

Dynamics of chiral molecules in the liquid state: Computer simulation and field effects

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The molecular dynamics of the *R* and *S* enantiomers of fluorochloroacetonitrile (HCFCINC), and of the racemic mixture, are investigated with computer simulation. Some novel single-molecule rotation-translation cross-correlation functions are reported in a moving frame of reference defined by that of the principal molecular moments of inertia. Two off-diagonal elements of these cross-correlation matrices have an equal and opposite time dependence for the two enantiomers and vanish for all t in the racemic mixture. The application of an external electric field to the chiral liquid generates *laboratory-frame* cross-correlation functions between the molecular center-of-mass translational momentum and the angular momentum of the same molecule. These cross-correlation functions are, therefore, seen in standard spectroscopic investigations of the molecular liquid state. As the intensity of the external field is increased, the following transient and field-on equilibrium effects become observable in the laboratory frame of reference: (i) Orientational rise transients are opposite in sign for the two enantiomers and vanish in the racemic mixture. (ii) These transients are field dependent, the dependence being qualitatively, but not quantitatively, that given by simple diffusion equations such as the Debye equation. (iii) At field-on equilibrium, the Grigolini decoupling effect is confirmed, i.e., the envelope of the oscillatory angular-velocity autocorrelation function decays more slowly than the field-off autocorrelation function at equilibrium as the external electric field strength is increased. (iv) The orientational fall transients are accelerated considerably with respect to the time dependence of the equivalent field-off orientational autocorrelation function. These results are interpreted with reduced-model theory, with use of Kramers equations with nonlinear potential terms.

I. INTRODUCTION

The dynamics of molecular liquids can be investigated with various types of external probe fields. By using computer simulation the field strength can be increased¹ to the point at which its energy of interaction begins to compete effectively with the natural thermal energy per molecule (kT). The computer simulations so far have involved electric and electromagnetic fields. Several field-induced effects are described in this paper using a combination of computer simulation and analytical theory. The latter is based on diffusion equations, such as the Kramers equation,² and new types of diffusion equations developed recently.³⁻⁵ The analytical theory is phenomenological in nature, i.e., descriptive rather than predictive, but the computer-simulation method can produce new effects quantitatively, in preparation for an experimental investigation. Fields with energy per unit time (i.e., power) far exceeding the ones used in this paper are now available from picosecond pulse lasers.

In previous work¹ the elementary Langevin and Kielich functions have been produced exactly by computer simulation, thus proving the validity of this new technique for all field strengths. These functions plot the $t \rightarrow \infty$ level of orientational rise transients of integer order versus the interaction energy of the external field with the sample in kT units. For dichloromethane liquid at room temperature it was found¹ that the rise transients were dependent on the external field strength. The greater the field strength the faster the rise transient. This result is inter-

preted for chiral symmetry in this paper with Morita's solution^{6,7} of the Debye diffusion equation.⁸ The theory and computer simulation agree qualitatively but there are large quantitative differences which are attributed⁹ to Debye's neglect of inertial,³ memory,⁵ and nonlinear⁴ effects.

At field-on equilibrium we confirm the field-induced decoupling effect of Grigolini,¹⁰ both in autocorrelation functions (ACF's) and cross-correlation functions (CCF's). The oscillation envelope of these functions becomes longer-lived as the external field strength increases and the Langevin function approaches its saturation point. This effect can be followed by the use of reduced-model theory^{3-5,11} (RMT). To do this memory effects⁵ are essential. The decoupling effect develops with the increasing predominance of the external field's strength and influence over the intermolecular forces themselves. In this paper it is confirmed both in the enantiomers and racemic mixture of fluorochloroacetonitrile. This body of detailed numerical and analytical evidence for the existence of the decoupling effect requires an experimental investigation. Field-induced decoupling delves deeply into the fundamental nature of the molecular liquid state of matter and requires for its basic description^{4,11} a rigorous theoretical analysis, based on fundamental equations of motion such as the Liouville equation. A quantitative description of the numerical results is still not possible analytically. Some purely phenomenological models¹² do not produce a decoupling effect at all because they do not relate rigorously to the Liouville equation. The analytical

theory of molecular diffusion is, generally speaking, still at the "one-particle" stage,¹³ where the intermolecular potential energy is ill-defined. This paper attempts to show that a clear representation of the pair potential is essential, and for chiral molecular dynamics some basic phenomena of chemical physics cannot be described without such a representation. These include the modification of physical and spectral properties observable when a racemic mixture is made up from two enantiomers.

At an equally fundamental level we report in this paper the direct observation of *laboratory frame*, single-molecule CCF's induced in the chiral molecular liquid by the use of directional fields of force such as an electric field. These CCF's are typified by the matrix¹⁴

$$\underline{c}_{lr} = \langle \vec{p}(t) \vec{J}^T(0) \rangle,$$

where \vec{p} is the molecular center-of-mass linear momentum and \vec{J} the angular momentum of the same molecule in the laboratory frame of reference. The normalized amplitude of \underline{c}_{lr} increases with increasing electric field strength for enantiomers and racemic mixture. We find in this paper that the parity theorem

$$\underline{c}_{lr} = 0, \quad 0 \leq t \leq \infty$$

no longer applies for chiral molecules subjected to external electric fields.¹⁵ Different off-diagonal CCF's ("elements") of \underline{c}_{lr} have different amplitude and time dependence for all field strengths greater than zero. Fundamental CCF's can be observed therefore in chiral molecular liquids (and, in general, in all liquids) with the use of external, directional force fields (electric, magnetic, and electromagnetic).

In the moving frame¹⁶ of the molecular principal moments of inertia the six off-diagonal CCF's of the matrix

$$\underline{c}_{lr}^{(m)} = \langle \vec{p}_{(m)}(t) \vec{J}_{(m)}^T(0) \rangle_{(m)}$$

exist in both enantiomers *but only four* in the racemic mixture. These CCF's are computed with both \vec{p} and \vec{J} defined in the moving frame of reference (1,2,3). The (1,3) and (3,1) elements have opposite and equal time-dependent characteristics (i.e., + or - in amplitude) for the *R* and *S* enantiomers. In the racemic mixture both of these CCF's vanish for all *t* in the moving frame of reference. The molecular dynamics of two enantiomers are therefore different when viewed in this frame, but, in the absence of a field, are identical in the laboratory frame. The dynamics of a racemic mixture differ in both frames from those of a component enantiomer.^{17,18} Electric field treatment in this paper produces two dominant CCF elements in the laboratory frame. For a field in the *z* axis these are the (*x,y*) and (*y,x*) elements of the laboratory frame matrix \underline{c}_{lr} . These are mirror images both in the two enantiomers and in the racemic mixture, where their amplitudes are decreased significantly with respect to their equivalents in each enantiomer. This paper also reports the existence of the (*z,x*) elements in the laboratory frame. These are much smaller than the (*x,y*) and (*y,x*) elements and do not mirror the (*x,z*) elements. This kind of detail is described further in the paper.

