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Molecular Dynamics Computer Simulation of the Rod-Like Molecule Methyl Hexa-tri-yne : Comparison with Doi/Edwards and Frenkel/Maguire Theories.

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Abstract

A large scale computer simulation of the rod like molecule methyl hexa-tri-yne has been carried out in the compressed gas and liquid states of matter. The intermolecular pair potential was constructed from a site model with 121 Lennard-Jones type interactions for each molecule pair, made up of a product of eleven atoms per molecule. The molecular dynamics for each number density were quantified in terms of various time auto and cross correlation functions, each element of which was computed by running time averaging over 6000 time steps of 5.0 fs each. This procedure allows the detailed investigation of translational, rotational and mixed dynamics for comparison with available analytical theories, such as those of Doi and Edwards and of Frenkel and Maguire. A large scale simulation such as this one, carried out with atom atom terms in the pair potential, reveals in detail the limitations of "hard rod" semi-empirical theories of elongated symmetric tops, such as methyl hexa-tri-yne. The "hard rod" theories are unlikely to be very accurate for liquid crystals or polymer liquid crystals on the evidence of this simulation, but are useful as approximations.

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Dedicated to Professor W.J. Orville-Thomas

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I. Introduction

There has been interest[1-6] in the last decade in analytical methods designed to mimick the diffusion of elongated molecules in liquids, liquid crystals and polymer liquid crystals. Several elegant theories are available in the literature and recently two of these, the Doi/Edwards[1,2] and Frenkel/Maguire theories,[3,4] have been compared with simulation[6] of an ensemble of hard rods. In this paper the ICAP1 supercomputer at I.B.M. Kingston is used to carry out a full scale simulation on 108 methyl hexa-tri-yne molecules over 6000 time steps of 5.0 fs each. This is an elongated symmetric top (Fig. (1)) with eleven atoms in a rigid rod-like configuration. It is weakly dipolar and to a good approximation the inter-molecular pair potential can be approximated with an 11x11 site site product of atom atom Lennard-Jones terms. Using standard constant volume simulation the rotational, translational, and mixed dynamics can be investigated in detail with time correlation functions developed in recent work[7-15].

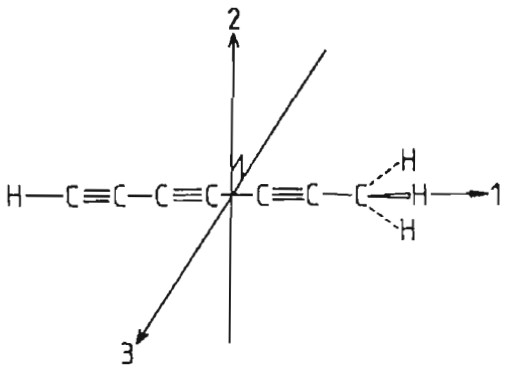


Figure 1 Schematic of the principal moment of inertia frame of methyl hexa-tri-yne.

Using these methods the simulation results can be compared with the analytical theory, usually based on the concept of hard rod diffusion, or Enskog theory applied to hard rods.

This is carried out in this paper using the available time correlation functions given in the theory, but the "real molecule" simulation also provides functions which are not available theoretically but which nevertheless provide considerable insight to the molecular dynamics. This is possible using two frames of reference, the laboratory frame (x,y,z) and the moving frame (1,2,3) of the principal molecular moments of inertia, defined in Fig. (1). For example, the results of this simulation reveal the time dependence of the lab frame cross correlation functions

$$C_1^{ij}(t) = \frac{< v(t).\mu(t) >}{(< v_i^2 >^{1/2} < \mu_j^2 >^{1/2})} \tag{1}$$

and

$$C_2^{ij}(t) = \frac{< v(t).\dot{\mu}(t) >}{(< v_i^2 >^{1/2} < \mu_j^2 >^{1/2})} \tag{2}$$

which the available theories do not consider. Here μ is the molecular dipole moment, $\dot{\mu}$ its time derivative, known as the rotational velocity, and v is the center of mass linear velocity of the same molecule. Further-

more this simulation reveals the presence in the moving frame (1,2,3) of intense cross correlation functions such as

$$C_3^{ij}(t) = \frac{< \mathbf{v}(t) \times \omega(t).\mathbf{v}(0) >}{< (\mathbf{v} \times \omega)_i^2 >^{1/2} < v_j^2 >^{1/2}} \tag{3}$$

and

$$C_4^{ij}(t) = \frac{< \mathbf{r}(t) \times \omega(t).\mathbf{r}(0) >}{< (\mathbf{r} \times \omega)_i^2 >^{1/2} < r_j^2 >^{1/2}} \tag{4}$$

where $\mathbf{v} \times \omega$ is the molecular Coriolis acceleration in frame (1,2,3), and r is the center of mass position defined in this frame. Neither the lab frame nor the moving frame cross correlation functions are available theoretically, but contribute fundamentally to spectral bandshapes generated by diffusing "rod like" molecules. It is reasonable to suggest that these cross correlations underpin the dynamics of liquid crystals and polymer liquid crystals, currently of interest in this field[16-18].

Computer Simulation Methods

The Doi/Edwards theory is primarily applicable to dilute ensembles of rod-like molecules, and for this reason a simulation was prepared at 296 K, molar volume = 150 cm^3/mole. It was observed that the total energy of the ensemble was positive, indicating that the positive translational and rotational kinetic energies outweighed the negative total potential energy summed over the 11x11 site-site interactions for the molecule pairs. This corresponds therefore to a compressed gas condition, whose mean pressure was computed to be 200 + 350 bar. This was calculated over 6,000 time steps of 5.0 fs each. In this condition no particular alignment of the molecules was observed, i.e. the sample was orientationally isotropic in frame (x,y,z).

Time correlation functions were computed in this state by running time averages using a program which eliminated data transfer from big disk to core. Correlation functions out to 8.0 ps from the time origin could be computed in a few minutes of elapsed ICAP1 time, using 3,000 configurations of 108 molecules each. This procedure was repeated for a range of auto and cross correlation functions, including those of the molecular linear velocity; angular momentum; angular velocity; orientation; rotational velocity; and cross correlation functions in frames (x,y,z) and (1,2,3).

Additionally, the special autocorrelation function

$$C_5^{ij}(t) = \frac{< \mathbf{v}(t).\mathbf{e}_1(0)\mathbf{v}(0)\mathbf{e}_1(0) >}{< (\mathbf{v}(0).\mathbf{e}_1(0))^2 >}$$

was computed for direct comparison with its equivalent from the Frenkel/Maguire theory of hard rod diffusion. Here $\mathbf{e}_1$ (0) is the initial orientation vector of each molecule in axis 1 of the dipole moment, the C_3 symmetry axis and therefore that of the "rod" (Fig. (1)). An analytical result for this a.c.f. has been given by Frenkel and Maguire and this was compared in this work with the simulation results on the "real" molecule methyl hexa-tri-yne.

A second state point was chosen at 50 K and with a molar volume of 130 cm^3/mole. This provided a computed mean pressure over 6,000 time steps of approximately 1 bar. In this condition the total energy was

negative, so that the ensemble had condensed into a liquid. Some alignment of the molecular ensemble was observed in this state through the simple average:

$$< e_{lz} > = 0.1 \pm 0.02 \tag{5}$$

In more elongated molecules and with much bigger molecular dynamics ensembles this may be indicative of the ordering characteristically observed in liquid crystals[19]. With a small sample however it is not meaningful to make the extrapolation because the "swarms" in a liquid crystal are thought to consist of upwards of one hundred thousand or a million molecules.

Time correlation functions were obtained in the liquid state of methyl hexa-tri-yne and compared with Doi/Edwards and Frenkel/Maguire theory on a qualitative level only. No quantitative comparison was attempted because the computer simulation results are clearly much more intricate in nature than the above simple theories.

Results and Discussion

In Fig. (2) are shown comparisons of the time correlation function

$$C_5^{ij}(t)$$

from the simulation at 296 K with the equivalent from Frenkel/Maguire theory for different choices of their parameter x in the theoretical expression

$$C_5(t) = (\cosh(xt))^{-1} \tag{6}$$

No further refinement was attempted because of the (expected) failure of the hard rod theory to produce the negative tail and superimposed oscillations of the simulation. This does not augur well for the hard rod theory in liquids and/or liquid crystals, despite its manifest mathematical elegance. The root cause of this failure is, furthermore, well known to protagonists of the memory function approach. A hierarchy of memory functions is required in general to mimick a computer simulation result or experimental data because of the inherently non-Markovian, non- linear, and non-Gaussian nature of the condensed molecular state of matter[20-22].

The Doi/Edwards theory is basically a "classical" rotational diffusion theory, based on the seminal Debye theory[23] of rotational diffusion modified for the special case of rod-like particles. It therefore has all the shortcomings of Debye's theory, which are by now well known and fully documented. The Doi/Edwards cannot therefore be used to describe the results of Fig. (2) or of Fig. (3), where are illustrated the linear center of mass velocity a.c.f.'s from the simulation in the lab frame (Fig. (3a)) and the moving frame (Fig. (3b)). The result in the fixed frame is deceptively simple, nearly exponential, but the more complex underlying diffusional dynamics are revealed clearly in the moving frame (1,2,3) of Fig. (3b). Similarly the angular velocity a.c.f., (Fig. (4)). For a hard rod theory of diffusion there can be no component of the angular velocity about the l axis, because the rod is assumed not to have inertia about this axis. Thus the Doi Edwards theory will not be able to account for the three components of Fig. (4b). Components such as these occur for most real molecules at all state points.

