simulated and discussed. Qualitative comparison between the Gibbs-DiMarzio theory and lattice cluster theory spans more than 40 years from the early lattice models to current research topics.

67 pages, 1 table, 7 graphs, 9 problems, 8 solutions

Membrane osmometry and the osmotic pressure expansion

The consequence of chemical equilibrium

Analogy with the virial expansion of real gases

Lattice models for athermal mixtures with excluded volume

Flory-Huggins lattice theory for flexible polymer solutions

Nomenclature

Assumptions

Conformational entropy of mixing, ΔS_{mixing}

Interaction free energy of mixing and the Flory-Huggins thermodynamic χ parameter

Energetic interactions within the pure solvent

Energetic interactions within the undiluted polymer

Energetic interactions within the polymer-solvent mixture

Complete expression for the Gibbs free energy of mixing, partial molar properties and the osmotic pressure expansion

Flory-Huggins entropy of mixing for concentrated polymer solutions, JPS (1983)

Chemical stability of binary mixtures, JPS (1986)

Shape of Δg_{mixing} vs. composition in binary and multicomponent mixtures

Intercepts and common tangents to Δg_{mixing} vs. composition in binary mixtures

The curvature criterion for chemical stability of binary mixtures via the composition dependence of the chemical potential

Chemical stability of polymer-solvent mixtures on the Flory-Huggins lattice

Strategy to determine if phase separation occurs

Phase equilibrium relations at the upper critical solution temperature (UCST)

Kinetics of phase separation within the spinodal region; spinodal decomposition via the unsteady state diffusion equation with negative binary molecular diffusion coefficients

Phase separation between the binodal and spinodal curves via nucleation and growth kinetics

Guggenheim's lattice theory of athermal mixtures

Gibbs-DiMarzio conformational entropy description of the glass transition for tetrahedral lattices

Flexible vs. rigid additives that decrease a polymer's glass transition temperature

Effect of molecular size of semi-flexible additives on T_g

Infinitely rigid diluents that increase a polymer's glass transition temperature

Conformational entropy description of T_g for lattices with higher coordination numbers

Lattice cluster theory analysis of conformational entropy and the glass transition in amorphous polymers

References on lattice cluster theory

Sanchez-Lacombe statistical thermodynamic lattice-fluid theory of polymer-solvent mixtures

Mixing rules for lattice fluids

Appendix: The connection between exothermic energetics (i.e., heats of mixing) and volume contraction of the mixture

Problems

(4) DC Electric Field Effects on First- and Second-Order Phase Transitions in Pure Materials and Binary Mixtures

Classical thermodynamics is employed to analyze electric field effects on phase transitions. Analogous to the Ehrenfest equations/inequality, volume and entropy continuity at T_g are invoked to describe field effects on second-order phase transitions. The modified Prigogine-Defay ratio contains dielectric properties of the material, and their dependence on temperature and pressure. Computational strategies for non-ideal binary mixtures are discussed to identify binodal and spinodal phase boundaries graphically as a function of field strength.

33 pages, 2 tables, 2 graphs

Overview, *Polymer* (2007)

Electric field effects on low-molecular-weight molecules and their mixtures

Electric field effects on polymers and their mixtures

Motivation for this analysis of electric field effects on phase transitions

Theoretical considerations

Electrostatic preliminaries

Classical thermodynamics in the presence of external fields

First-order transition temperatures via phase equilibrium on the binodal curve

Second-order phase transitions in pure materials

Entropy continuity

Volume continuity

Electric-field analog of the Prigogine-Defay ratio (i.e., equality)

Chemical stability limits in binary mixtures via the spinodal curve

Incorrect description of the spinodal phase boundary

Classical thermodynamic analysis of the Gibbs free energy of mixing in the presence of uniform dc electric fields

Reformulation of the Gibbs free energy of mixing based on a reference state in which both pure components experience the electric field

Numerical simulations of the compositional dependence of Δg_{mixing} in binary mixtures

Parameter declaration

Aqueous solutions of methyl acetate at 40°C and 1 atm.

Organic mixtures of carbon disulfide and acetone at 40°C and 1 atm.

Trends

Chapter summary

Nomenclature

Literature references

Polymer and small-molecule phase behaviour in the presence of electric fields

Effects of mechanical stress on phase transitions in polymers

(5) Order Parameters for Glasses; Pressure and Compositional Dependence of the Glass Transition Temperature

Volume and entropy continuity at second-order phase transition temperatures are discussed within the framework of classical thermodynamics using two order parameters to identify structural characteristics of glasses that yield the Ehrenfest inequality for the pressure dependence of T_g . Then, the “order-parameter approach” is combined with statistical lattice models to describe the compositional dependence of T_g for plasticized polymer-diluent blends. The temperature derivative of the Flory-Huggins thermodynamic interaction parameter is discontinuous at T_g .