It is clear, therefore, that the statistical correlation of a

molecule's rotational properties with its own translational properties is a factor that must be accounted for even with a rudimentary description, in molecular dynamical terms, of the observable differences (e.g., spectral differences) that exist between an enantiomer and its racemic mixture. Laboratory-frame spectra (e.g., far infrared spectra)^{3,4} incorporate information on rotational-translational (RT) coupling in their frequency-dependent characteristics at equilibrium, or in rise and fall transients of orientation. In order to interpret these data satisfactorily we must rely on computer simulation until analytical techniques become available to match in detail the new, numerically generated¹⁷ CCF's. The theory must also be able to describe a variety of spectra (i.e., ACF's) self-consistently.

Finally, in this paper the applied electric fields are released instantaneously in the computer simulation, thus producing orientational fall transients¹ as the molecular liquid adjusts to field-off equilibrium at constant temperature. For the *R* and *S* enantiomers the fall transient is accelerated at constant temperature with respect to the time dependence of the equivalent field-off equilibrium orientational ACF. The first fluctuation-dissipation (FD) theorem of statistical thermodynamics¹⁹ is therefore invalidated as the external field energy approaches and exceeds the natural thermal energy per molecule. The effect persists at low field strengths and the validity of the FD theorem is restored only in the limit $\vec{E} \rightarrow \vec{0}$. The single most significant implication of field-induced fall-transient acceleration is that it is evidence for the future use of well-defined, nonlinear (i.e., "multiparticle") theories of molecular diffusion at *field-off equilibrium*.^{4,5,11} Again, as in the decoupling effect, long accepted theories of molecular liquid dynamics miss the fall-transient acceleration completely, i.e., cannot be used to describe the effect. In this paper transient acceleration is reproduced phenomenologically with the use of a "two-particle" theory, a cosinal itinerant oscillator in two dimensions.¹¹ Transient acceleration means that theories of molecular diffusion, in and out of equilibrium, must be non-Markovian and nonlinear. For consistency, it follows that all other observable (e.g., spectral) features of molecular diffusion also need the same ingredients and conversely supply information about them.

The paper is arranged as follows. Section I describes the computer-simulation algorithm, explaining the choice of the fluorochloroacetonitriles for this study. The pair potential is tabulated in terms of Lennard-Jones atom-atom terms and partial charges located on each atom. In Sec. III orientational rise transients are described as a function of field energy of interaction (μE) for enantiomers and racemic mixture and the field dependence interpreted theoretically with Morita's results^{6,7} modified and extended by Marchesoni⁹ for this purpose. In Sec. IV field-on equilibrium CCF's are illustrated in both (*x,y,z*) and (1,2,3) frames. The prime results are summarized in symmetry tables and interpreted qualitatively with a laboratory frame theory of coupling due originally to Condiff and Dahler.¹⁴ Section V illustrates the decoupling effect^{10,11} at field-on equilibrium and describes some field-on and field-off equilibrium ACF's of interest to spectroscopy, produced self-consistently in our computer simula-

TABLE I. Intermolecular pair potential for fluorochloroacetonitrile, Lennard-Jones and partial charge terms.

Atom ^a	x (\vec{e}_3)	y (\vec{e}_1)	z (\vec{e}_2)	z (\underline{e}_2)	ϵ/k (K)	σ (\AA^{-1})	$q/ e $
N	0.75	-2.28	0.35	-0.35	47.8	3.0	-0.16
C	0.27	-1.29	-0.03	0.03	35.8	3.4	-0.02
C	-0.34	-0.05	-0.51	0.51	35.8	3.4	0.03
H	-0.34	-0.38	-1.59	1.59	10.0	2.8	0.51
Cl	0.61	1.33	0.07	-0.07	127.9	3.6	-0.16
F	-1.64	0.06	0.02	-0.02	54.9	2.7	-0.20

^aAtom coordinates relative to center of mass frame of the molecular principal moments of inertia.

tion. Finally, in Sec. VI, field-induced transient acceleration is illustrated for the *R* enantiomer and interpreted with the Suzuki equation,¹¹ a nonlinear Langevin equation to which the cosinal itinerant oscillator reduces in a well-defined limiting case.

II. COMPUTER-SIMULATION ALGORITHM

The algorithm integrates the classical equations of motion for 108 interacting molecules of fluorochloroacetonitrile. The potential energy is assumed pairwise additive and is built up from the atom-atom terms of Table I. There are 36 atom-atom terms per molecular pair. The numerical integration technique and assumptions involved are described fully elsewhere by Ferrario *et al.*²⁰ The input temperature of the simulation was 133 K and the input molar volume was taken to be 91.4 cm³. This corresponds to fluorochloroacetonitrile in a supercooled condition below the normal freezing point at 1 bar. In this state the effect of the external field is accentuated because kT is small. In this condition field-off and field-on ACF's and CCF's were computed by running-time averaging.^{3,21} The racemic mixture was investigated with

54 *R* molecules and 54 *S* molecules with the same site-site pair potential terms of Table I. The equilibrium averaged *R-R* and *S-S* potentials are the same but the *R-S* potential is slightly different. This is sometimes known as "chiral discrimination." The atom-atom terms of the table reproduce this small effect approximately.

The effect of an external electric field on the molecular dynamics was simulated by the addition in the forces loop of the algorithm of an extra torque¹ $-\vec{\mu} \times \vec{\mathcal{E}}$. Here $\vec{\mu}$ is the net molecular dipole moment and $\vec{\mathcal{E}}$ the electric field strength. The field was applied in the z axis of the laboratory frame of reference. The fluorochloroacetonitrile molecule was chosen for the simulation because the reflection needed to generate the *R* enantiomer from the *S* fortuitously reverses the sign of the molecular dipole moment in the laboratory frame. The effect of this is that an orientational rise transient $\langle e_{2z} \rangle (\vec{e}_2 \approx \mu / |\mu|)$ for the *R* enantiomer mirrors that of the *S* enantiomer. There is no observable transient in the racemic mixture because of cancellation. A sufficiently strong field aligns the *R* (or *S*) enantiomer parallel and the racemic mixture antiparallel. This property maximizes an observable laboratory-frame difference between aligned enantiomers

TABLE II. Thermodynamic data from the computer simulation of fluorochloroacetonitrile, $T=133$ K. [] denotes output from different runs; checks constancy of the total energy.

Liquid	Potential energy (kJ/mole)	Kinetic energy		Total energy (kJ/mole)	$\mu E/kT$
		Trans. (kJ/mole)	Rot. (kJ/mole)		
<i>R</i>	[-48.33]	[1.70]	[1.74]	[-44.89]	0
	[-48.46]	[1.76]	[1.83]	[-44.87]	0
	[-48.20]	[1.80]	[1.75]	[-44.65]	0
<i>S</i>	-47.65	-1.75	1.75	-44.15	0
<i>R-S</i>	-47.78	1.75	1.75	-44.28	0
<i>R</i>	-48.54	1.76	1.80	-44.99	0.5
<i>R</i>	-43.36	1.79	1.74	-39.83	2.0
<i>R</i>	[-31.23]	[1.78]	[1.75]	[-27.28]	[10.0]
	[-30.83]	[1.78]	[1.76]	[-27.70]	[10.0]
<i>S</i>	[-31.38]	[1.81]	[1.74]	[-27.84]	[10.0]
	[-30.95]	[1.80]	[1.76]	[-27.40]	[10.0]
<i>R-S</i>	[-32.54]	[1.71]	[1.76]	[-29.07]	[10.0]
	[-32.11]	[1.73]	[1.75]	[-28.63]	[10.0]
<i>S</i>	-27.51	1.76	1.75	-24.00	50.0
<i>R-S</i>	-30.54	1.72	1.82	-27.01	50.0

and racemic mixture, providing an extra experimental variable.