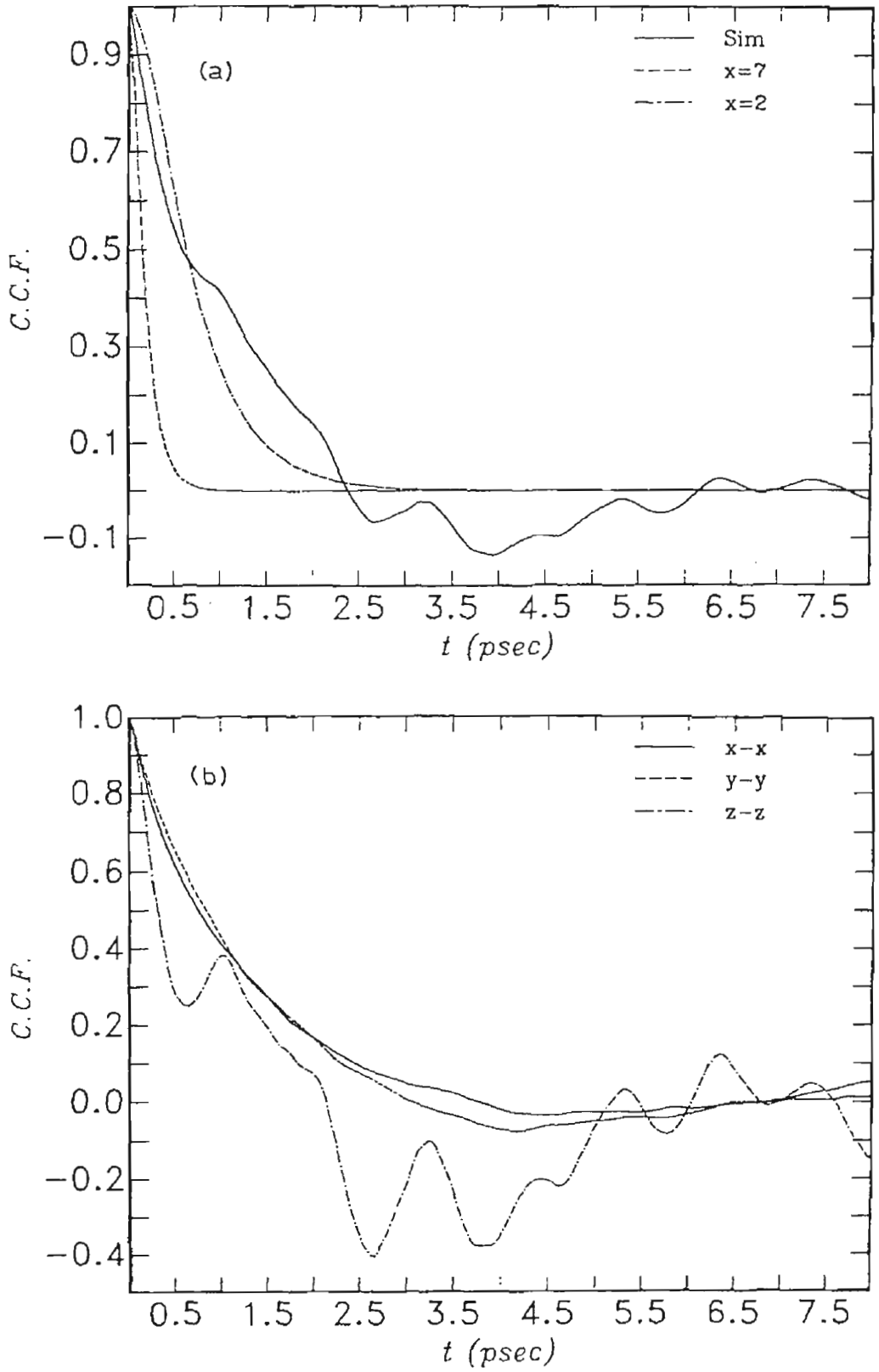


Figure 2 (a) Comparison of C_{ξ}^{ij} from the computer simulation with two results from the Frenkel Maguire theory of hard rod diffusion for different x (see text).Compressed Gas (b) Individual computer simulated elements in the lab. frame.Compressed gas

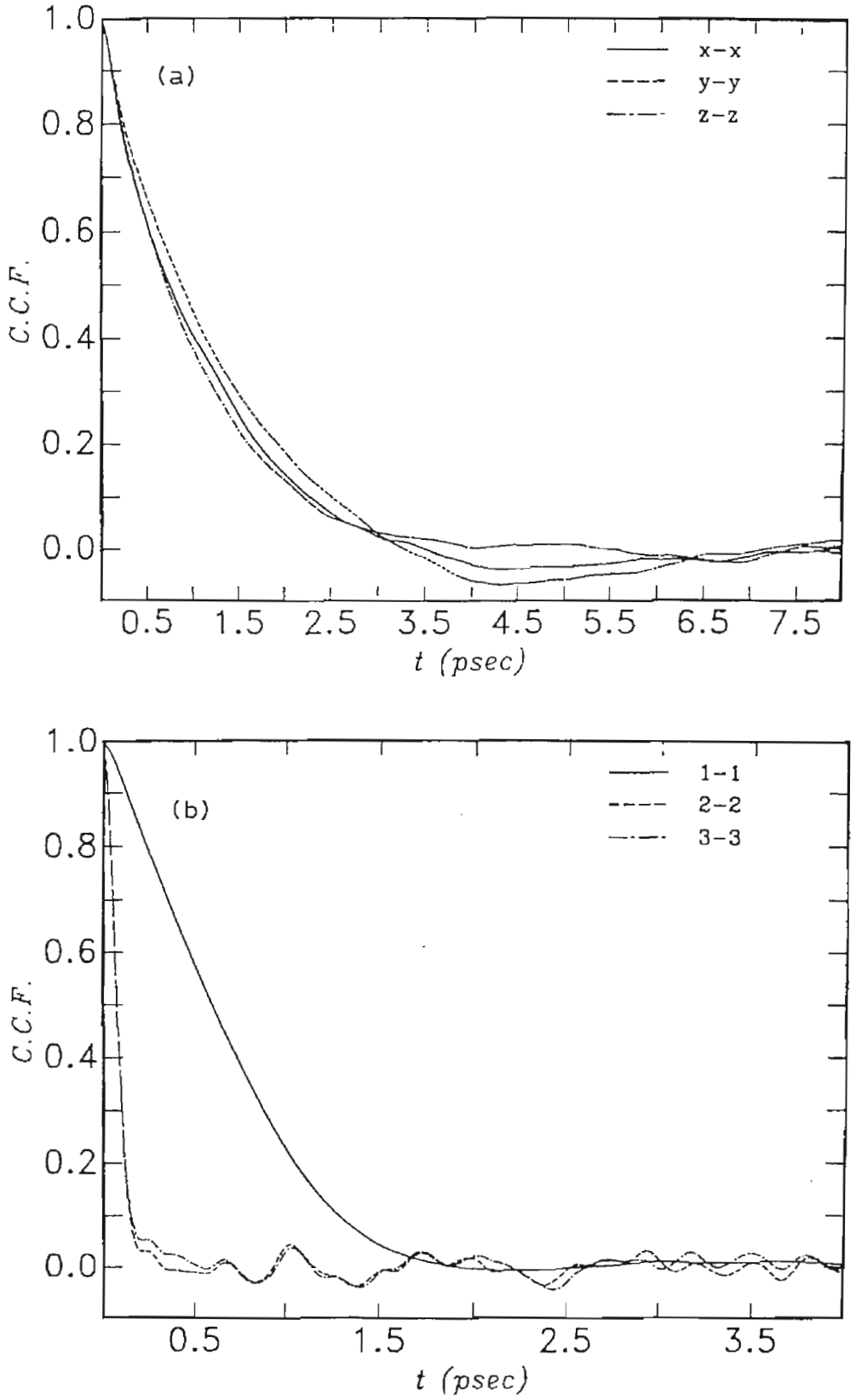


Figure 3 (a) Elements of the centre of mass velocity a.c.f., frame (x, y, z). (b) As for (a), frame (1, 2, 3).Compressed gas