19 pages, 1 table, 1 graph

Ehrenfest inequalities

Two independent internal order parameters identify an inequality between the two predictions for the pressure dependence of the glass transition temperature

References for order parameters and the Ehrenfest equations/inequalities

Compositional dependence of the glass transition temperature, *JPS* (1983)

Calorimetric results and objectives

Assumptions of the theory

Diluent concentration dependence of the glass transition temperature via classical thermodynamics

Compositional dependence of the glass transition temperature via lattice theory models

Comparison with other theories

Model calculations

Temperature dependence of the Flory-Huggins intermolecular interaction parameter near the glass transition temperature

Limitations of the theory

(6) Macromolecule-Metal Complexes: Ligand Field Stabilization and Glass Transition Temperature Enhancement

Inorganic models of transition-metal coordination between d-block salts and functional polymers are introduced and analyzed to explain increases in T_g via coordination crosslinks. d-Electron configurations and stabilization of metal d-electrons due to the surrounding ligands in the first-shell coordination sphere are correlated with thermal synergy in several macromolecule-metal complexes. These energetic models that exhibit reduced local symmetry about the metal center in the molten state, relative to the glassy state, can be extended to binary systems for which glass transition data are not available.

61 pages, 26 tables, 8 figures/graphs

Overview, *Macromolecules containing metals and metal-like elements* (2006)

Methodology of transition metal coordination in polymeric complexes

Polymeric coordination complexes with d-block salts that exhibit an increase in T_g

Chemical bonding, coordination, and transition metal compatibilization

Ligand field stabilization energy description of the enhancement in T_g for polymeric complexes with transition metal ions

Energetic ligand field models and the methodology of transition metal coordination

Well-defined low-molecular-weight transition metal complexes

Attractive polymeric ligands

Identifying attractive interactions via hard-and-soft acids and bases

Displacement of weak neutral bases in the first-shell coordination sphere

Anionic ligands are the last ones that should be displaced to the 2nd shell

Complexes with the same local symmetry above & below the glass transition

Complexes with reduced symmetry above T_g

Consideration of interelectronic repulsion and ligand field splitting when there is ambiguity in the d-electron configuration

Jorgensen's parametric representation of ligand field splitting and interelectronic repulsion

Polymeric complexes with enhanced glass transition temperatures

Polymeric complexes with reduced glass transition temperatures

Other considerations

Pseudo-octahedral d^8 nickel complexes with poly(4-vinylpyridine)

Ligand field stabilization energies

Coordination crosslinks vs. coordination pendant groups

Ligand field model of the glass transition in macromolecule-metal complexes

Linear least squares analysis of $\Delta(LFSE)$ via the concentration dependence of T_g

d^6 Molybdenum carbonyl complexes with poly(vinylamine) that exhibit reduced symmetry above the glass transition temperature

Experimental results

Ligand field splitting parameters for molybdenum hexacarbonyl

Ligand field stabilization for complexes of $Mo(CO)_6$ and poly(vinylamine) in the glassy state

Quantum mechanical model parameters and trigonal bipyramid 5-coordinate d^6 complexes of $Mo(CO)_6$ and poly(vinylamine) with D_{3h} symmetry above T_g

Square pyramid 5-coordinate d^6 complexes of $Mo(CO)_6$ and poly(vinylamine) with C_{4v} symmetry above T_g

Pentagonal planar 5-coordinate d^6 complexes of $Mo(CO)_6$ and poly(vinylamine) with D_{5h} symmetry above T_g

Ligand field stabilization of 5-coordinate d^6 complexes of $Mo(CO)_6$ and poly(vinylamine) above T_g

Cobalt, nickel, and ruthenium complexes with poly(4-vinylpyridine) and poly(L-histidine) that exhibit reduced symmetry in the molten state

Polymeric coordination complexes with d-block salts

Ruthenium d^6 complexes

Cobalt d^7 complexes

Nickel d^8 complexes

Five-coordinate complexes with reduced symmetry in the molten state

d-Orbital energies for five-coordinate complexes above T_g

Trigonal bipyramid d^n complexes with D_{3h} symmetry

Square pyramid d^n complexes with C_{4v} symmetry

Pentagonal planar d^n complexes with D_{5h} symmetry

Summary of LFSE calculations for 5-coordinate d^n complexes

Stabilization of metal d-electrons in mixed-ligand complexes

Consideration of interelectronic repulsion and Δ_o when there is ambiguity in the d-electron configuration for complexes with pseudo-octahedral symmetry

Correlation between T_g enhancement and the difference between ligand field stabilization energies in the glassy and molten states

Tetrahedral Co^{2+} complexes below T_g and 3-coordinate complexes in the molten state

Total energetic requirements to induce the glass transition via consideration of the first-shell coordination sphere in transition metal and lanthanide complexes

Density functional estimates of metal-ligand bond dissociation energies

The energetics of ligand dissociation reactions in model systems; comparison with experimental T_g -enhancements for d-block and f-block complexes

Summary

Epilogue

Appendix: Physical interpretation of the parameters in the Kwei equation for synergistic enhancement of the glass transition temperature in binary mixtures

Literature references

Figure captions

(7) Basic Concepts and Molecular Optical Anisotropy in Semicrystalline Polymers

Introductory crystallization topics are followed by a discussion of semicrystalline polymers that form spherulites. Then, optical anisotropy is analyzed from the interaction of birefringent materials with polarized light in spherical coordinates. Segment orientation distribution functions are developed via entropy maximization with constraints. This Langevin distribution is employed to predict the molecular optical anisotropy of random-coil and rigid-rod polymers. The connection between the morphology of semicrystalline polymers and their mechanical properties is discussed qualitatively.