The potential energy of the sample at field-on equilibrium (Table II) increases with external field strength. The potential energy of the racemic mixture for strong fields is consistently a little lower (more negative) than that of either enantiomer. The kinetic energy is always maintained the same in the simulation with temperature rescaling to the input temperature. This is the standard technique used in constant-volume molecular-dynamics simulation.²² The application of an external field means that the molecules of the sample adjust from low to high potential energy at constant temperature. The adjustment process is isothermal, i.e., the sample is thermostated. The efficiency of this thermostat can be varied by varying the frequency of temperature rescaling. We have verified that rescaling, with very strong fields, produces small, spurious oscillations in the rise transient, but has little or no effect on its underlying time dependence. For intermediate field strengths there is very little abnormal temperature fluctuation after field application. The input, equilibrium, fluctuation range was ± 25 K.

With field-effect computer simulation it is possible therefore to compute rise and fall transients for different applied field strengths for the enantiomers, ACF's and CCF's for enantiomers and racemic mixture at field-on and field-off equilibrium, and thermodynamic properties.

III. ORIENTATIONAL RISE TRANSIENTS

There have been recent attempts at^{6-8,23} solving the Debye diffusion equation⁸ in the presence of strong external fields. These approximate solutions suggest a field dependence of the characteristic rise-transient time, defined for convenience as the e^{-1} time. Morita's solution, for example, is expressed^{6,7} as a Laplace space continued fraction. Marchesoni⁹ has extended the validity of Morita's result for comparison with the results of a computer simulation¹ of dichloromethane at 296 K. Morita obtains for the Laplace transform of the rise transient [$\langle \cos\theta(t) \rangle$]

$$\mathcal{L}_a(\langle \cos\theta(t) \rangle) = \frac{2e_0}{3} \frac{\Lambda}{p} (p, e_0), \quad (3.1)$$

where

$$\Lambda(p, e_0) = \frac{1}{p + \lambda_0 + \frac{\Delta_1^2}{p + \lambda_1 + \frac{\Delta_2^2}{p + \lambda_2 + \frac{\Delta_3^2}{p + \lambda_3 + \dots}}}}$$

in which

$$\lambda_n = (n+1)(n+2),$$

$$\Delta_n^2 = \frac{n(n+1)^2(n+2)e_0^2}{(2n+3)(2n+1)}$$

The same result can be obtained straightforwardly²⁴ as a continued fraction⁵ of the Mori type.²⁵ From Eq. (3.1) it follows that⁹

$$\lim_{k \rightarrow \infty} \langle \cos\theta(t) \rangle = \lim_{p \rightarrow 0} \frac{2}{3} e_0 \Lambda(0, e_0) = L(e_0), \quad (3.2)$$

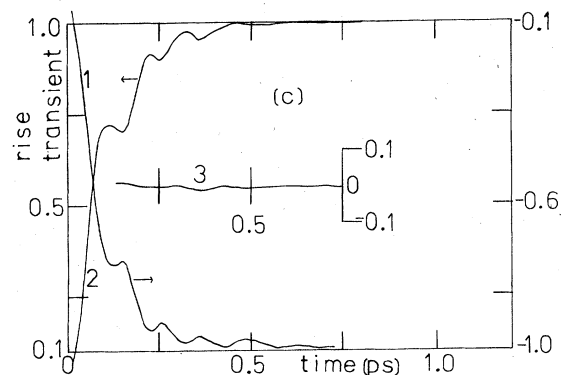
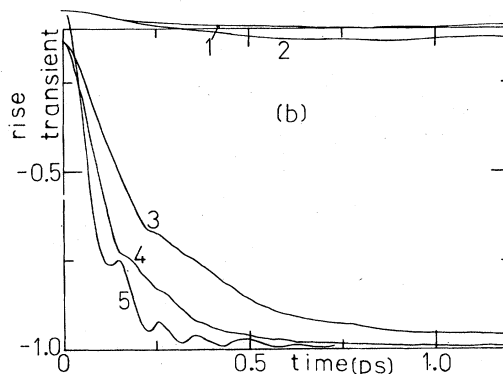
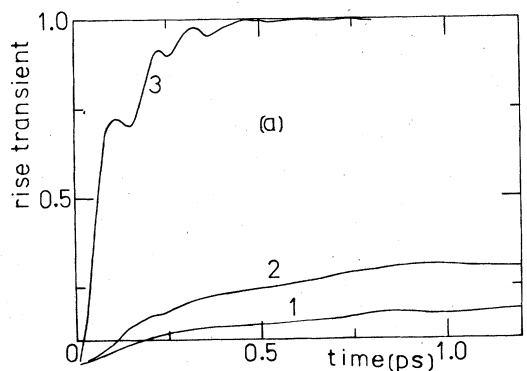


FIG. 1. Rise transients for fluoroacetonitrile. (a) Curve 1, $\mu E/kT=1.0$; curve 2, 2.0; curve 3, 50.0; *S* enantiomer. (b) Curve 1, 0.5; curve 2, 1.0; curve 3, 10.0; curve 4, 20.0; curve 5, 50.0; *R* enantiomer. (c) 50.0 kT field. Curve 1, *R* enantiomer, (right-hand-side scale); curve 2, *S* (left-hand-side scale). Inset: racemic mixture, same abscissal scale. Ordinate: $\langle e_{2z} \rangle$.

where $L(e_0)$ is the well-known Langevin function. The $t \rightarrow \infty$ limits of the rise transients in Fig. 1 fall on mirror-image Langevin functions for *R* and *S* enantiomers. This check has been used before by Evans¹ to test the basic validity of field-effect computer simulation. If we normalize the rise transient by

$$A_1(t) = 1 - \frac{\langle \cos\theta(t) \rangle}{\langle \cos\theta(\infty) \rangle} \quad (3.3)$$

the corresponding function from Morita's theory is, in Laplace transform,

$$A_1(p) = \frac{\Lambda(0, e_0) - \Lambda(p, e_0)}{p \Lambda(0, e_0)} \quad (3.4)$$

The clear dependence of our computer simulation $A_1(p)$ on electric field strength is shown in Fig. 2 with curves calculated from the rise transients by numerical Laplace transformation. Morita introduces a characteristic rise-transient time τ_R by fitting with a simple exponential e^{-t/τ_R} . Marchesoni has shown⁹ that this is equivalent to setting $p=0$ in all the denominators of Eq. (3.1) except the first, so that he obtains a characteristic time

$$\tau_e^M = \Lambda(0, e_0) = \frac{3}{2} \frac{L(e_0)}{e_0} \quad (3.5)$$

of Morita's theory. This is compared with the e^{-1} levels of the normalized rise transients for the *R* enantiomer from the computer simulation in Table III. There is a big difference between the theory and the simulation. The qualitative trend is, however, the same, but it would be surprising if this were not so. This result is similar to the comparison made by Evans *et al.*⁹ for dichloromethane at 296 K, but for the chiral case the discrepancy is more pronounced. For the purposes of comparison the Debye relaxation time has been estimated directly from the computer simulation of the field-off dipolar ACF. An improvement of the analytical theory is possible using the theorems and methods of RMT incorporating memory, inertial, and nonlinear (two-particle) effects.³⁻⁵ This is expected to close the gap (Table III) between the theory and computer simulation. It is essential, for further progress, to initiate the *experimental* study of the field dependence of rise transients. This seems to be possible using laser fields,²⁶ generating second-order rise transients via the molecular polarizability (the Buckingham effect).