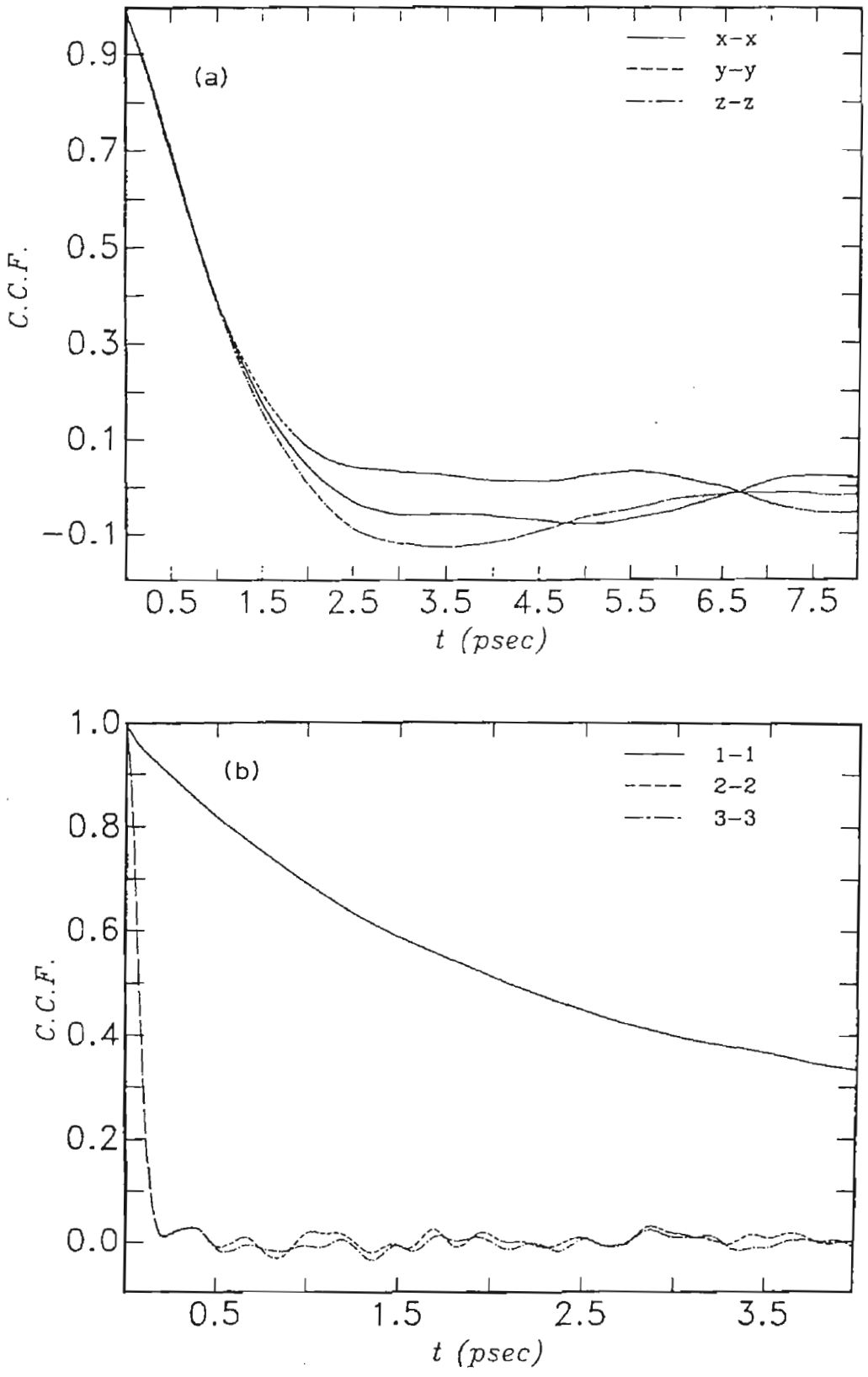


Figure 4 As for fig (3), molecular angular velocity.Compressed gas

The anisotropy of both the linear and angular molecular motion is therefore revealed in the moving frame (1,2,3).

A further, subtle, and often overlooked feature of anisotropic diffusion is the different time dependence of the angular velocity and angular momentum a.c.f.'s, and this is shown for clarity by comparison of Figs. (4a) and (5). This stems from the anisotropy of the molecular moment of inertia tensor in an elongated symmetric top such as methyl hexa-tri-yne.

The orientational a.c.f. of Fig. (6) is that of a vector in the dipole axis 1 of the molecule. It has a slight negative overshoot which is characteristic of the compressed gas state, and therefore of a low concentration of elongated rod like molecules for which the Doi/Edwards theory is appropriate. It may be possible to force fit the theory to the results of Fig. (6), taken in isolation of all the other correlation functions of the simulation, but this would be a meaningless procedure for reasons outlined already. Similarly for the rotational velocity a.c.f. of Fig. (7), i.e. the a.c.f. of the dipole moment derivative, roughly speaking the Fourier transform of the far infra-red power absorption coefficient. For a rotational diffusion theory the rotational velocity a.c.f. is, moreover, ill defined, and in classical Debye theory does not exist, and has no Fourier transform. A memory function hierarchy is required for the proper definition of a result such as that of Fig. (7).

The most severe and analytically intractable limitations of a translational (Frenkel/Maguire) or rotational (Doi/Edwards) theory is brought out, however, by time cross correlation functions.

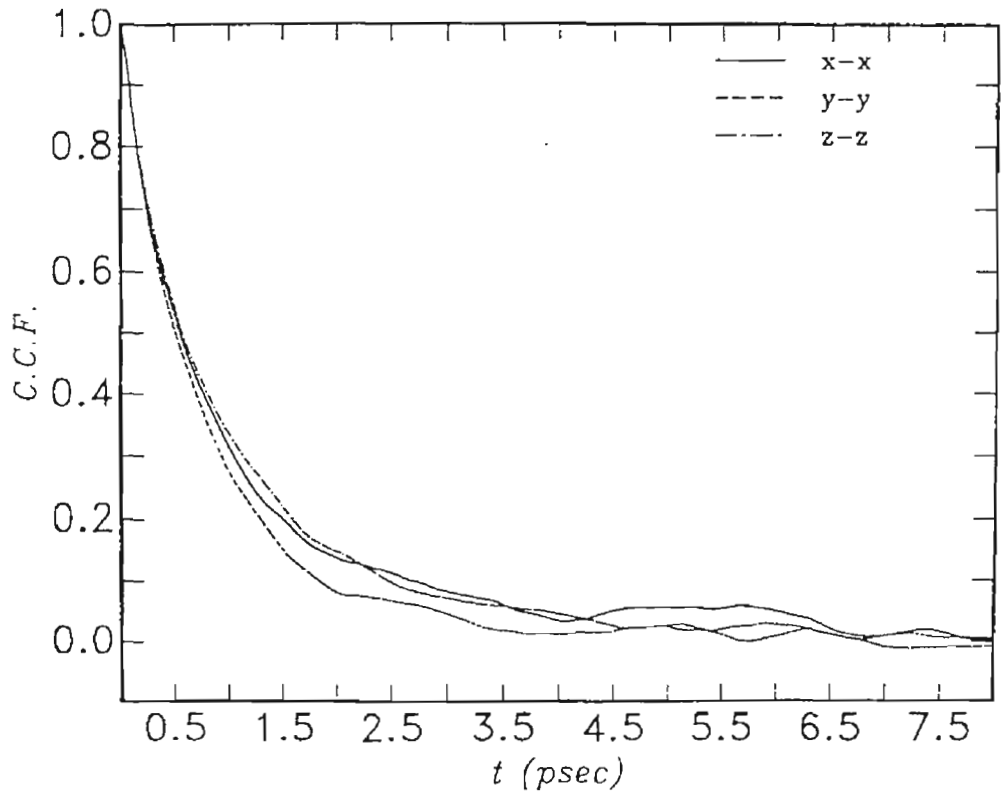


Figure 5 Molecular angular momentum a.c.f. in the lab. frame.Compressed gas.

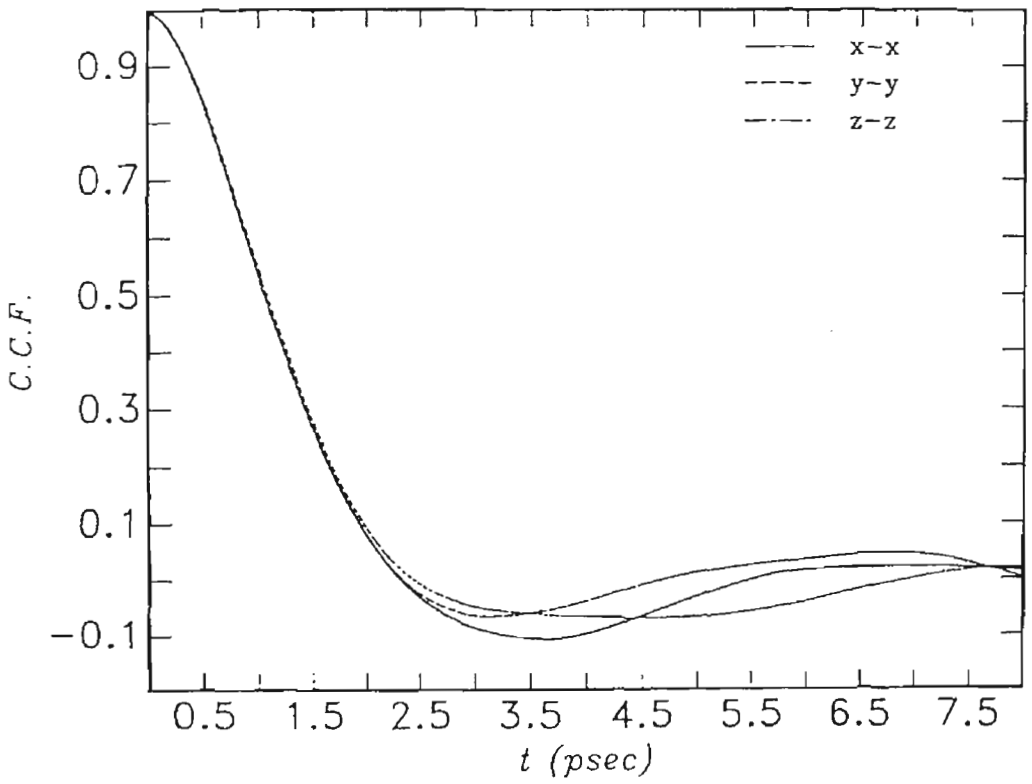


Figure 6 Orientational a.c.f. components, lab frame, compressed gas.

