

## CONTENTS

<b>1. GENERAL PHYSICAL PROPERTIES OF RUBBER</b>	
1.1. What is a rubber?	1
1.2. Chemical constitution of rubbers	3
1.3. Early theories of rubber elasticity	6
1.4. The kinetic theory of elasticity	7
1.5. Cross-linking and vulcanization: network theory	11
1.6. The glass-rubber transition	13
1.7. Crystallization in raw rubber	16
1.8. Crystallization in the stretched state	20
<b>2. INTERNAL ENERGY AND ENTROPY CHANGES ON DEFORMATION</b>	
2.1. Stress-temperature relations	24
2.2. Thermodynamic analysis	28
2.3. Application to experimental data	32
2.4. Interpretation of thermoelastic data	34
2.5. Thermal effects of extension	37
2.6. Conclusion	40
<b>3. THE ELASTICITY OF LONG-CHAIN MOLECULES</b>	
3.1. Statistical properties of long-chain molecules	42
3.2. Statistical form of long-chain molecule	43
3.3. The randomly jointed chain	46
3.4. Properties of Gaussian functions	48
3.5. The distribution of <i>r</i> -values	50
3.6. Equivalent random chain	53
3.7. The entropy of a single chain	55
3.8. The tension on a chain	57
<b>4. THE ELASTICITY OF A MOLECULAR NETWORK</b>	
4.1. The nature of the problem	59
4.2. Detailed development of the theory	60
4.3. Significance of theoretical conclusions	64
4.4. The principal stresses	65
4.5. Significance of single elastic constant	67
4.6. The elastic properties of a swollen rubber	68
4.7. Development of the theory by James and Guth	71

4.8. Network imperfections: 'loose end' corrections	74
4.9. The absolute value of the modulus	77
<b>5. EXPERIMENTAL EXAMINATION OF THE STATISTICAL THEORY</b>	
5.1. Introduction	80
5.2. Particular stress-strain relations	81
5.3. Experimental examination of stress-strain relations	85
5.4. Deviations from theory: Mooney equation	95
5.5. General conclusions	99
<b>6. NON-GAUSSIAN CHAIN STATISTICS AND NETWORK THEORY</b>	
6.1. Introduction	101
6.2. Statistical treatment of randomly jointed chain	102
6.3. Entropy and tension	106
6.4. Alternative derivation of tension on chain	108
6.5. The exact distribution function	109
6.6. Application to real molecular structures	111
6.7. Non-Gaussian network theory	113
6.8. Comparison with experiment	122
6.9. Possible influence of crystallization	123
6.10. The equivalent random link	124
<b>7. SWELLING PHENOMENA</b>	
7.1. Introduction	128
7.2. General thermodynamic principles	129
7.3. Experimental data	131
7.4. Significance of thermodynamic quantities	134
7.5. Statistical treatment of swelling	136
7.6. Comparison with experiment	139
7.7. The swelling of cross-linked polymers	140
7.8. Relation between swelling and modulus	142
7.9. The cohesive-energy density	147
7.10. The dependence of swelling on strain	150
7.11. Experiments on swelling of strained rubber	155
7.12. Swelling under torsional strain	158
<b>8. CROSS-LINKING AND MODULUS</b>	
8.1. Introduction	160
8.2. Early work	161
8.3. The experiments of Moore and Watson and of Mullins	164
8.4. Effect of entanglements	168
8.5. Discussion and conclusion	170

<b>9. PHOTOELASTIC PROPERTIES OF RUBBERS</b>	
9.1. Refractive index and polarizability	174
9.2. Optical properties of long-chain molecules	175
9.3. The Gaussian network	178
9.4. The effect of swelling	182
9.5. The non-Gaussian network	182
9.6. Measurement of birefringence	186
9.7. Investigations on natural rubber	189
9.8. The effect of the degree of cross-linking	195
9.9. Polyethylene	198
9.10. Optical properties of the monomer unit	202
9.11. The equivalent random link	204
9.12. The effect of swelling on stress-optical coefficient	206
9.13. Temperature dependence of optical anisotropy	209
<b>10. THE GENERAL STRAIN: PHENOMENOLOGICAL THEORY</b>	
10.1. Introduction	211
10.2. The theory of Mooney	212
10.3. Rivlin's formulation	214
10.4. Pure homogeneous strain	218
10.5. The general strain: early experiments	220
10.6. The experiments of Rivlin and Saunders	223
10.7. Interpretation of Mooney plots	225
10.8. Molecular significance of deviations from statistical theory	227
<b>11. ALTERNATIVE FORMS OF STRAIN-ENERGY FUNCTION</b>	
11.1. Survey of alternative proposals	230
11.2. Ogden's formulation	233
11.3. The Valanis-Landel hypothesis	236
11.4. Experimental examination of Valanis-Landel hypothesis	238
11.5. Form of the function $w'(\lambda)$	242
11.6. Re-examination in terms of strain invariants	246
<b>12. LARGE-DEFORMATION THEORY: SHEAR AND TORSION</b>	
12.1. Introduction: components of stress	252
12.2. Stress components in simple shear	253
12.3. Torsion of a cylinder	258
12.4. Generalization of preceding results	260
12.5. Experimental verification	262

12.6. Further problems in torsion	265
12.7. Simultaneous extension, inflation, and shear of cylindrical annulus	267
12.8. Application of Ogden formulation	269
<b>13. THERMODYNAMIC ANALYSIS OF GAUSSIAN NETWORK</b>	
13.1. Introduction	270
13.2. Force-extension relation for Gaussian network	271
13.3. Stress-temperature relations	272
13.4. Internal energy and entropy changes	274
13.5. Measurements at constant volume	276
13.6. Values of $f_e/f$	281
13.7. Alternative experimental methods	283
13.8. Theoretical analysis of torsion	287
13.9. Experimental data for torsion	291
13.10. Volume changes due to stress	293
13.11. Experimental examination	294
13.12. Volume changes in torsion	296
13.13. Calorimetric determination of internal-energy contribution to stress	297
13.14. Temperature dependence of chain dimensions	299
13.15. Conclusion	300
<b>REFERENCES</b>	302
<b>AUTHOR INDEX</b>	307
<b>SUBJECT INDEX</b>	309