Finally, in this section, we note that for strong (50.0 *kT*) electric field [Fig. 1(c)] there is, essentially speaking, complete alignment in the *R* and *S* enantiomers and complete antiparallel alignment in the racemic mixture, where the transient average vanishes.

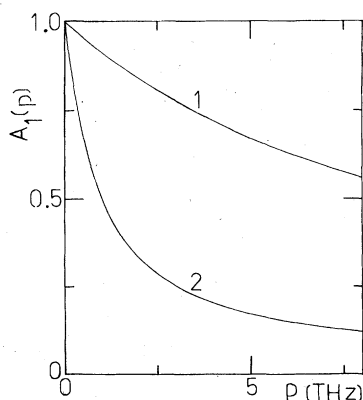


FIG. 2. Laplace transform of normalized rise transients, *S* enantiomer: curve 1, 50.0 *kT* field; curve 2, 2.0 *kT* field. Ordinate, $A_1(p)$; abscissa, p/THz .

TABLE III. Comparison of characteristic rise-transient times from the simulation of the *R* enantiomer with Morita's solution of the Debye equation. Debye relaxation time equals 30.0 ps [$1/e$ time of the field off $\langle \vec{\mu}(t) \cdot \vec{\mu}(0) \rangle$] from the computer simulation.

$\mu E/kT$	Simulated (ps)	Theoretical (ps)
50.0	0.06	1.80
10.0	0.12±0.01	2.91
2.0	0.35±0.02	23.62
1.0	0.70±0.10	23.40

IV. RT COUPLING

The available single-particle diffusional theories of the molecular liquid state cannot yet deal very effectively with the fact that molecules can both translate and rotate at the same time, and that the two types of motion are not statistically independent.¹⁴ The attempts at adapting Langevin or Kramers equations for such a description have not been useful in practice because of inconsistencies and great complexity. For this reason Debye's idea of "rotational" diffusion⁸ is still used almost universally in the analytical interpretation of, for example, spectra, in the liquid state. Of the recorded attempts at deriving c_{tr} analytically the first and clearest is that of Condiff and Dahler.¹⁴ This important paper shows that several fluid mechanical phenomena can arise from the coupling between molecular rotation and mass flow, and may be stimulated by the interaction of molecular electromagnetic multipoles with external fields. Recently Evans²⁷ has induced bulk translation in molecular liquids such as CCl_4 with inhomogeneous electric fields. Papers on the analytical theory of RT coupling are reviewed in Ref. 3, Chap. 5. A recent paper by Steiger and Fox²⁸ claims that there are basic inconsistencies in the earlier treatments of Hwang and Freed²⁹ and Evans.³⁰ The theory should satisfy the parity law^{15,16} $c_{tr} = 0$ in the laboratory frame for an *isolated* sample of molecular liquid. However, Ryckaert *et al.*¹⁶ have used computer simulation to show that CCF's such as c_{tr} exist in a moving, molecular frame of reference. This work for linear molecules has been extended to other molecular symmetries by Evans *et al.*^{17,18,31-37}

The symmetry characteristics of the off-diagonal CCF's of $c_{tr}^{(m)}$ are summarized in Table IV for the enantiomers and racemic mixture of fluorochloroacetonitrile. The numbers in this table denote the maximum levels attained by the first peak of the normalized off-diagonal CCF's at field-off equilibrium. The noise level in each entry is estimated at about $\pm(\mp)0.01$ and the symbol δ is used to denote that the signal is below the noise, i.e., the CCF is either very small in amplitude or must vanish (diagonal terms) by symmetry. (We have checked that the diagonal elements are indeed all buried in the background noise.) It is clear from Table IV that the symmetry characteristics of $c_{tr}^{(m)}$ for the racemic mixture are different from those of either enantiomer. *There is also a difference between the two enantiomers.* In particular the (3,1) and (1,3) ma-

TABLE IV. $\underline{c}_{tr}^{(m)}$ symmetry table for the fluorochloroacetonitriles.

Enantiomers			S			Racemic mixture		
R			S			Racemic mixture		
δ	δ	$-(0.09)$	δ	δ	$+(0.08)$	δ	δ	δ
$-(0.08)$	δ	$+(0.12)$	$-(0.08)$	δ	$+(0.11)$	$-(0.06)$	δ	$+(0.10)$
$+(0.12)$	$-(0.13)$	δ	$-(0.13)$	$-(0.13)$	δ	δ	$-(0.11)$	δ

trix elements for the *R* and *S* enantiomers change sign. These elements vanish in the mixture. The other off-diagonal CCF's retain the same sign and magnitude (approximately) in all three cases. The diagonal elements are always below the noise. The time dependence of the (3,1) and (1,3) elements of $\underline{c}_{tr}^{(m)}$ is illustrated in Fig. 3. They mirror each other in amplitude, within the noise, for the *R* and *S* enantiomers but the (3,1) element is not the mirror image of the (1,3) element, i.e., the two CCF's have a different time dependence. The (2,3) and (3,2) elements are illustrated in Fig. 4 for the two enantiomers and this time they do not change sign and look similar in the racemic mixture. The same is true for the (2,1) CCF's of Fig. 5. The (1,2) elements (Table IV) cannot be detected above the noise of the simulation, but are not precluded on symmetry grounds.¹⁶

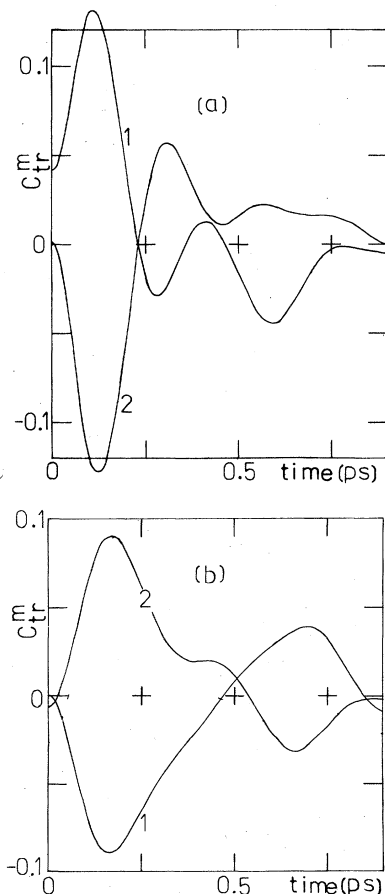


FIG. 3. Moving frame CCF elements for the *R* and *S* enantiomers. (a) Curve 1, *R*; curve 2, *S*; (3,1) element, defined as $(3,1) \equiv \langle p_3(t)J_1(0) \rangle / (\langle p_3^2 \rangle^{1/2} \langle J_1^2 \rangle^{1/2})$. (b) Curve 1, *R*; curve 2, *S*; (1,3) element.