40 pages, 1 table, 4 figures/graphs, 11 problems, 1 solution

Comments about crystallization

Tacticity

Helical conformations

Predicting the melting temperature

Single crystals, lamellae, and chain folding

Molecular optical anisotropy

Spherulitic superstructures that exhibit molecular optical anisotropy

Interaction of a birefringent spherulite with polarized light

Interaction of disordered lamellae with polarized light

Interaction of disordered lamellae with unpolarized light

Molecular optical anisotropy of random coils and rigid rod-like polymers

Segment orientation with respect to the end-to-end chain vector; inverse Langevin distribution

Rectangular Cartesian components of the polarizability tensor for cylindrically symmetric bonds in the chain backbone

Ensemble averaging of α_{jk} in rectangular coordinates with respect to the Langevin segment orientation distribution function

Optical anisotropy of rigid rod-like polymers in the completely extended conformation

Birefringence calculations via optical microscopy with cross polars

Simplified analysis of the Lorentz-Lorenz equation

Optical anisotropy of random coil polymers that exhibit Gaussian chain statistics

Birefringence of rubbery polymers subjected to external force fields

The connection between the refractive index tensor in anisotropic media and depolarization

Intrinsic birefringence

Orientation birefringence

Optical properties of crosslinked polymers

Chain folding, interspherulitic connectivity, and mechanical properties of semicrystalline polymers, *ACS Division of Polymer Chemistry discussion list*

Problems

(8) Crystallization Kinetics via Spherulitic Growth

Quantitative models of nucleation and growth rates for impinging and non-impinging spherulites are discussed within the framework of classical thermodynamics that include effects of supercooling and fractional free volume. Mathematical analysis of the Avrami equation is useful to parameterize the kinetics of crystallization and identify actual experimental annealing temperatures where maximum rates should yield significant fractions of crystallinity. Thermodynamic descriptions of chain folding in semicrystalline-amorphous polymer-polymer blends identify optimum lamellar thicknesses when hydrogen bonding between dissimilar chains competes with the crystallization process. Flory-Huggins lattice models are employed to describe melting-point depression in binary systems. Linear least squares analysis of T_m -

depression data yields quantitative information about the enthalpy of fusion and the interaction free energy of mixing (i.e., Flory-Huggins χ parameter).

48 pages, 6 tables, 15 figures/graphs, 22 problems, 6 solutions

Heterogeneous nucleation and growth prior to impingement

Avrami equation for heterogeneous nucleation that accounts for impingement of spherulites

Crystallization kinetics and the Avrami equation for homogeneous nucleation of spherulites

Linear least squares analysis of the kinetics of crystallization via the generalized Avrami equation

Half-time analysis of crystallization isotherms

Maximum rate of isothermal crystallization

Thermodynamics and kinetics of homogeneous nucleation

Temperature dependence of crystallization rate constants

Optimum crystallization temperatures; comparison between theory and experiment

Suggested literature on crystallization kinetics

The energetics of chain folding in semicrystalline polymer-polymer blends that exhibit multiple melting endotherms, *Chuan Qin (1991)*

Overview

Dependence of multiple melting behaviour on the chemical structure of the crystallizable component in polymer-polymer blends

Theoretical considerations that account for strong interactions

Geometric considerations

Energetic considerations for chain folds, chain ends, and the presence of lateral surfaces

Melting

Hydrogen bonding in the amorphous phase and on the periphery of the lamellae

Total free energy function for the formation of an N-stem surface layer

Optimum lamellar thickness

Summary of multiple melting behaviour

Melting point depression in polymer-polymer and polymer-diluent blends that contain a high-molecular-weight semicrystalline component

Hoffman-Weeks analysis

Problems

(9) Experimental Analysis of Semicrystalline Polymers

Isothermal crystallization kinetic data from calorimetry are analyzed using the formalism of coupled heat and mass transfer in constant-volume batch reactors. Rate constants and scaling exponents in the generalized Avrami equation are obtained from linear least squares analysis of crystallization exotherms. Simple pycnometry measurements are discussed to calculate densities of semicrystalline polymers and thermal expansion coefficients of solids.