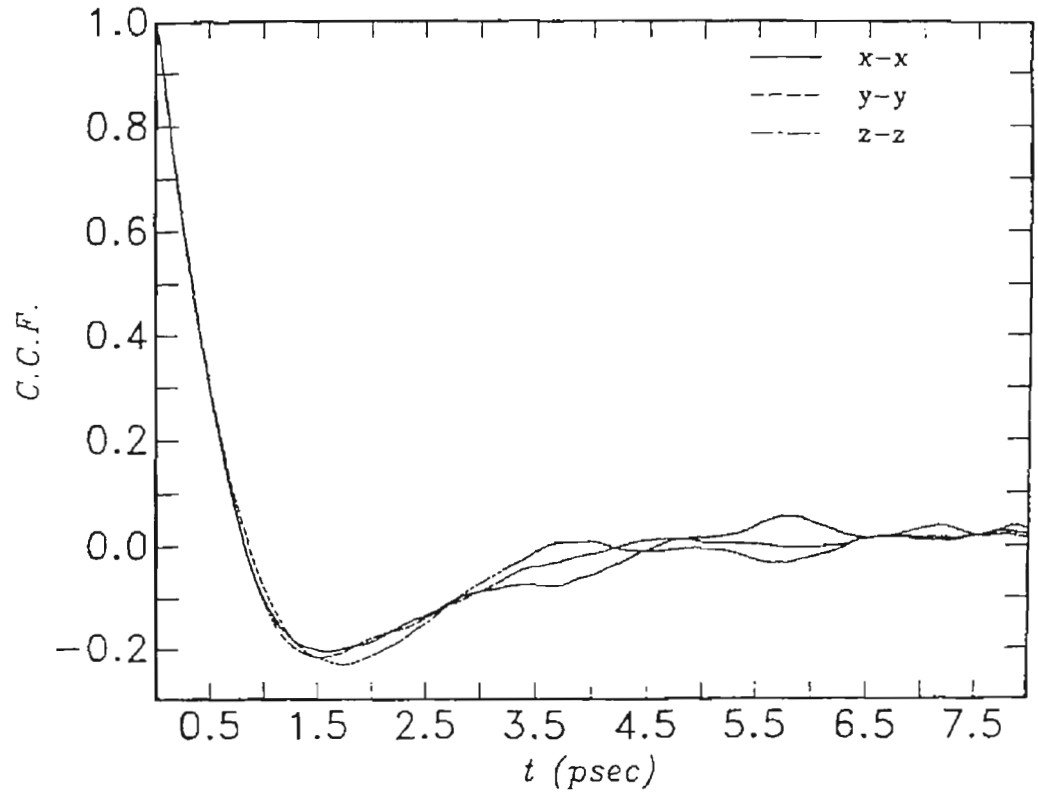


Figure 7 As for fig. (6), rotational velocity a.c.f.

Cross Correlation Functions from the Computer Simulation

In the laboratory frame of reference the velocity of an atom in the molecule is given by

$$v_a = v + 1/2\omega \times \mu$$

where v is the velocity of the center of mass,ω the molecular angular velocity and μ the axis vector from the atom to the center of mass. From this well known result the following relation appears direct in the lab. frame (x,y,z)

$$< v_a(t).v_a(0) > = < v(t).v(0) > + 1/2 < v(t).\dot{\mu}(0) > + 1/4 < \omega(t) \times \mu(t).\omega(0) \times \mu(0) > \quad (7)$$

It follows in turn that the cross correlation function

$$< v(t).\mu(0) > \quad (8)$$

is symmetry allowed in frame (x,y,z) and simultaneously measures both the rotational and translational diffusion of the molecule. Neither of the analytical hard rod theories cover this aspect of molecular diffusion, which is slowly being explored in the literature[7-15, 24]

The cross correlation function

$$< v(t).\dot{\mu}(0) > \quad (9)$$

between the molecular center of mass velocity and molecular rotational velocity also exists in the lab. frame, and no theory of far infra red absorption can be complete which cannot follow its time dependence in the lab. frame. Both types of cross correlation function (c.c.f.) have been simulated in this work and are illustrated in Figs. (8) and (9). These figures reveal that their intensity is substantial, even at compressed gas concentrations. The only other results available for comparison of these functions at present were also obtained in this laboratory, for liquid water[25] over a 250 kbar range of pressure and a thousand degree range of temperature. In normalized peak intensity the c.c.f.'s for methyl hexa-tri-yne in the compressed gas are comparable with those for water in the liquid. In the lab. frame the three elements of these c.c.f.'s are isotropic within the noise.

The analytical interpretation of these c.c.f.'s requires a radically new approach, and one such theory, based on linked Langevin equations, has been suggested elsewhere in the literature[25]. It is reasonable to expect the existence of such c.c.f's in liquid crystals, whose molecules are typically highly elongated and also fairly strongly dipolar. The theory of liquid crystal dynamics would therefore involve such c.c.f.'s from the outset. Naturally the same is true of polymer liquid crystals. Neither the Doi/Edwards nor Frenkel/Maguire theories are appropriate for this purpose.

In the moving frame of reference defined by the frame of the three principal molecular moments of inertia, (1,2,3), recent computer simulations have revealed the existence of cross correlation functions which are symmetry allowed in this frame but disappear in the lab. frame. The first and simplest to be discovered was[7-15, 26]

$$< v(t)\omega^T(0) > \quad (10)$$

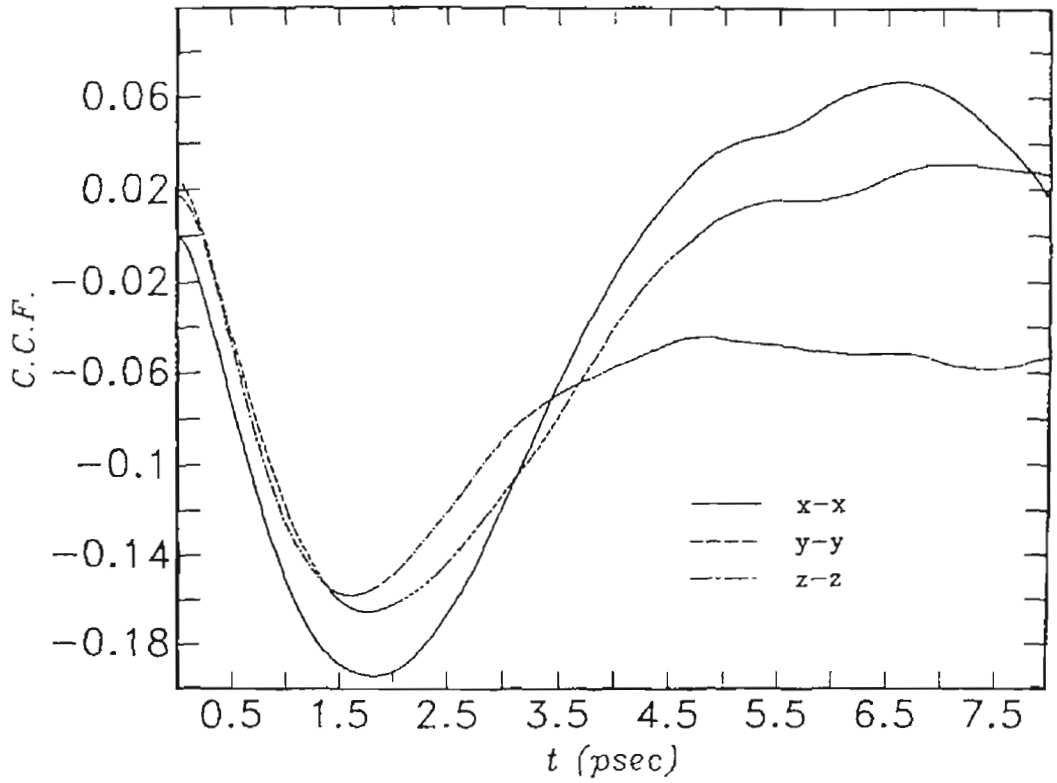


Figure 8 Velocity orientation c.c.f., C_{γ}^{ij}, lab. frame.Compressed gas.