The effect on the CCF's of a strong external electric field is to make them more oscillatory and longer-lived. At field-on equilibrium, therefore, there is a decoupling^{10,11} of the rototranslational molecular dynamics from the thermal background as a result of the competition between the interaction energy (μE) and kT . This is exactly analogous to the Grigolini decoupling effect in the angular velocity^{3-5,10,11} ACF at field-on equilibrium (Sec. V). For an energy ratio $\mu E/kT=50.0$ the (2,3) and (2,1) elements are oscillatory (Fig. 6) in the racemic mixture. The extent of field induced decoupling is different for different elements. It seems to be smaller for the (3,2) element of Fig. 6. There is also, of course, a decoupling effect in each enantiomer.

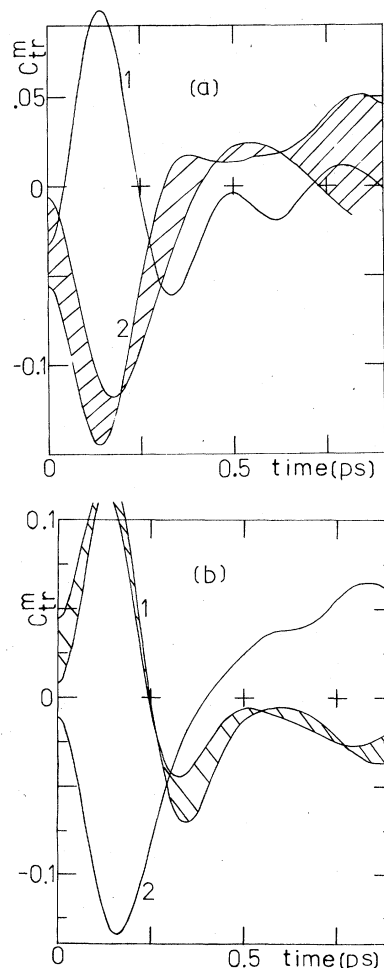


FIG. 4. Moving frame CCF elements. (a) *S* enantiomer: curve 1, (2,3); curve 2 (3,2). (b) As for (a), *R* enantiomer. The hatched area denotes the statistical noise level, i.e., the difference between consecutive runs.

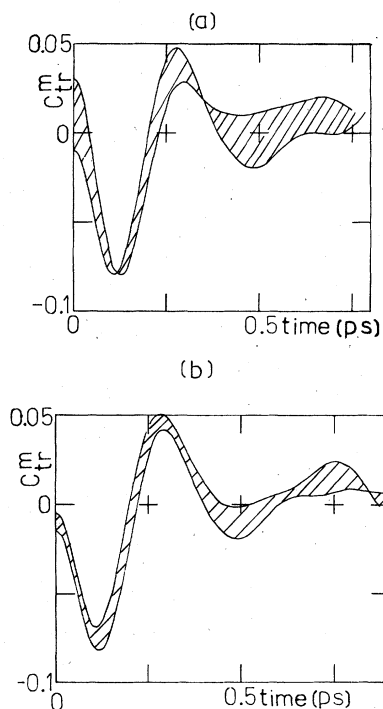


FIG. 5. Moving frame CCF elements. (a) *R* enantiomer, (2,1) element; (b) as for (a) *S* enantiomer.

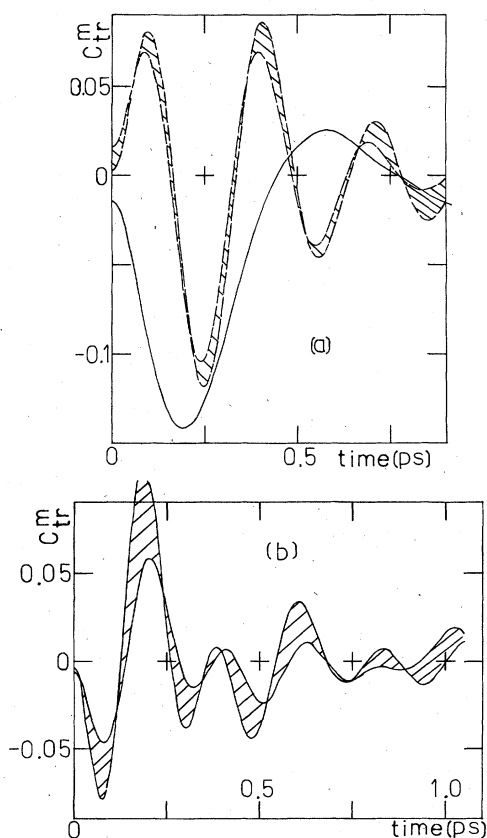


FIG. 6. Moving frame CCF elements, field-on equilibrium. (a) —, (3,2) element, 50.0kT field; ---, (2,3) element; racemic mixture. (b) As for (a), (2,1) element.

A fundamentally important result of the electric field treatment is illustrated in Fig. 7. The application of an electric field makes \underline{c}_{tr} visible in the laboratory frame of reference. Its dominant elements for a z axis electric field are the (x,y) and (y,x) elements in the laboratory frame (x,y,z) . The normalized amplitude of these elements increases with the strength of the external electric field. These elemental CCF's are mirror images, within the noise, for all $\vec{E} > \vec{0}$. They reach a maximum normalized amplitude at $\mu E/kT \approx 10$ for both enantiomers and racemic mixture, and thereafter become more oscillatory with increasing \vec{E} (Fig. 8). These elements are illustrated for $\mu E/kT = 10.0$ in Fig. 9. As in Fig. 8 there is a small but significant difference between the CCF's for the racemic mixture and an enantiomer. Most of the other elements of \underline{c}_{tr} vanish in the noise of the simulation runs, but at $\mu E/kT = 50.0$ it is just possible to quantify the (z,x) elements. These are low in amplitude compared with the (x,y) or (y,x) elements but are more oscillatory in time dependence (Fig. 10). Again there seems to be a significant difference between the behavior of the enantiomer and the racemic mixture. We have not been able to see the other elements of \underline{c}_{tr} above the noise, but they may exist for $t > 0$. The general symmetry characteristics of \underline{c}_{tr} are summarized in Table V.