8 pages

Differential scanning calorimetry---thermograms of semicrystalline polymers during heating and cooling traces

Isothermal analysis of crystallization exotherms via differential scanning calorimetry, *JPS* (1996)

Kinetic analysis of the mass fraction of crystallinity via the generalized Avrami equation

(10) Mechanical Properties of Viscoelastic Materials: Basic Concepts in Linear Viscoelasticity

Linear viscoelasticity is introduced and Maxwell's constitutive equation is developed by combining Hooke's law of elasticity and Newton's law of viscosity. Time dependence of stress and strain is analyzed for creep, stress relaxation, dynamic mechanical testing, and the torsion pendulum. The concept of the dimensionless Deborah number is used to introduce the principle of time-temperature superposition. The Boltzmann superposition integral for linear viscoelasticity connects dynamic properties and stress relaxation moduli via Fourier transformation. The irreversible degradation of mechanical energy to thermal energy in forced-vibration and free-vibration experiments is analyzed quantitatively and related qualitatively to the fluctuation-dissipation theorem in statistical physics.

107 pages, 5 tables, 1 graph, 48 problems, 8 solutions

Objectives

Simple definitions of stress, strain, and Poisson's ratio

Stress tensor

Strain and rate-of-strain tensors

Hooke's law of elasticity

Newton's law of viscosity

Simple analogies between mechanical and electrical response

Phase angle difference between stress & strain and voltage & current in dynamic mechanical & dielectric experiments

Maxwell's viscoelastic constitutive equation

Integral forms of Maxwell's viscoelastic constitutive equation

Suggestions for further reading about polymer viscoelasticity

Mechanical model of Maxwell's viscoelastic constitutive equation

Four well-defined mechanical experiments

Creep and creep recovery

Stress relaxation

Dynamic mechanical testing

Fracture testing

Linear response of the Maxwell model during creep experiments

Creep recovery of the Maxwell model
 Linear response of the Maxwell model during stress relaxation
 Temperature dependence of the stress relaxation modulus and definition of the Deborah number
 Other combinations of springs and dashpots
 Equation of motion for the Voigt model
 General solution to the equation of motion for the Voigt model
 Linear response of the Voigt model in a creep experiment
 Creep recovery of the Voigt model
 Creep and stress relaxation for a series combination of Maxwell and Voigt elements
 Creep response
 Stress relaxation
 Convolution integrals
 Leibnitz rule for differentiating one-dimensional integrals when the limits of integration are not constant
 Boundary conditions
 The principle of time-temperature superposition
 Stress relaxation via the equivalence between time and temperature
 Semi-theoretical justification for the empirical form of the WLF shift factor $a_T(T; T_{\text{reference}})$
 Temperature dependence of the zero-shear-rate polymer viscosity via fractional free volume and the Doolittle equation
 Apparent activation energy for a_T and the zero-shear-rate polymer viscosity
 Comparison of the WLF shift factor a_T at different reference temperatures
 Vogel's equation for the time-temperature shift factor
 Effect of diluent concentration on the WLF shift factor a_c in concentrated polymer solutions
 Stress relaxation moduli via the distribution of viscoelastic time constants
 Stress relaxation moduli and terminal relaxation times
 The critical molecular weight required for entanglement formation
 Zero-shear-rate polymer viscosity via the distribution of viscoelastic relaxation times
 The Boltzmann superposition integral for linear viscoelastic response
 Alternate forms of the Boltzmann superposition integral for $\sigma(t)$
 Linear viscoelastic applications of the Boltzmann superposition principle; elastic free recovery
 Dynamic mechanical testing of viscoelastic solids via forced vibration analysis of time-dependent stress and *dynamic modulus* $E^*(t; \omega)$
 Phasor analysis of dynamic viscoelastic experiments via complex variables
 Fourier transformation of the stress relaxation modulus yields dynamic moduli via complex variable analysis
 Frequency-temperature dependence of viscoelastic loss maxima; Arrhenius activation energies for molecular motion of the main-chain vs. sidegroup
 Energy dissipation and storage during forced vibration dynamic mechanical experiments
 Free vibration dynamic measurements via the torsion pendulum

Problems, Solutions to Problems, and the Appendix (27 pages)

Boltzmann superposition principle for time-dependent strain via continuous stress history
Alternate form of the Boltzmann superposition integral for time-dependent strain $\gamma(t)$
Laplace transform analysis of the relation between creep compliance J_c and stress relaxation modulus E_R via Boltzmann superposition integrals
Distribution of viscoelastic relaxation times via the continuous analog of the Voigt-Kelvin model
Dynamic mechanical spectroscopy of viscoelastic liquids via forced vibration analysis of time-dependent strain and *dynamic compliance* $J^*(t;\omega)$

(11) Finite Strain Theory of Viscoelastic Materials

Elastic materials are discussed from an “engineering mechanics” viewpoint. Stress and strain ellipsoids are defined and evaluated for simple flow fields.

9 pages

Introductory comments

Deformation and the strain ellipsoid

Rigid translation

Isotropic dilation or contraction

Uniaxial tensile deformation

Simple two-dimensional shear

Stress ellipsoid

Perfectly elastic isotropic solids

Principal values of stress when a perfectly elastic isotropic solid is subjected to two-dimensional shear

Evaluation of the principal axes of the stress ellipsoid for simple two-dimensional shear

Analysis of homogeneous isotropic shear in elastic solids via orthogonal transformation matrices

(12) Distribution of Linear Viscoelastic Relaxation Times

Advanced mathematical techniques are introduced to analyze relaxation time distributions for linear viscoelastic response. Fourier transforms and double-Laplace transforms are employed to evaluate frequency response functions from time-dependent stress relaxation data.

