Contents

1.	THE	DELTA	PROJECT	1
	1.1.	Introd	uction	1
	1.2.	The Tl	hree Dimensions of the Delta Project	1
	1.3.	The Pr	roblem	2
	1.4.	Spectr	al Properties of Liquid Dichloromethane	6
		1.4.1.	Infrared Spectroscopy	6
		1.4.2.	Raman Spectroscopy	7
		1.4.3.	Relaxation of Nuclear Magnetic Resonance	8
		1.4.4.	Light Scattering and Ultrasound Relaxation	9
		1.4.5.	Dielectric and Far-Infrared (Zero-to-Terahertz	
			Frequency) Spectroscopy	11
		1.4.6.	Incoherent, Inelastic Neutron Scattering	13
		1.4.7.	Vibrational-Population Lifetime of Liquid CH ₂ Cl ₂	14
		1.4.8.	High-Field-Induced Birefringence	14
	App	endix: 7	The First Experimental Data from the Delta Project	18
	Refe	erences		19
2.	CON	MPUTE	R SIMULATION OF LIQUID CH ₂ Cl ₂	21
	2.1.	Introd	luction	21
	2.2.	Correl	ation Functions from TETRAH	22
		2.2.1.	Detailed Description of the Algorithm	24
		2.2.2.	Atom-Atom Pair Distribution Functions	26
		2.2.3.	Dynamical Results	28
		2.2.4.	Summary of the CH ₂ Cl ₂ Computer Simulation	45
	2.3.	The Ir	nteraction of Rotation and Translation in CH ₂ Cl ₂	
		and C	H ₃ CN	46
		2.3.1.	Symmetry Properties in Fixed and Moving Frames	
			of Reference	47
		2.3.2.	The Frame Transformation and	
			Moving-Frame A.C.F.	49

	 2.3.3. Theoretical Treatment of A.C.F.'s. 2.3.4. Nonlinear Effects 2.4. Suggestions for Further Work Appendix A. Taylor Series Expansion of the Mixed A.C.F.'s Appendix B. Frame Changes in Rotation-Translation Coupling References 	54 59 60 61 61 64
3.	MODELS FOR THE EFFECT OF DIPOLE-DIPOLE COUPLING ON DIELECTRIC RELAXATION AT LOW FREQUENCIES	65
	3.1. The Debye Theory3.2. The Effects of Dipole-Dipole Coupling When Inertia Is	65
	Neglected 3.3. Zwanzig's Lattice Model References	67 80 86
4.	INERTIAL EFFECTS AND ELECTRICAL INTERACTIONS I: MODELS WHICH LEAD TO LINEAR FOUNTIONS	
	OF MOTION	87
_	 4.1. Preliminary Remarks 4.2. The Disk Model with Inertial Effects 4.2.1. Corrections for Inertia 4.2.2. A Theorem about Gaussian Random Variables 4.2.3. Autocorrelation Functions for the Disk Model 4.3. The Torsional-Oscillator Model for Molecular Motion 4.3.1. Polarizability of the Torsional Oscillator 4.3.2. Frequency Dependence of α_μ(ω) 4.3.3. Discussion 4.4. Itinerant-Oscillator Model Appendix. The Wiener Process and Wiener Integrals References 	87 87 88 89 90 95 100 103 108 108 124 129
5.	INERTIAL EFFECTS AND ELECTRICAL INTERACTIONS II: MODELS WHICH LEAD TO NONLINEAR EQUATIONS OF MOTION	131
	5.1. Probability-Density Diffusion Equations 5.1.1 The Simple Pendulum: The Dependence of the	131
	J.I.I. The bimple rendulum. The Dependence of the	

Contents

x

Period of Oscillation on the Amplitude 132 5.1.2. Complete Revolutions 134 5.2. The Brownian Movement of a Particle in a One-Dimensional Periodic Potential 136

5.3.	Differential–Difference Equations for the Time Dependence	
	of the Distribution Function	137
5.4.	Expression of the Set of Equations (5.3.6) as a Matrix	
	Differential Equation	140
5.5.	Some Numerical Results	142
	5.5.1. Behavior of the Model in the Frequency Domain	149
	5.5.2. Summary of the Cosine-Potential Model	150
5.6.	Inclusion of Inertial Effects in Dielectric Relaxation of	
	Molecules Containing Polar Groups	153
	5.6.1. The Kramers Equation for the Rotating Dipoles	153
	5.6.2. Solution of Equation (5.6.1.10)	156
	5.6.3. Solution of Equation (5.6.2.12)	161
5.7.	Exact Inclusion of Inertial Effects	166
5.8.	The Itinerant-Oscillator Model When the Small-Oscillation	
	Constraint Is Relaxed	173
	5.8.1. The Kramers Equation for the Itinerant Oscillator	175
	5.8.2. Initial Conditions	179
	5.8.3. Angular-Velocity Correlation Functions	180
	5.8.4. Orientational Correlation Functions	181
Refe	rences	182
App	endix A. Calculation of the $A_p^n(t)$ in Equation (5.4.1) by	
	Means of Continued Fractions.	183
App	endix B. Frequency Dependence in Onsager's Model of a	
	Polar Dielectric—Some General Conclusions	193
THE	MACROSCOPIC PROPERTIES OF DIFLECTRICS	
AND	THEIR INTERPRETATION IN TERMS OF	
COR	RELATION FUNCTIONS	107
con		137
6.1.	The Field Equations in Free Space	197
6.2.	The Field Equations in a Dielectric	198
	6.2.1. The Relation between \vec{D} , \vec{E} , and \vec{P}	201
	6.2.2. The Differential Equation for the Potential V in a	
	Dielectric Medium	202
	6.2.3. Conditions for the Vanishing of the Divergence	
	of the Polarization	203
	6.2.4. Boundary Conditions for the Potential	203
	6.2.5. Uniqueness Theorems	203
6.3.	Analysis of Dielectric Absorption Spectra in Terms of	
	Correlation Functions	204
	6.3.1. The Relation between the Dipole Unit-Vector	-01
	Autocorrelation Function and the Observed	
	Spectral Data for Noninteracting Rigid Dipoles	205
	I Brade Sthotes	