As in Table IV the entries in these matrices denote the sign of the first peak of each elemental CCF so that the (y,x) entry is + and so on. Table V holds for all field strengths $\vec{E} > \vec{0}$. The (z,x) entry is negative because there is a negative trend in the first peak of this oscillatory CCF at $\mu E/kT = 50.0$ (Fig. 10). This may persist at lower field strengths. It is clear that the symmetry characteristics of Table V are different from those of the Table IV. Both tables are generated *self-consistently* in the computer simulation. The analytical theory of RT coupling must be able at some stage to account for this finding. In principle, all the off-diagonal elements of \underline{c}_{tr} and $\underline{c}_{tr}^{(m)}$ may exist in the enantiomers, but two of these disappear, as we have seen,

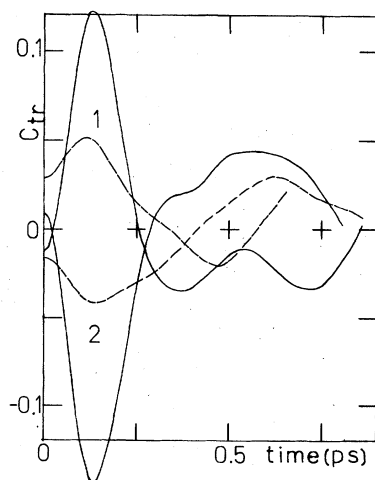


FIG. 7. Laboratory frame CCF elements, *S* enantiomer. Curve 1, —, (y,x) , 20.0kT field; ---, (y,x) ; 2.0kT field. Curve 2, as for curve 1, (x,y) elements. Elements normalized as in $(x,y) \equiv \langle p_x(t)J_y(0) \rangle / (\langle p_x^2 \rangle^{1/2} \langle J_y^2 \rangle^{1/2})$.

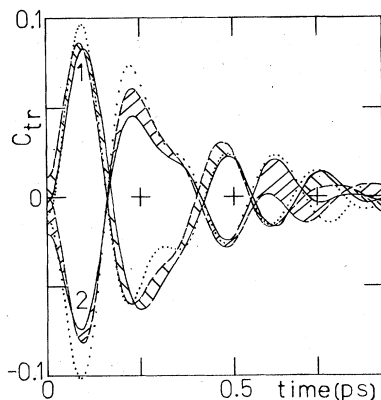


FIG. 8. Laboratory frame CCF elements, 50.0kT field. Curve 1, . . . , racemic mixture; hatched area is the difference (assumed to be noise) between the two enantiomers; (y,x) element. Curve 2, as for curve 1, (x,y) element.

in the racemic mixture for $\underline{\epsilon}_{tr}^{(m)}$ but not for $\underline{\epsilon}_{tr}$. Observable spectral differences between enantiomer and racemic mixture therefore hold information on CCF's and their time dependence. This can be extracted provided that the spectroscopy is backed up by computer simulation as an aid to interpretation.

As pointed out by Condiff and Dahler¹⁴ the properties of CCF matrices are fundamental to the understanding of fluid-mechanical phenomena generated from the application of fields to molecular liquids. In a parallel simulation of the achiral asymmetric top dichloromethane, we have verified³⁸ that $\underline{\epsilon}_{tr}$ also appears in the laboratory frame upon electric field treatment, but that for a *homogeneous* electric field the computer-simulation sample as a whole does not translate. The observation of $\underline{\epsilon}_{tr}$ in the laboratory frame is an important result, because it means that RT coupling is directly observable by standard spectroscopic methods, in particular by field-induced birefringence.³⁹ In general the parity theorem $\underline{\epsilon}_{tr} = 0$ is always violated for any molecular symmetry by an imposed directionality, i.e., a field of force in the laboratory frame. Birefringence has been observed with electric, magnetic,

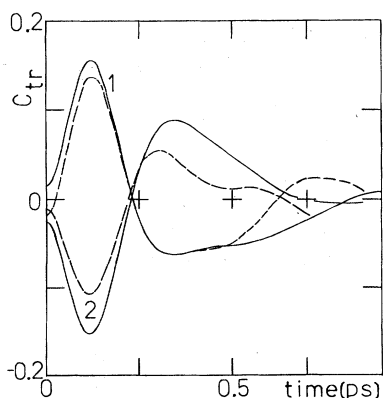


FIG. 9. As for Fig. 8; ---, R enantiomer; —, racemic mixture; 10.0kT field.

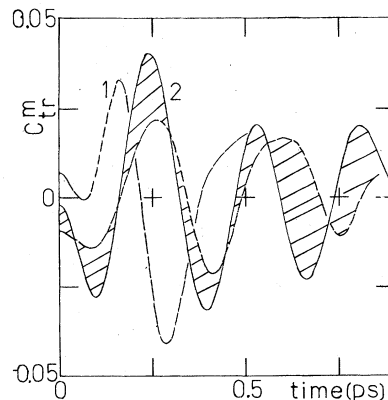


FIG. 10. As for Fig. 8, (z,x) element of the laboratory frame. Curve 1, racemic mixture; curve 2, difference between R and S enantiomers, hatched, assumed to be noise.

and electromagnetic²⁶ fields (Kerr, Faraday, and Buckingham effects) and the apparatus used is capable of picking up a minute level of birefringence. In doing this it is automatically observing CCF's by imposing directionality via the probe field. In fact $\underline{\epsilon}_{tr}$ never vanishes with any known spectroscopic technique because the sample is always probed with a parity-breaking field, however weak. It is precisely the presence of this field that allows us to see spectra, and it is precisely this that induces the presence of CCF's in the laboratory frame. (They are always there in the moving frame.) It is questionable, therefore, whether the protagonists of induced birefringence, for example, have been seeing what they think they were seeing.

With strong inhomogeneous or polarized fields the RT effects become obvious (i.e., there is bulk translation), as shown in a striking series of experiments by Evans²⁷ with a very simple apparatus.

It is important to simplify the formidably difficult theory of RT coupling as exemplified in the work of Steiger and Fox.²⁸ This would aim to produce a general description of RT effects of technological importance. Using the theory of Condiff and Dahler¹⁴ it is possible to obtain a basic, qualitative description of the computer-simulation results. Assuming that the parity theorem is invalidated by the lack of inversion symmetry in chiral liquids¹⁵ it is possible to calculate $\underline{\epsilon}_{tr}$ analytically provided we assume that this has only one dominant element and that the three moments of inertia of the molecule are roughly equal. In this limit the RT CCF's are illustrated by the curves of Fig. 11. The available analytical theory of RT coupling, however sophisticated, cannot yet provide more than a shadow of the detail available from computer

TABLE V. $\underline{\epsilon}_{tr}$ symmetry table for fluorochloroacetonitrile.

Enantiomers		Racemic mixture
R	S	
$\begin{bmatrix} \delta & -\delta \\ + & \delta \end{bmatrix}$	$\begin{bmatrix} \delta & -\delta \\ + & \delta \end{bmatrix}$	$\begin{bmatrix} \delta & -\delta \\ + & \delta \end{bmatrix}$
$\begin{bmatrix} -\delta & \delta \\ - & \delta \end{bmatrix}$	$\begin{bmatrix} -\delta & \delta \\ - & \delta \end{bmatrix}$	$\begin{bmatrix} -\delta & \delta \\ - & \delta \end{bmatrix}$