9 pages, 2 tables

Overview

Inverse moments of the distribution of viscoelastic relaxation times

Numerical results when the relaxation modulus E_R follows a single exponential decay

Numerical results when E_R follows an exponential decay with 2 relaxation times

Frequency response via Fourier transformation of the step response (i.e., stress relaxation modulus) or Stieltjes (i.e., double Laplace) transformation of the distribution function

(13) Nonlinear Stress Relaxation in Macromolecule-Metal Complexes

Experimental stress relaxation data at large jump strains are analyzed for palladium complexes with polybutadiene that contain transition-metal catalyzed chemical crosslinks. Relaxation moduli are discussed in terms of a “correlated-states” model that employs nonlinear exponential functions. The effect of strain on viscoelastic relaxation times is discussed in terms of time-strain separability of the relaxation functions and conformational rearrangements of several neighboring segments that respond in cooperative fashion. Relaxation time constants increase when (i) experiments are performed at higher strain, and (ii) higher concentrations of palladium chloride produce larger crosslink densities.

16 pages, 1 table, 4 graphs

Overview, JAPS (2004)

Relevant background information about palladium complexes with macromolecules that contain alkene functional groups

Effect of palladium chloride on the stress-strain behaviour of triblock copolymers containing styrene and butadiene

Crosslinked polymers and limited chain extensibility

Nonlinear stress relaxation

Time-dependent relaxation functions via the “correlated states” model

Previous investigations of stress relaxation in the nonlinear regime

Experimental design of nonlinear stress relaxation experiments

Nonlinear relaxation moduli

Effect of strain on stress relaxation

Time-strain separability of the relaxation function

Characteristic length scales for cooperative reorganization and the effect of strain on viscoelastic relaxation times

Summary

Figure captions

Literature references

(14) Molecular Weight Distributions in Linear Polymers

Continuous and discrete molecular weight distribution functions are analyzed from a chemical kinetics viewpoint for condensation, free radical, and anionic polymerization

mechanisms. Comparisons between these distributions and the output curves from gel permeation chromatographic columns are illustrated graphically and numerically. Moments generating functions are introduced to evaluate number-average and weight-average degrees of polymerization. The Appendix contains additional examples of kinetic mechanisms for transition-metal catalyzed hydrogenation and chemical-crosslinking reactions in industrially important polymers.

64 pages, 2 tables, 1 problem, 1 solution

- The “Most Probable Distribution” for polycondensation reactions; statistical considerations
Discrete vs. continuous distributions for condensation polymerization
Comments about the “degree of polymerization” (DP) for polycondensation reactions, *ACS Division of Polymer Chemistry discussion list*
Moments generating functions for discrete distributions via z-transforms
Kinetics, molecular weight distributions, and moments generating functions for free radical polymerizations
Free radical mechanism that includes termination by recombination
Discrete moments generating function F_z
Peak of the GPC output curve for vinyl polymers produced by free radical mechanisms
Continuous distribution functions for free radical polymerizations that terminate by recombination
Termination by disproportionation
Anionic “living” polymerizations and the Poisson distribution
Kinetic mechanism, rate expressions, and the mole fraction distribution of x-mers
Discrete moments generating function, average degrees of polymerization, and polydispersity for anionic polymerization
Continuous distribution functions for anionic polymerization
Comparison of molecular weight distributions for condensation, free radical, and anionic polymerization mechanisms via GPC output curves
Connection between Laplace transforms and the moments generating function for any distribution in the continuous limit
Polycondensation reactions
Free radical polymerizations that terminate by recombination
Anionic polymers described by the Poisson distribution
Expansion of continuous distribution functions via orthogonal Laguerre polynomials
Use of the zeroth-, first-, second-, and third-moments to reconstruct the Most Probable Distribution for polycondensation reactions
Problem *Unsteady state batch reactor analysis of the Most Probable Distribution function*
Appendix A *Mechanism and kinetics of alkene hydrogenation reactions via transition metal catalysts*
Introduction and overview
Sequence of independent elementary steps
Kinetic analysis of the rate of alkene consumption

(15) Gaussian Statistics of Linear Chain Molecules and Crosslinked Elastomers

Statistical analysis of chain dimensions is presented for ideal chains in non-interacting solvents and real chains in good solvents with excluded volume. Scaling concepts are introduced for real chains, intrinsic viscosity, and concentrated polymer solutions. Capillary viscometry is discussed in the Appendix. The Gaussian distribution is combined with Boltzmann's entropy law to calculate retractive forces for ideal elastomers via entropy elasticity. This simplified statistical thermodynamic analysis of ideal elastomers in the presence of external fields yields relations between stress and strain that are discussed further in the following chapter.