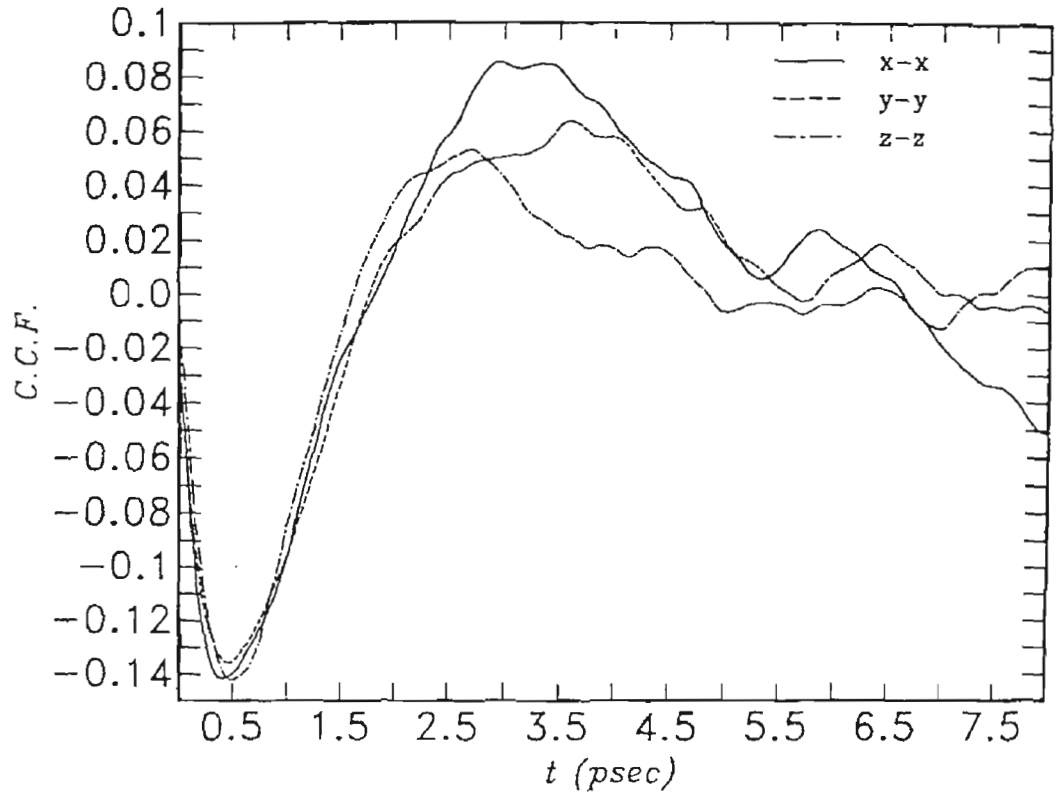
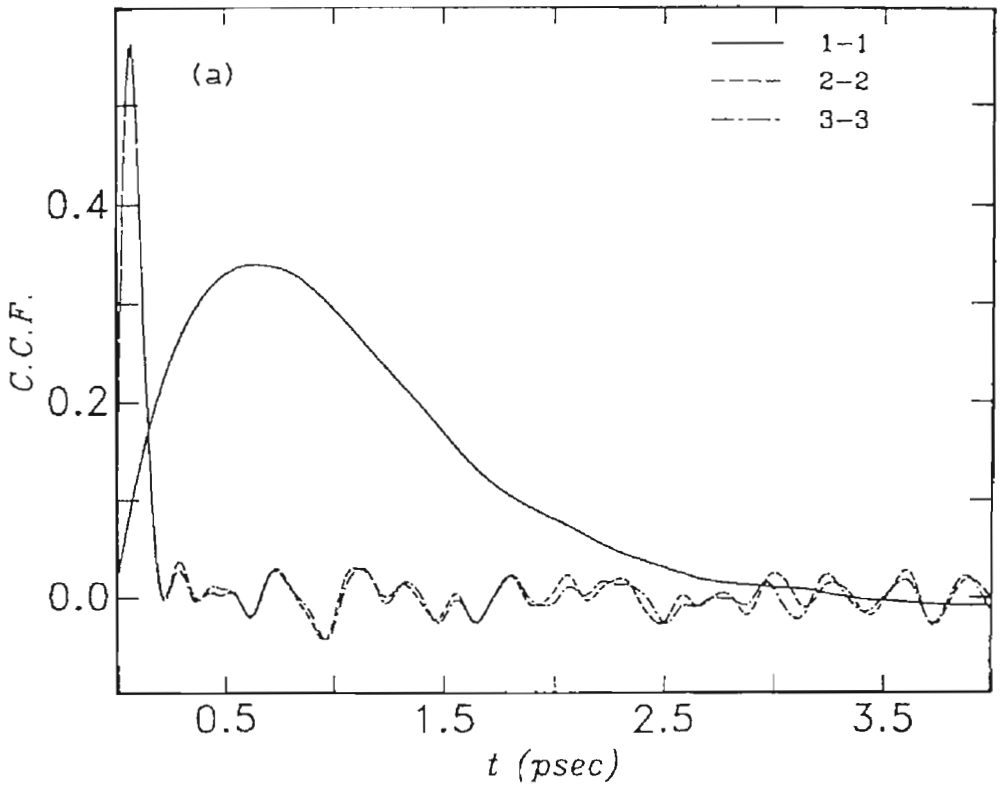
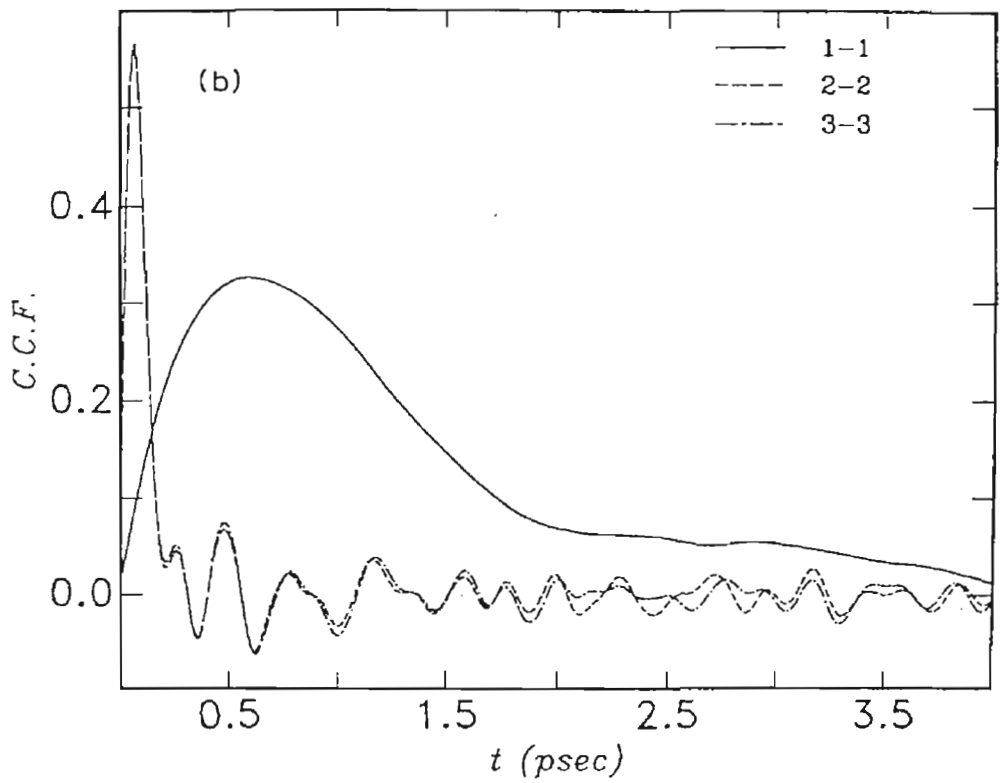


Figure 9 Velocity-rotational velocity c.c.f., C_{γ}^{ij}, lab frame, Compressed gas.


(a)
1-1
2-2
3-3
0.4
0.2
0.0
C.C.F.
0.5
1.5
2.5
3.5
t (psec)


(b)
1-1
2-2
3-3
0.4
0.2
0.0
C.C.F.
0.5
1.5
2.5
3.5
t (psec)

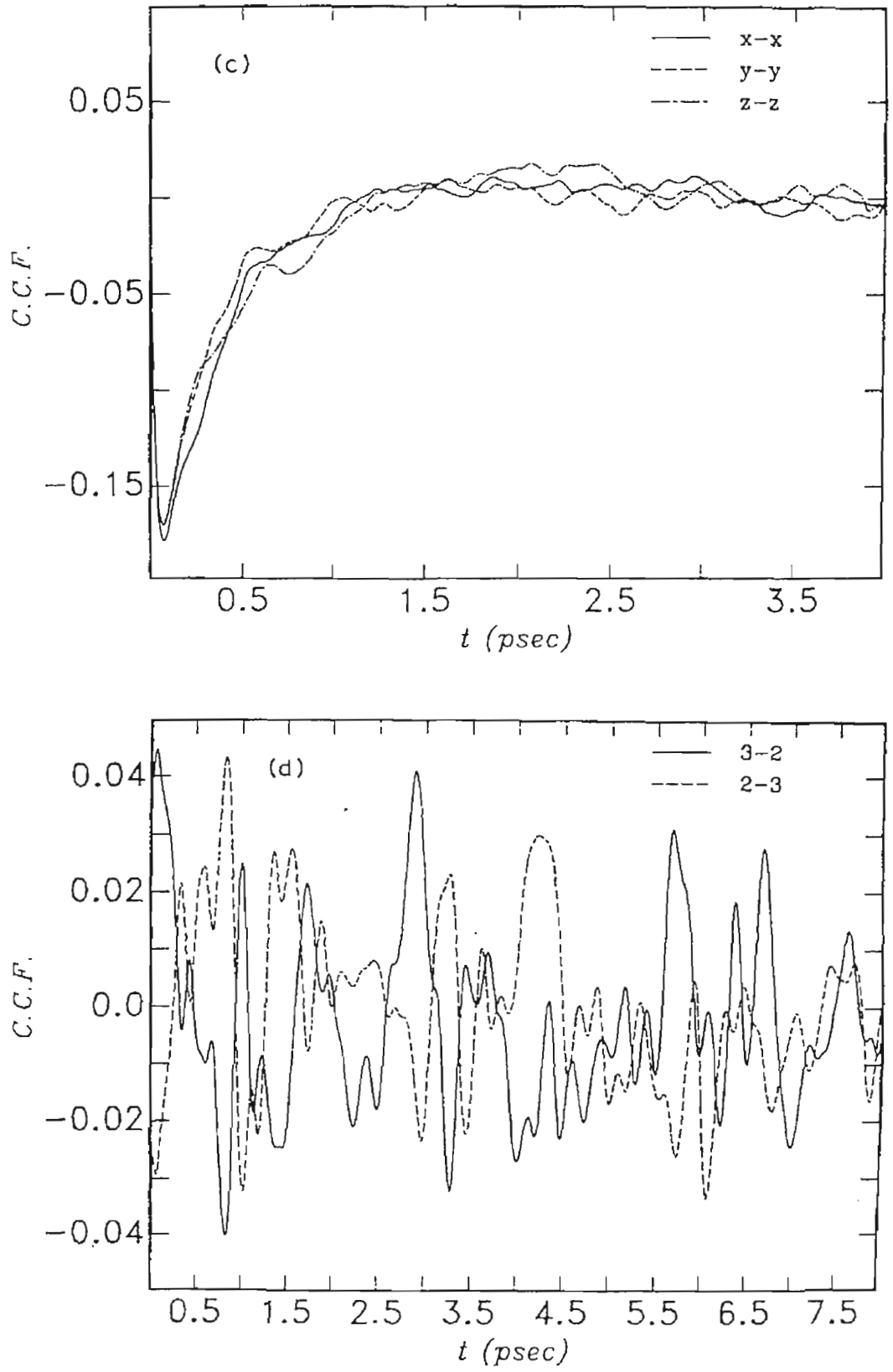


Figure 10 Higher order c.c.f.'s, compressed gas. (a) Components in frame (1, 2, 3) of C^{ij}_{ij} (b) Components in frame (1, 2, 3) of C^{ij}_{ij} (c) Components in frame (x, y, z) of Csub6supij (d) Components in frame (1, 2, 3) of C^{ij}_{ij}

by Ryckaert, Bellemans and Ciccotti[26]. Subsequently, many others have been brought to light by a combination of computer simulation and analytical (including group) theory. The set of non vanishing c.c.f.'s in frame (1,2,3) and also in frame (x,y,z) is of general interest for condensed molecular and possibly ionic matter, including useful semiconductors and epitaxials. In this context "condensed molecular" includes compressed gases, liquids, liquid crystals, polymer liquid crystals, polymers, rotator phases, supercooled liquids and glasses. It may be extended to include electrolyte solutions, single crystals and polymorphs, alloys, and so forth. In other words the time c.c.f.'s are fundamental properties of matter, and are therefore useful for and appear in situations of interest to the individual researcher.