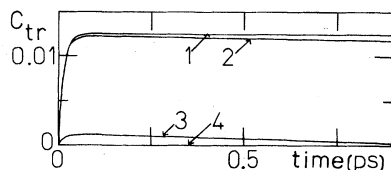


FIG. 11. Some RT cross-correlation functions calculated from a simplified version (see text) of the theory in Ref. 14: Laboratory frame of reference (Ref. 3). Curve 1, $\gamma_r = \gamma_t = \gamma_n = 10^{12}$ Hz (r , t , and rt friction coefficients); curve 2, $\gamma_r = \gamma_t = 10^{13}$ Hz, $\gamma_n = 9.8 \times 10^{12}$ Hz; curve 3, $\gamma_r = \gamma_t = 10^{13}$ Hz, $\gamma_n = 1.0 \times 10^{12}$ Hz; curve 4, $\gamma_r = \gamma_t = 10^{13}$ Hz, $\gamma_n = 0.1 \times 10^{12}$ Hz. In the case of curve 1 the CCF becomes a plateau as $t \rightarrow \infty$. In this limit the RT friction coefficient is set to be the same as the rotational and translational friction coefficients.

simulation, which could be used to investigate the technological applications of field-induced fluid dynamics, reviewed by Dahler.⁴⁰

V. ACF'S AT FIELD ON EQUILIBRIUM: GRIGOLINI'S FIELD DECOUPLING EFFECT

The numerical results reported in detail in this paper have *all* been produced self-consistently from a numerical solution of Hamilton's equations of motion for 108 interacting molecules. Their analytical understanding is aided by RMT developed by Grigolini and co-workers³⁻⁵ at Pisa. In this section and in Sec. VI we interpret some features of the computer simulation using some results of RMT, which approximates the Liouville equation rigorously using projection operators, and develops nonlinear (multiparticle) diffusion equations for molecular dynamics, e.g., generalized Kramers equations.⁴ Solutions for these equations have been obtained numerically by Grigolini *et al.* with continued-fraction expansions⁴¹ truncated for a given problem at a given approximant. FORTRAN listings are available for this purpose and have been documented as the "Pisa Algorithm."

One of the prime outcomes of RMT was the discovery by Grigolini¹⁰ of his field-decoupling effect. This was verified by Oxtoby *et al.*⁴²⁻⁴⁴ with Monte-Carlo simula-

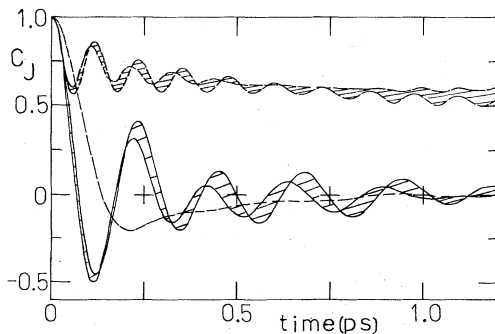


FIG. 12. Illustration of the Grigolini decoupling effect (Refs. 10 and 11) for the angular velocity ACF of the racemic mixture in the laboratory frame at field-off equilibrium (---) and field-on equilibrium (hatched curve): 50.0 kT field. Upper hatched curve is the second moment of the ACF—the ACF of the rotational kinetic energy. Hatching denotes noise.

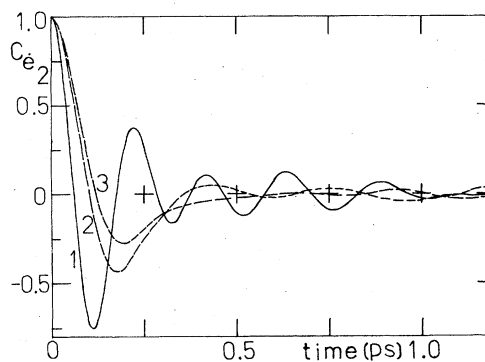


FIG. 13. Rotational velocity ACF $\langle \vec{e}_2(t) \cdot \vec{e}_2(0) \rangle / \langle e_2^2 \rangle$. Curve 1, racemic mixture, 50.0 kT field; curve 2, *S* enantiomer, 20.0 kT field; curve 3, *R* enantiomer, 2.0 kT field.

tion and by Evans *et al.*^{1,11} with molecular-dynamics simulation. As mentioned in the Introduction, it requires for its description non-Markovian statistics and self-consistency in approximating the basic equations of motion. The essential feature of the decoupling effect is illustrated in Fig. 12 for the angular velocity ACF of the racemic mixture at field-off and field-on equilibrium ($\mu E/kT = 50.0$). Measured through the envelope of its oscillations, the ACF becomes longer-lived as the field-strength increases. This is the effect of the external field which contends with the thermal motion via the torque $-\vec{\mu} \times \vec{E}$, i.e., decouples the dynamics of a given molecule from the influence of the thermal background. The standard Debye diffusion equation,⁸ used as the starting point in analyses^{6,7} such as that of Morita (Sec. III) does not produce the decoupling effect at all because of its Markovian structure. The same is true¹¹ of other purely phenomenological models that are basically Markovian in nature.¹² In this respect, field-induced decoupling resembles far-infrared spectroscopy⁴⁵ and spectral moment analysis⁴⁶ as tests for the analytical models which proliferate in the literature.⁴⁷⁻⁵¹

The Fourier transform of the far-infrared power absorption coefficient $\alpha(\bar{\nu})$ is a rotational velocity correlation function.¹⁹ This may be approximated in well-

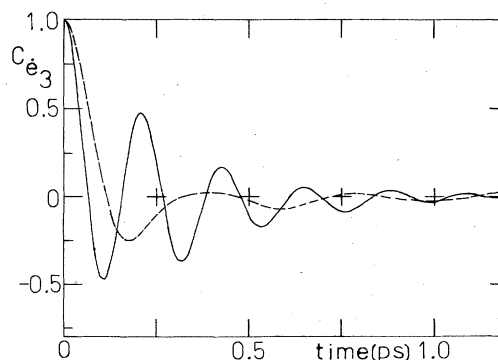


FIG. 14. Rotational velocity ACF $\langle \vec{e}_3(t) \cdot \vec{e}_3(0) \rangle / \langle e_3^2 \rangle$. —, racemic mixture, 50.0 kT field; ---, *S* enantiomer, 20.0 kT field.

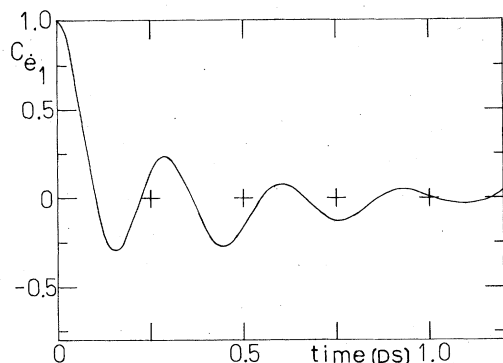


FIG. 15. Rotational velocity ACF $\langle \dot{\vec{e}}_1(t) \cdot \dot{\vec{e}}_1(0) \rangle / \langle \dot{\vec{e}}_1 \rangle$, racemic mixture, $50.0kT$ field.

defined limits²¹ by the ACF $\langle (\vec{\mu}(t) \cdot \vec{\mu}(0)) \rangle$, where $\vec{\mu}$ is the net molecular dipole moment. For fluorochloroacetonitrile $\vec{\mu}$ is a combination of the unit vectors \vec{e}_1 , \vec{e}_2 , and \vec{e}_3 of the principal moment of inertia frame (Table I). In Fig. 13 we illustrate the effect of increasing field strength on the ACF $\langle \dot{\vec{e}}_2(t) \cdot \dot{\vec{e}}_2(0) \rangle$ for *R* enantiomer, *S* enantiomer, and racemic mixture. The decoupling effect develops with increasing field strength. Similar features are observed for $\langle \dot{\vec{e}}_3(t) \cdot \dot{\vec{e}}_3(0) \rangle$ (Fig. 14) and $\langle \dot{\vec{e}}_1(t) \cdot \dot{\vec{e}}_1(0) \rangle$ (for $\mu E/kT=50.0$ in the racemic mixture, Fig. 15). Figures 13–15 imply that field decoupling is easily visible in the far infrared as a pronounced frequency blue-shift and sharpening of the broadband absorption in response to a powerful external force-field (e.g., a train of MW pulses from a Nd:YAG laser). Experimental verification of these simulations is necessary.