59 pages, 2 tables, 2 graphs, 13 problems, 5 solutions

Summary of three-dimensional Gaussian chain statistics

Vector analysis of the mean-square end-to-end chain distance

One-dimensional random walk statistics via Bernoulli trials and the binomial distribution

Asymptotic expression for $P(m;n)$ via Bernoulli trials

Extrapolation of one-dimensional Gaussian statistics to three dimensions

Properties of three-dimensional Gaussian distributions & their moments generating function

Mean-square radius of gyration of freely jointed chains

Mean-square end-to-end distance of freely rotating chains

Characteristic ratios, persistence length, and statistical segment length

Excluded volume and the expansion factor α for real chains in "good" solvents; athermal solutions

Excluded volume parameter φ via probability analysis on a cubic lattice and the radius of gyration distribution function

Conformational entropic contribution to the multiplicity of states for real chains in "good" solvents

Helmholtz free energy minimization yields the equilibrium chain expansion factor in athermal solutions

deGennes scaling analysis of Flory's law for real chains in "good" solvents

Intrinsic viscosity of dilute polymer solutions and universal calibration curves for gel permeation chromatography

Einstein's theory for the viscosity of a dilute suspension of spherical particles in a Newtonian solvent

Intrinsic viscosity of dilute polymer solutions

Scaling laws for intrinsic viscosity and the Mark-Houwink equation

Intrinsic viscosities of polystyrene and poly(ethylene oxide)

Effect of pH during dilute-aqueous-solution preparation of solid films on the glass transition
deGennes scaling analysis of the threshold overlap molar density c^* in concentrated polymer solutions, and the concept of “blobs”

Entropically elastic retractive forces via statistical thermodynamics of Gaussian chains

Characteristic mechanical response of elastomers

The connection between entropy and probability density distribution functions

Classical thermodynamics in the presence of external force fields

Hooke’s law of elasticity for ideal rubber-like materials

Constitutive relation between stress and elongation for ideal rubber-like materials

Appendix---Capillary viscometry:

Transient analysis of draining an incompressible Newtonian fluid from a spherical bulb with a tilted capillary tube to simulate the performance of capillary viscometers for the determination of momentum diffusivities and fluid viscosities

Detailed evaluation of the capillary constant and comparison with experimental results

Draining power-law fluids from a right circular cylindrical tank via a tilted capillary tube; comparison of efflux and half-times

Problems

(16) Classical and Statistical Thermodynamics of Rubberlike Materials

Classical thermodynamics is employed to analyze the equation of state for ideal elastomers, using some results from the previous chapter. Flory’s approximations are discussed in detail, allowing one to obtain equation-of-state information from experimental data. Statistical analysis is based on three-dimensional Gaussian chains and Boltzmann’s entropy law. Another view of chain expansion on the Flory-Huggins lattice is presented and compared with a similar analysis from the previous chapter. There is a significant amount of complementary discussion in Chapters 15 and 16.

35 pages, 4 problems, 1 solution

Overview

Analogies

Classical thermodynamic analysis of the ideal equation of state for retractive force from the previous chapter

Classical thermodynamic strategy

Analogous development for the effect of sample length on internal energy; the concept of ideal rubberlike solids

Thermoelastic inversion

Temperature dependence of retractive forces that accounts for thermal expansion

Derivation of Flory's approximation for isotropic rubberlike materials that exhibit no volume change upon deformation
Statistical thermodynamic analysis of the equation of state for ideal rubberlike materials
Effect of temperature on chain conformations
Affine deformation
Gaussian statistics
Multiplicity of network strand conformations after deformation
Manipulation of the multiplicity function and extrapolation to the continuous limit
Boltzmann's entropy expression for isochoric deformation with isotropic lateral contraction
Stress-strain relations
Effect of biaxial deformation at constant volume on Boltzmann's entropy and stress vs. strain
Effect of isotropic chain expansion in "good" solvents on the conformational entropy of linear macromolecules due to excluded volume
Effect of polymer-solvent energetics on chain expansion via the Flory-Huggins lattice model
Gibbs free energy minimization yields the equilibrium chain expansion factor
Appendix: Chemical or diffusional stability of polymer-solvent mixtures
Problems

(17) Molecular Dynamics via Magnetic Resonance (i.e., NMR), Viscoelastic, and Dielectric Relaxation Phenomena

Relaxation phenomena for NMR are developed from the Liouville equation and compared with mechanical relaxation via the fluctuation-dissipation theorem. Connections between correlation functions and spectral densities are discussed for NMR and stress relaxation. Correlation times for stress relaxation are introduced via Rouse dynamics with negligible hydrodynamic interaction. Relations between the real and imaginary parts of the complex dynamic viscosity, and the complex dynamic modulus, are discussed within the context of the Kramers-Kronig theorem using the Maxwell model as an illustrative example. Experimental results for bisphenol-A polycarbonate are used to compare measurements from NMR, mechanical, and dielectric relaxation on this industrially important polymer. Complex impedance analysis of dielectric relaxation measurements for Maxwell and Voigt models is compared with thermally stimulated discharge of polarized electrets. This chapter illustrates how motional-induced relaxation across a broad spectrum of physical chemistry and rheological experiments provides complementary information about the solid-state dynamics of polymeric materials.