A typical example is

$$C_3^{ij}(t) \tag{11}$$

in which is illustrated in frame (1,2,3) in Fig. (10a). Note the anisotropy of the time dependence in this frame, caused by the anisotropy of the molecule itself. It is reasonable to expect diffusion theories to attempt to envelope such a result, self consistently with those already described. This c.c.f. is described formally as that between the molecular Coriolis acceleration and its own center of mass linear velocity, v. It vanishes by fundamental symmetry in frame (x,y,z). The symmetry arguments are developed elsewhere.[11-15, 24] A new application of group theory, due to Whiffen, provides detailed rules with which to define the existence of c.c.f.'s such as that in Fig. (10(a)).

A similar looking c.c.f. is that of Fig. (10(b)), viz. :

$$C_4^{ij}(t)$$

where r is the center of mass position vector rotated into frame (1,2,3) as defined elsewhere. This is also allowed by group theory and is also highly anisotropic in its individual elements because of the molecular geometry and diffusional characteristics in the compressed gas.

The powerful and fundamental symmetry rules of chemical physics allow relatively few cross correlation functions to exist directly in frame (x,y,z). The components of the c.c.f.have to pass tests of parity, time reversal and reflection recently developed in terms of group theory by Whiffen. The two lab. frame c.c.f.'s already described obviously survive the symmetry tests, and another example is shown in Fig. (10c)

$$C_6^{ij}(t) = \frac{< v(t) \times \omega(t)(F(0) \times \omega(0))^T >}{< (v(0) \times \omega(0))_i^2 >^{1/2} < (F(0) \times \omega(0))_j^2 >^{1/2}} \tag{11}$$

where F is the net force on the molecule at time t. Existing lab. frame c.c.f.'s of this type have recently been catalogued systematically by Evans using a rotating frame theory of diffusion[7-15].

A complete analytical theory of rod like diffusion must account for all c.c.f.'s self consistently. This reveals starkly the limitations of the available theories such as the two considered in this paper. Such theories are elegant and useful in some circumstances, but in comparison with computer simulation are severely limited in what they can do. This is true of nearly all contemporary theories of diffusion, including those based on hierarchies of memory functions, probably the most sophisticated "state of the art" theories of molecular dynamics.

Finally for the compressed gas the simple c.c.f.

$$C_7^{ij}(t) = \frac{< v(t)\omega^T(0) >}{(< v_i^2 >^{1/2} < \omega_j^{1/2})}$$

exists in two of its off diagonal elements in frame (1,2,3). These are illustrated in Fig. (10d), and are the (3,2) and (2,3) elements. They are allowed by Whiffen's group theoretical rules and do not involve motion about axis 1. Fig. (10d) shows that they are small in intensity, barely rising above the noise, indicating that there is little direct cross correlation in frame (1,2,3) between v and ω. By symmetry there is no direct cross correlation in frame (x,y,z) of this type. This illustrates the care needed in establishing in rod-like molecules the precise nature of rotation / translation coupling. The latter reveals itself only through the right types of c.c.f., and the fact that one c.c.f.may be small is no indication of the absence of correlation.

Time Correlation Functions in the Liquid State.

Some orientational order was observed in the simulation of the liquid state at 50 K, 130 cm^3 / mole. The total energy was conserved to one part in 100,000, and pressure fluctuations were typically those of the liquid state, i.e. much greater than in the compressed gas for the same molecule. The thermodynamic condition could thus be described as that of an isotropic liquid, with no sign of mesophase behavior typified by long range order about a director axis in the lab frame. For direct comparison with the compressed gas results the same set of time correlation functions were computed in both frames of reference and are described here.

In Fig. (11) it is shown that the correlation function of $C_7^{ij}(t)$ from the simulation of the liquid methyl hexa-tri-yne is radically different in time dependence from the simple result of the Frenkel/Maguire theory. There is an initial rapid decay, followed by a change of slope at about 0.25 ps, with superimposed irregular oscillations. This is far more complex than anything envisaged in the Frenkel/Maguire theory. The simulated behavior is likely to be even more involved in the highly elongated and structurally more complex molecules making up liquid crystal and polymer liquid crystal mesophases.

In Fig. (12a) the time dependence of the center of mass velocity a.c.f. in the lab frame is similar in overall terms, i.e. there is a relatively rapid fall-off, followed by a slope change at about 0.3 ps into a much slower tail. In the moving frame, (1,2,3), the three components of the a.c.f. are anisotropic but less so than in the compressed gas.

The angular velocity a.c.f. in the lab frame and moving frames is illustrated in Fig. (13), and the angular momentum a.c.f. in the lab. frame in Fig. (14). From a comparison of Figs. (13a) and (14) it is clear that the change of slope is much more pronounced in the angular momentum a.c.f., and again occurs at about 0.25 ps. It is impossible to follow the variety of results in Figs. (13) and (14) with either the Doi/Edwards or Frenkel/Maguire theory, even in qualitative terms, across the phase transition from compressed gas to liquid.

The orientational a.c.f. components of Fig. (15), apart from the physically correct zero slope at the time origin, look like a combination of exponentials, indicating that the dielectric loss may have more than one component, as observed in anisotropic liquid crystal mesophases. This is a small step towards the goal of simulating a liquid crystal mesophase in terms of molecular dynamics with site/site potential terms.

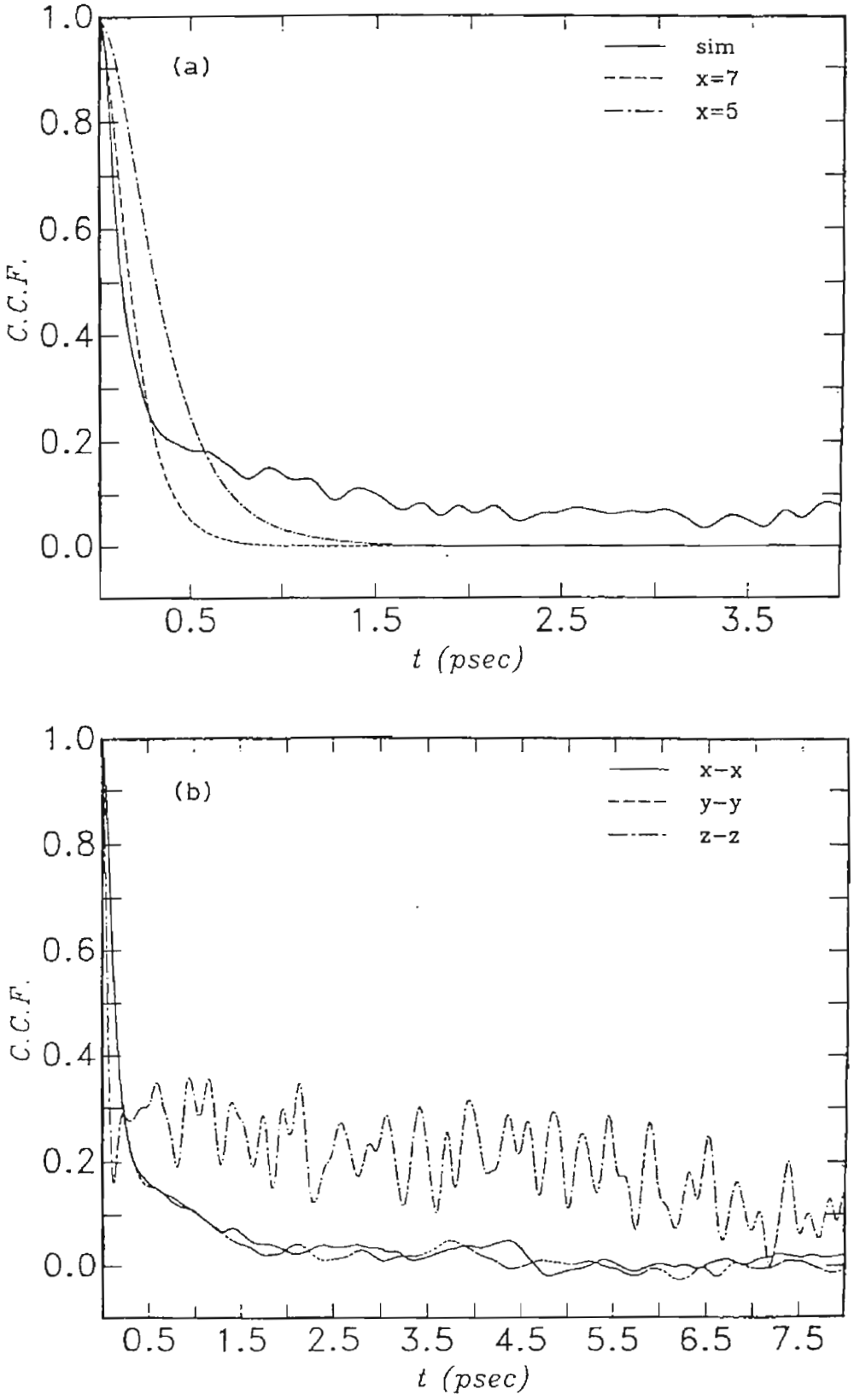


Figure 11 As for fig (2), liquid.