VI. FIELD-INDUCED FALL-TRANSIENT ACCELERATION

If the electric field is turned off instantaneously the sample adjusts from a state of high potential energy to one of thermal equilibrium (Table II). The temperature rescaling routine of the standard constant volume molecular-dynamics algorithm maintains the temperature of the sample within the input bounds (e.g., ± 25 K). There is no temperature effect of releasing the field because the sample is thermostated in this way. The kinetic energy at field-on and field-off equilibrium is the same (Table II). Orientational averages such as $\langle e_{2z}^2 \rangle$ decay to equilibrium as fall transients. The fluctuation-dissipation theorem of nonequilibrium statistical thermodynamics⁴⁷ implies that the normalized fall transient and the equilibrium, field-off orientational ACF are identical in time dependence for a given orientational vector. The great majority of analytical models^{45–51} produce this result, including the Debye diffusion equation⁸ for all field strengths \vec{E} .

This picture is, however, illusory, as the simulation results, summarized in Fig. 16, now show clearly. *The time dependence of the fall transient depends on the field strength applied in the field-on equilibrium state prior to*

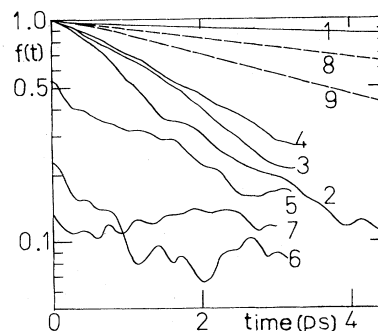


FIG. 16. Field-induced fall-transient acceleration. Dashed lines are theoretical fall transients from the Suzuki equation. Curve 1, field-off equilibrium orientational ACF $\langle \vec{e}_2(t) \cdot \vec{e}_2(0) \rangle$. Curve 2, $50.0kT$ field, orientational fall transient $\langle e_{2z}(t) \rangle$. Curve 3, as for 2, $20.0kT$ field; curve 4, as for 2, $10.0kT$ field; curve 5, as for 2, $2.0kT$ field; curve 6, as for 2, $1.0kT$ field; curve 7, as for 2, $0.5kT$ field; curves 8 and 9, increasing nonlinear friction coefficient γ' of Eq. (5.1).

releasing the field. For strong fields (e.g., $\mu E/kT=50.0$) there is a striking *acceleration* (Fig. 16) of the fall transient with respect to the field-off orientational ACF. Fall-transient acceleration persists with weaker applied fields. In the limit $\vec{E} \rightarrow \vec{0}$ fall transient and ACF become similar in time dependence from the computer simulation. (When $\vec{E} = \vec{0}$ there is, of course, no fall transient.) Fall-transient acceleration has been detected before, in a computer simulation^{1,4,5,11} of dichloromethane at 296 K, but the effect in Fig. 16, in the low-temperature state, is very much more pronounced.

Grigolini was the first to understand the significance of fall-transient acceleration to *field-off, equilibrium* molecular dynamics. This has been discussed briefly in the Introduction. With Marchesoni he has developed and solved numerically a cosinal itinerant oscillator model for its interpretation.^{4,5,11} The key property of this model is the nonlinear dependence of the potential energy of interaction between the diffusing particle and a representation of its immediate surroundings, termed by Grigolini the “virtual” particle. The virtual particle is also diffusing and is assumed to interact with the rest of the molecular ensemble (the thermal bath) with friction and stochastic terms as in the Langevin equation.²¹ The cosinal itinerant oscillator model is therefore a two-particle model. Its mathematical structure can be obtained by following the principles^{3–5} of RMT, i.e., by applying repeatedly to the basic equation of motion, e.g., the Liouville equation, suitable projection operators. The ACF’s of interest produced by this analytical model are non-Markovian.²¹ The nonlinear nature of the cosine function implies analytically that these ACF’s (such as that of the molecular angular velocity at field-off equilibrium) are also *non-Gaussian*.^{3–5} The latter property is by now well known from many different molecular-dynamics simulation runs.^{3–5} The most important property of this model is its ability to reproduce fall-transient acceleration in a qualitative but entirely self-consistent manner.¹¹ *It be-*

comes clear, therefore, that the root cause of transient acceleration is the nonlinear nature of the interaction between a diffusing molecule and its immediate surroundings, termed by Grigolini the virtual particle.

It is important to realize that the existence of fall-transient acceleration means that the traditional one-particle theory of molecular diffusion at field-off equilibrium is too limited. This is true even if we ignore, for the sake of argument, the new RT coupling effects of Sec. IV and fall back into the habit of using terms such as "rotational" or "translational" diffusion.

The Suzuki equation. Finally, in this paper, we use a simple nonlinear diffusion equation to reproduce qualitatively the simulation results of Fig. 16. This is the Suzuki equation:¹¹

$$\dot{\vec{\omega}} = -\gamma\vec{\omega} + \gamma'\langle\omega^2(t)\rangle\vec{\omega} + \vec{F}(t) \quad (6.1)$$

to which the cosinal itinerant oscillator reduces in the Markov ("long-time") limit. [Note that RT coupling is ignored in Eq. (6.1).] In the Suzuki equation $\vec{\omega}$ is the molecular angular velocity at field-off equilibrium, γ the friction coefficient, \vec{F} a stochastic angular acceleration term, $\langle\omega^2(t)\rangle$ the field-off equilibrium mean square angular velocity, and γ' a nonlinear friction term. In the limit $\gamma' \rightarrow 0$ the Suzuki equation reduces to the rotational Langevin equation²¹ for the isotropic diffusion in three dimensions of a spherical top with embedded dipole. Grigolini *et al.*^{4,5,11} have solved this equation for the fall transient $\langle\cos\theta(t)\rangle$. The field-acceleration effect is repro-

duced qualitatively as illustrated in Fig. 16. A quantitative description would involve, self-consistently, a description of RT coupling.

VII. CONCLUSIONS

Computer simulation of the molecular dynamics of chiral molecules is a means of describing in detail some fundamental new features of the molecular liquid state. Some, like the modification of properties brought about by mixing enantiomers, have been detected experimentally; others, like field-induced decoupling and fall-transient acceleration, have not yet been observed experimentally; still others, the manifestations of RT coupling, are fundamental features of liquid-state broadband³ and transient⁴ spectroscopy which have not been recognized as such in the literature. Future work is intended to describe the experimental measurement of field-induced transient acceleration and field decoupling with the use of powerful laser fields.

ACKNOWLEDGMENTS

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