51 pages, 1 table, 7 figures/graphs

Overview, *Polymer International* (2007)

A brief introduction to quantum statistical mechanics

The density matrix

The “ergodic” problem of statistical thermodynamics

NMR relaxation via spin temperature equilibration with the lattice

Analysis of spin-lattice relaxation rates via time-dependent perturbation theory and the density matrix

Development of the Liouville equation

Effect of small time-dependent fluctuations on the Liouville equation for ρ_{22}

Numerical solution of the Liouville equation for the simple two-state problem

Classical description of stress relaxation via auto-correlation functions and the fluctuation-dissipation theorem

Single-chain dynamics via the Rouse model

Solution of the unsteady state diffusion equation for the position vector to the i^{th} bead in high-molecular-weight chains

Kramers-Kronig theorem via Fourier transformation

Kramers-Kronig theorem via complex variables and Cauchy’s integral

Comparisons among NMR, mechanical (i.e., viscoelastic), and dielectric relaxation via molecular motion in polymeric materials; activated rate processes

NMR relaxation

Mechanical relaxation

Dielectric relaxation, Polymer (1984)

Complex impedance analysis of dielectric relaxation measurements via electrical analogs of the Maxwell and Voigt models of linear viscoelastic response

Maxwell model

Voigt model

Thermally stimulated discharge currents in polarized dielectric materials (i.e., electrets)

Charging process

Discharge process

Depolarization currents and activation energies for rheologically simple materials

Chapter summary

Literature references

(18) Magnetic Spin Diffusion at the NanoScale in Multiphase Polymers and Molecular Complexes

Solid state NMR spectroscopy is discussed extensively throughout this chapter as a diagnostic probe of nanoscale dimensions in phase-separated copolymers and hydrogen-bonded molecular complexes. Magnetic spin diffusion measurements are modeled phenomenologically via Fick’s second law, and an optimization algorithm is presented to determine the best parameters in the diffusion equation. An example of two-dimensional ^1H spin-diffusion spectroscopy identifies dipolar communication between ^1H nuclei in different species on a time scale of 100 μs , which is 3-orders of magnitude shorter than the spin diffusion mixing time employed by RR Ernst and

coworkers to illustrate miscibility in a blend of polystyrene and poly(vinyl methyl ether) that was prepared in toluene. The chapter concludes with a summary of NMR experiments on suggested polymers and metal complexes.

39 pages, 27 figures/graphs

Overview, *Polymer International* (2007)

Statement of the problem

Description of the modified Goldman-Shen experiment

Materials

Magnetic spin diffusion experiments on random copolymers that contain disorganized lamellae

Magnetic spin diffusion experiments on triblock copolymers that contain spherically dispersed hard segments

Cross-polarization dynamics

Interdomain communication via magnetic spin diffusion

Phenomenological transient diffusion models (i.e., Fick's second law) in two-phase systems with spherical polystyrene domains in a polybutadiene matrix

Diffusion in a core-shell morphology

Coupled partial differential equations and their supporting boundary and initial conditions

Bulk magnetization that diffuses across the mobile-rigid interface into the central core

Finite-difference simulations for Kraton™ triblock copolymers

Multi-variable parameter estimation via nonlinear least squares analysis

The algorithm

Solid state NMR analysis of molecular complexes

Spectroscopic detection of phase coexistence

Solid state NMR detection of molecular complexes

High-resolution carbon-13 solid state NMR spectroscopy of PEO molecular complexes; correlations with phase behaviour

Biectetic blends of poly(ethylene oxide) and resorcinol

Molecular proximity and spin diffusion in PEO-resorcinol complexes via ¹H CRAMPS; combined rotation and multiple pulse spectroscopy

Interdomain communication via magnetic (¹H) spin diffusion; the modified Goldman-Shen experiment

Chapter Summary

Carbon-13 solid state NMR spectroscopy; laboratory experiments

Chemical shift interactions

Power spectrum without magic-angle sample spinning

Molecular mobility via dipolar dephasing experiments

Molecular mobility via selective cross-polarization experiments

Detection of molecular proximity in polymer-polymer and polymer/small-molecule blends via ^1H - ^{13}C spin diffusion when one of the components is completely deuterated

Detection of molecular proximity in poly(4-vinylpyridine)/ Ru^{2+} complexes when one of the components does not contain protons (i.e., ^1H nuclei)

Questions for discussion

(19) Thermo-Reversible Gelation in Macromolecule-Metal Complexes that Contain Visible-Photon-Emitting Lanthanides

This chapter outlines experimental procedures to develop thermo-reversible gels when metal complexation with functional groups in the sidechain of the polymer competes with polymer-solvent interactions. Metal complexes from the lanthanide series, like Pr^{3+} , Eu^{3+} , and Tb^{3+} , emit visible radiation in response to laser excitation at shorter wavelengths. The overall objective is to design gelatinous materials that emit visible light for potential sensor applications.