6.

		6.3.2.	Dilute Solutions of Polar Materials in	205
	64	Comp	arison of Experimental and Model $\phi(t)$'s	207
	Refe	rences	arison of Experimental and Woder $\varphi(t)$ s	210
			*	21.
7.	TWC TO F) THEO RELAXA	RETICAL TOOLS FOR A RIGOROUS APPROACH TION PHENOMENA IN CONDENSED MATTER	215
	7.1.	Introd	uction	215
	7.2.	The A	diabatic Elimination Procedure (AEP)	218
	7.3.	A Wig	ner-Moval-Type Equation as a Correct	=10
		Pertur	bation Expansion	222
	7.4.	The Co	ontinued-Fraction Procedure	230
	Refe	rences		236
8.	EXA/	MPLES (OF JOINT USE OF THE AEP AND CFP	239
	8.1.	Introd	uction	239
	8.2.	Analyt	tical Results for the Lowest-Order	
		Adiaba	atic Approximation	241
	8.3.	Escape	e over Potential Barriers	244
	8.4.	Suzuki	Time Scale	256
	8.5.	A Prel	iminary "Microscopic Model" for Noise-Induced Phase	
		Transi	tions and Change from Kramers to Suzuki Decay	262
		8.5.1.	Escape from a Potential Well in the Presence of	
			Multiplicative Noise	263
		8.5.2.	The Time Behavior of the Activation Process	266
	8.6. A Second Model for Noise-Induced Phase Transitions: The Presence of "Standard" Adiabatic Effects		ond Model for Noise-Induced Phase Transitions:	
			resence of "Standard" Adiabatic Effects	270
		8.6.1.	First Scheme of Calculation: Case 1	273
		8.6.2.	Second Scheme of Calculation: Case 2	274
	8.7.	Genera	alized Brownian Motion in a Double-Well Potential	280
		8.7.1.	On the Simulation of the Nonwhite Noise via a	
			Multidimensional Langevin Equation of the	
			Markovian Kind	281
		8.7.2.	Generalized Brownian Motion in a Double-Well	
			Potential: Quantitative Results	284
		8.7.3.	Adiabatic Elimination of Fast Relaxing Variables	
			for the Study of the Generalized Brownian Motion	
			in a Double-Well Potential	290
	8.8.	The R	ole of High-Frequency Fields: The Influence of	
		Short-	Time Dynamics on Long-Time Dynamics	294
		8.8.1.	Excitation by an External Radiation Field	
			Expressed in Terms of a Time-Independent	
			Fokker–Planck Operator	295

295

	8.8.2. Brownian Motion in a Double-Well Potential in the	
	Presence of a Partially Coherent Radiation Field	300
	8.8.3. Electromagnetic Excitation as a Source of	
	Noise-Induced Phase Transitions	304
	8.8.4. High-Frequency Radiation Fields	305
	Appendix	308
	References	310
9.	RMT AND MOLECULAR DYNAMICS IN THE LIQUID STATE	313
	9.1. Introduction	313
	9.2. Transient Non-Gaussian Effects	314
	9.3. An Example of a "Microscopic Model" That Is	
	Purely Phenomenological	321
	9.4. On Some Recent Key "Experiments"	326
	9.5. Long-Time Formal Constraints	330
	9.6. Non-Gaussian Behavior as an Effect of Short-Time Dynamics	335
	9.7. The RMT as a Link between Long- and Short-Time Behavior	341
	9.8. The Cosine Potential Model (Translational Case)	345
	9.9. The RMT and DEIEF Effects	348
	9.9.1. Decoupling Effects in the Quasi-Markovian Case	349
	9.9.2. Effects of Thermal-Bath Excitation	350
	9.10. The RMT and DASE Effects	353
	9.10.1. The Time Evolution of $\langle \cos \theta(t) \rangle$	354
	9.10.2. Short-Time Excitation Process	357
	9.10.3. Long-Time Behavior after Excitation	360
	References	363
AU	THOR INDEX	365
SUI	BJECT INDEX	369