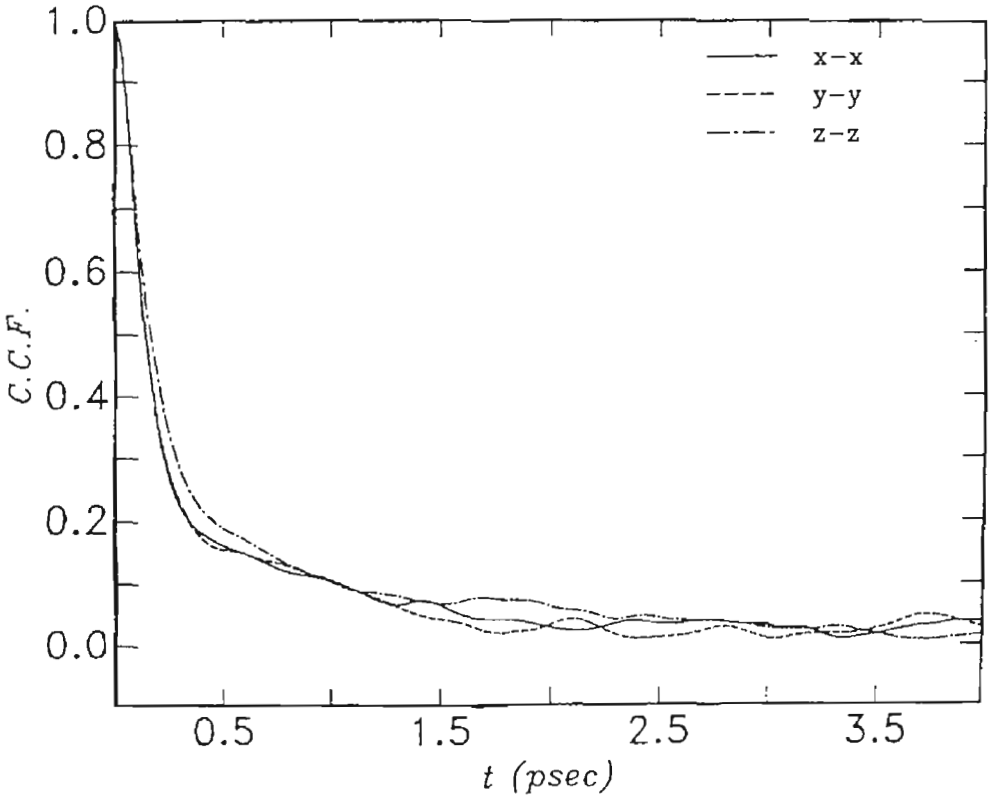


Figure 12 As for fig (3), liquid.

The rotational velocity components of Fig. (16) again show the change of slope at about 0.25 ps, followed by a long, slow tail. Unusually for such an a.c.f., this remains positive for all t. This may be interpreted through a rapid initial loss of correlation due to libration of the dipole axis at high frequencies, followed by a much slower relaxation process, the diffusion of the long axis. A hierarchy of memory functions is certainly needed to follow such a non Markovian process.

The character of the functions C_1^{ij} , (Fig. (16)), and C_2^{ij} , (Fig. (17)), is markedly different in the liquid from their equivalents in the compressed gas. The change of slope at 0.25 ps in the a.c.f.'s is echoed in the c.c.f. C_2^{ij} by a sharp negative peak at the same point followed by a long diffusive tail. This indicates that cross correlation of this type in the lab frame is a long lived process. In a liquid crystal made up of long molecules it is likely therefore that cross-correlation between the molecular center of mass linear velocity and the same molecule's orientation vector, μ, or rotational velocity, $\dot{\mu}$ will be persistent and characteristic of a mesophase. In other words the orientational diffusion is "locked in" to the translation of the molecule of a mesophase. This promotes long range order along the director axis. Orientational freedom is restricted and it requires little additional energy (e. g. a weak electric field), to align the director axis in one direction, thus making the sample birefringent. The role of cross-correlation functions in this process is fundamental and illuminating.

The correlation between molecular Coriolis acceleration and its own center of mass velocity is a faster overall process, and in this case Figs. (18(a)) and (18(b)) show that the moving frame correlations of this type have lost intensity compared to their counterparts in the compressed gas. The (1,1) component for example has lost

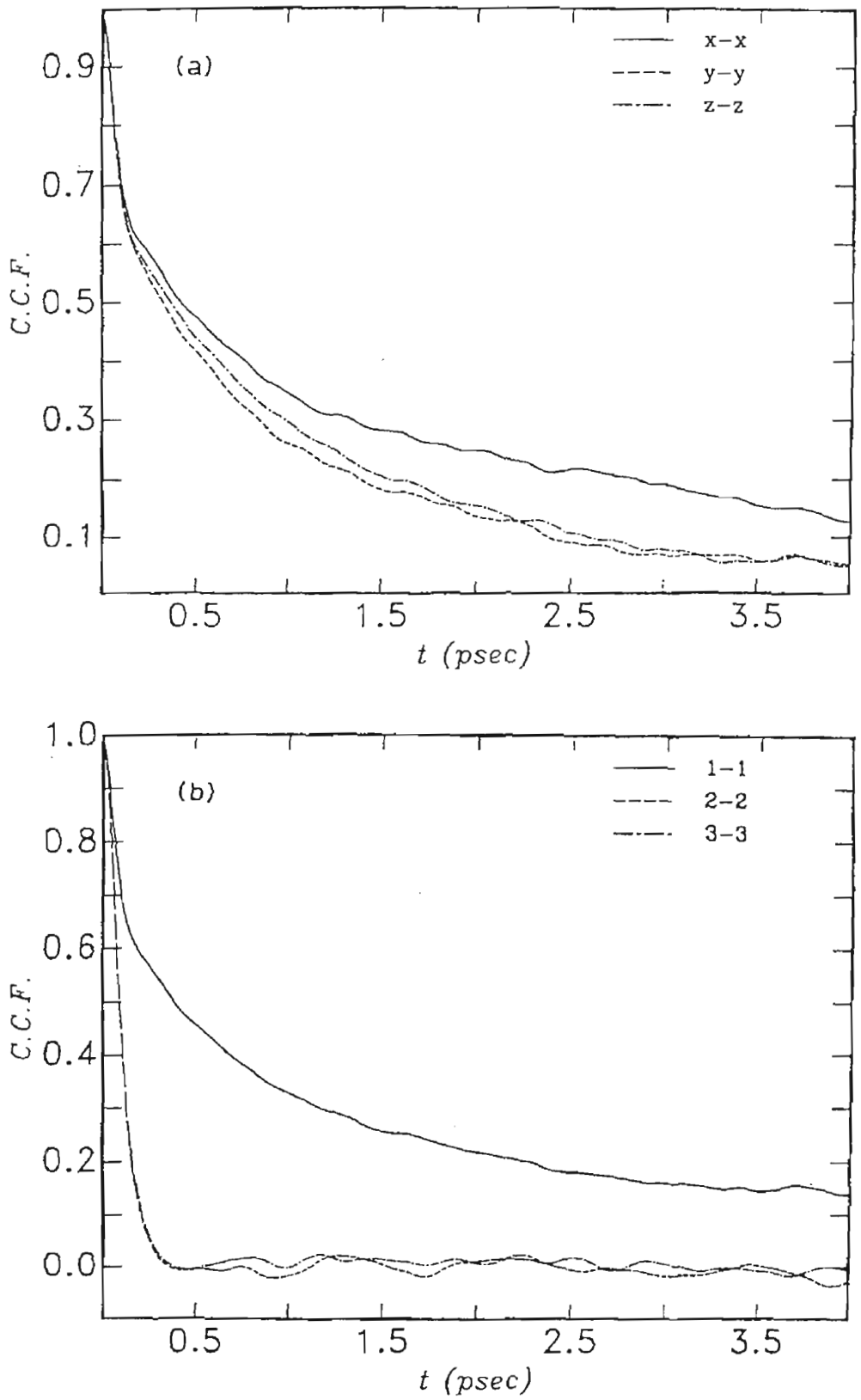


Figure 13 As for fig (4), liquid.