17 pages

Published manuscripts that appear in “Physical Properties of Macromolecules”

Chapter#3; Flory-Huggins conformational entropy of concentrated polymer solutions

Chapter#4; Order parameter analysis of the diluent concentration dependence of T_g

LA Belfiore & SL Cooper, **Bisphenol-A Polycarbonate-Diluent Interactions** *Journal of Polymer Science; Polymer Physics Edition*, 21 (10), 2135-2157 (1983).

Chapter#3; Chemical stability of binary mixtures via the Gibbs free energy of mixing

AA Patwardhan & LA Belfiore, **Prediction of Thermodynamic Properties of Polymer Solutions by a Group Contribution Method**, *Journal of Polymer Science; Polymer Physics Edition*, 24 (11), 2473-2486 (1986).

Chapter#4; DC electric field effects on phase transition in pure materials and binary mixtures

LA Belfiore, **DC Electric Field Effects on Ehrenfest-like Relations at the Glass Transition**, *Polymer*, submitted for publication, February (2007).

Chapter#6; Macromolecule-metal complexes; enhancement in T_g

LA Belfiore, MP McCurdie & PK Das, **Macromolecule-Metal Complexes: Ligand Field Stabilization and Thermophysical Property Modification**, *Polymer*, 42 (25), 9995-10006 (2001).

LA Belfiore & SE Fenton, **Nanocluster Assemblies and Molecular Orbital Interactions in Macromolecule-Metal Complexes**, in *Macromolecules Containing Metal & Metal-Like Elements, Volume 7, Nanoscale Interactions of Metal-Containing Polymers, Chapter 1*; edited

by AS Abd-El-Aziz; CE Carraher, Jr; CU Pittman, Jr; & M Zeldin; Wiley-Interscience: New York (2006), pp. 1-53, ISBN# 0-471-68440-6.

Chapter#8; Chain folding and multiple melting endotherms in blends and complexes
JG Tang, CKS Lee & LA Belfiore, **Effects of Several Lanthanide Trichloride Hydrates on the Melting Behaviour and Spherulitic Superstructure of Poly(ethylene oxide)**, *Journal of Polymer Science; Polymer Physics Edition*, **41** (18), 2200-2213 (2003).

Solid state NMR data in the carbonyl chemical shift region for amorphous/semicrystalline polymer-polymer blends of poly(vinyl phenol) with main-chain polyesters;
LA Belfiore, C Qin, E Ueda & ATN Pires, **Carbon-13 Solid State NMR Detection of the Isotropic Carbonyl Lineshape in Blends of Poly(vinylphenol) with Main-Chain Polyesters**, *Journal of Polymer Science; Polymer Physics Edition*, **31** (4), 409-418 (1993).

Chapter#9; Isothermal analysis of crystallization kinetics via calorimetric endotherms
F Bossé, PK Das & LA Belfiore, **Annealing Effects on the Solid State Properties of Transition Metal Coordination Complexes & Networks based on Diene Polymers with Palladium Chloride**, *Journal of Polymer Science; Polymer Physics Edition*, **34** (5), 909-924 (1996).

Chapter#12; Distribution of linear viscoelastic relaxation times and moments of the distribution function
LA Belfiore, **Transient Viscoelastic Response in Multiphase Thermoplastic Elastomers**, *ACS Proceedings; Division of Polymeric Materials Science & Engineering*, **56**, 817 (1987).

Chapter#13; Nonlinear stress relaxation and effect of strain on viscoelastic relaxation times
PK Das & LA Belfiore, **Nonlinear Stress Relaxation in Palladium(II) Complexes with Triblock Copolymers of Styrene and Butadiene**, *Journal of Applied Polymer Science*, **93** (3), 1329-1336 (2004).

Chapter#14; Appendix B
Alkene dimerization and Pd-catalyzed compatibilization of diene polymers
LA Belfiore, X Sun, PK Das & JY Lee, **High-Temperature Infrared Kinetics of Transition-Metal-Catalyzed Chemical Reactions in Solid State Complexes of Polybutadienes with Palladium Chloride**, *Polymer*, **40** (20), 5583-5599 (1999).

Chapter#17; Dielectric and solid state NMR relaxation phenomena in carbon-13 labelled bisphenol-A polycarbonate
LA Belfiore, PM Henrichs & SL Cooper, **Diluent Effects on Carbonate Mobility in Bisphenol-A Polycarbonate in the Solid State**, *Polymer*, **25** (4), 452-458 (1984).

Chapter#18; Magnetic spin diffusion in multiphase polymers

LA Belfiore & AA Patwardhan, **Interdomain Communication via Spin Diffusion in Multiphase Polymers**, *ACS Proceedings; Division of Polymeric Materials Science & Engineering*, **54**, 638 (1986).

LA Belfiore, HRJ Graham, E Ueda & Y Wang, **Solid State NMR Detection of Molecular Mixing in Biectetic Blends, d-Metal Complexes and Phase-Separated Copolymers**, *Polymer International*, **28** (1), 81-94 (1992).