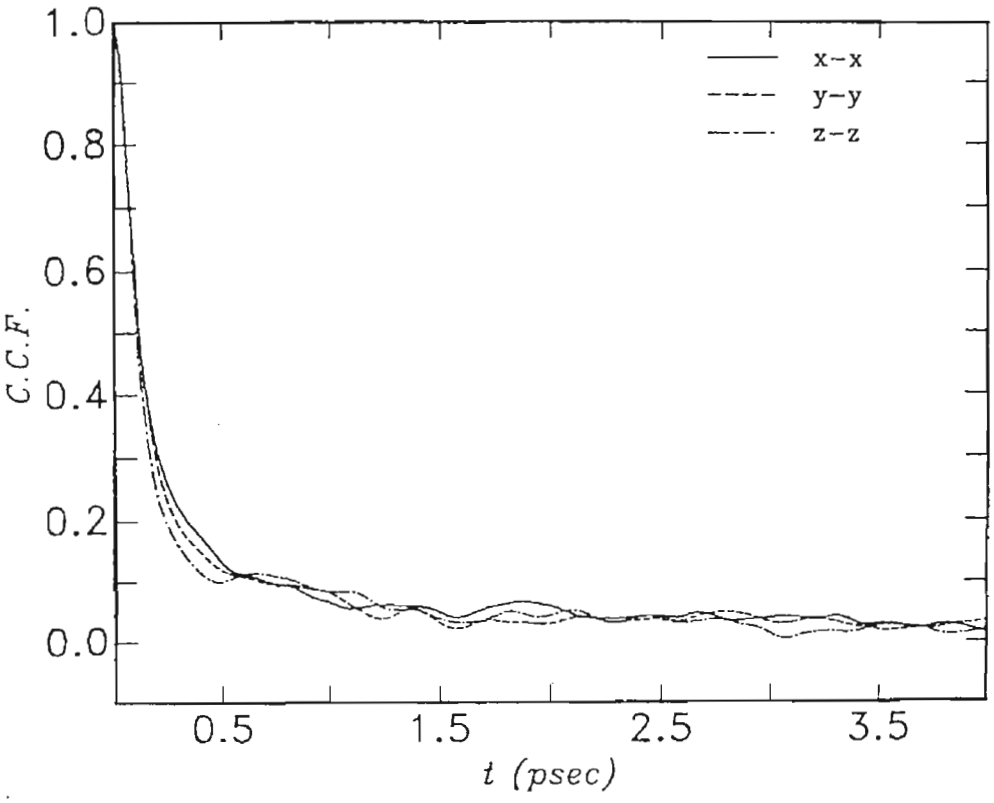


Figure 14 As for fig (5), liquid.

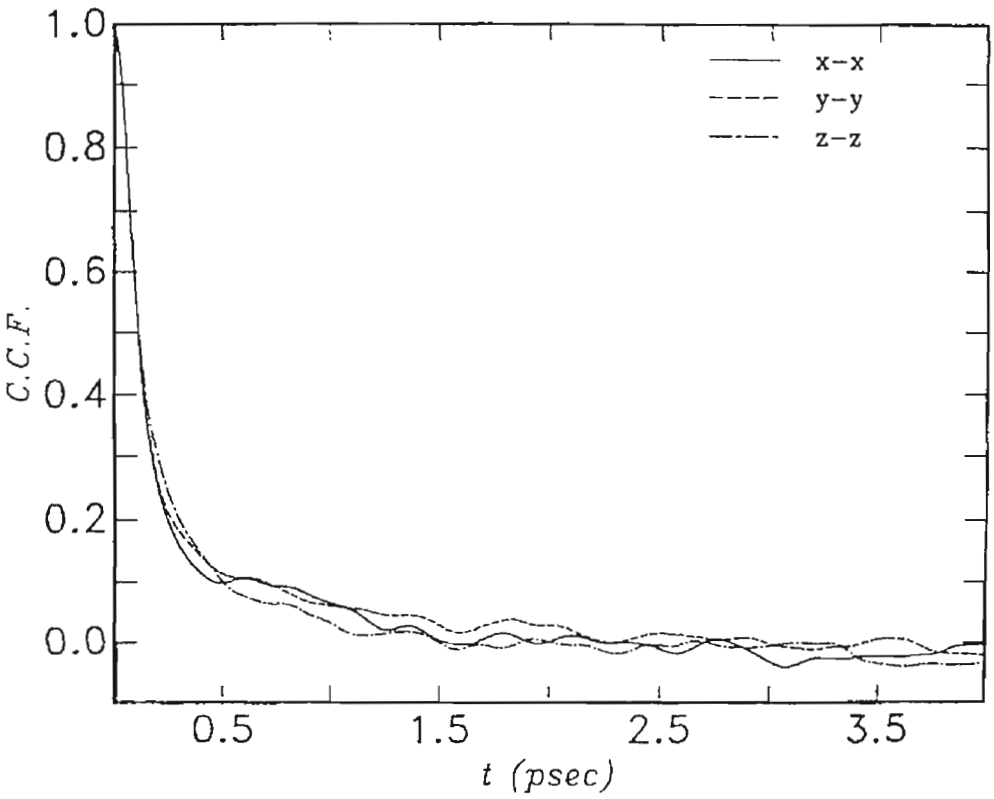


Figure 15 As for fig (6), liquid.

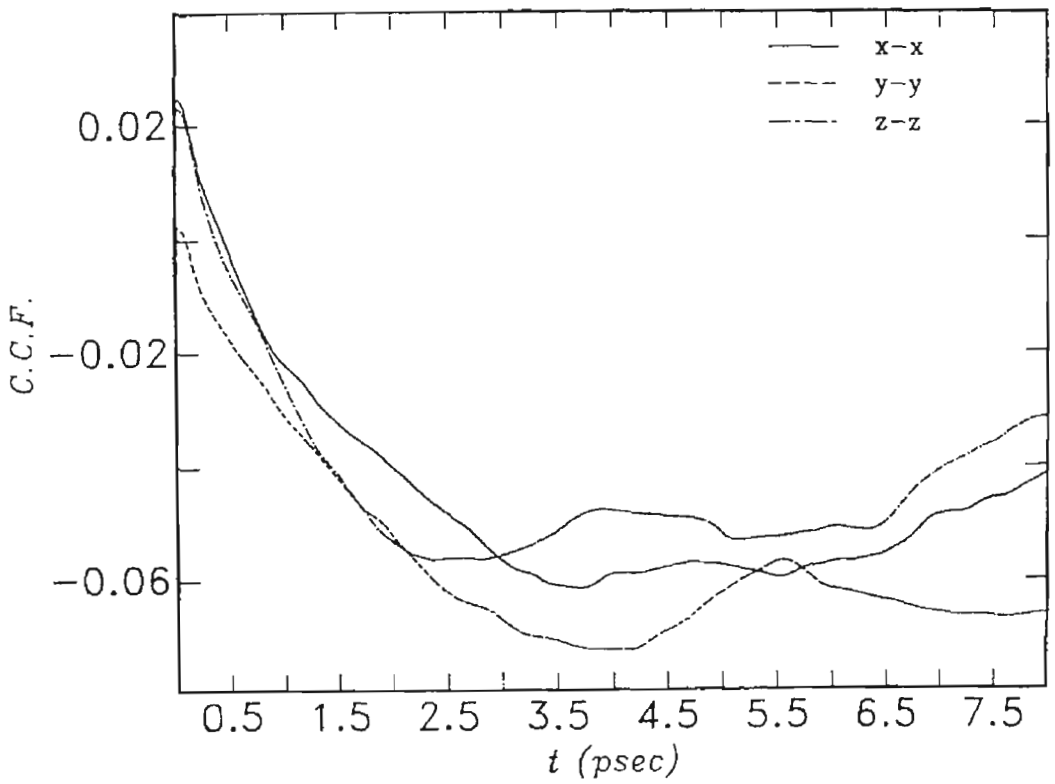


Figure 16. As for fig (8), liquid.

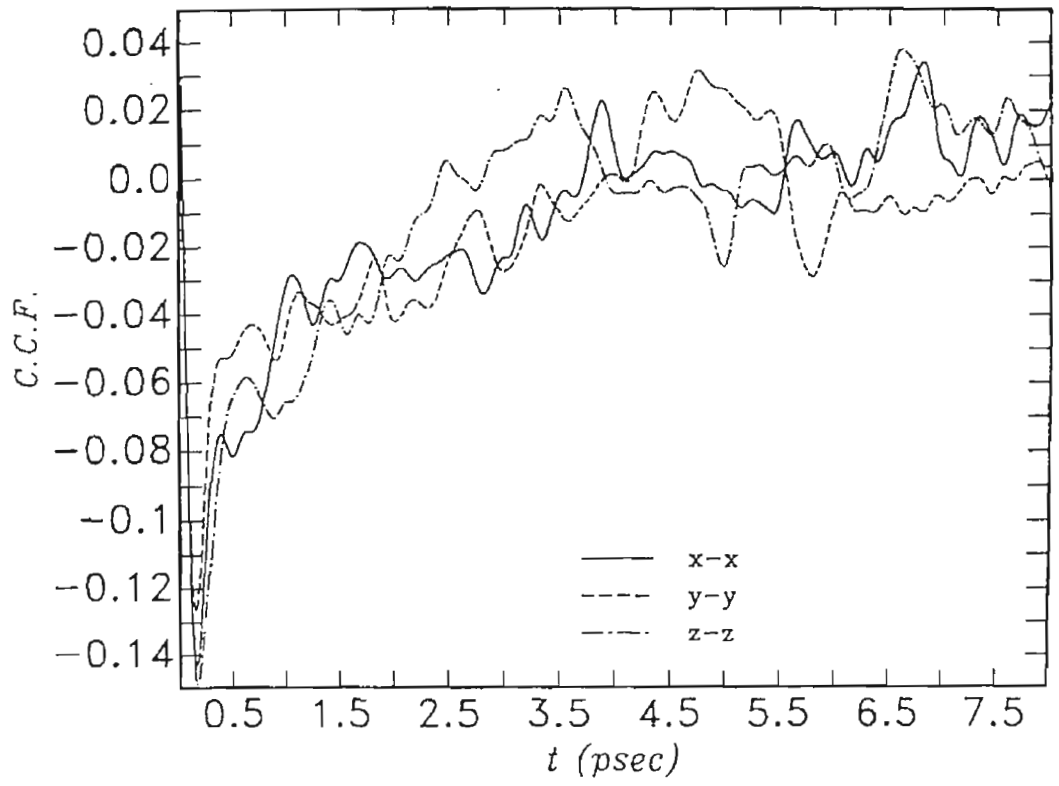
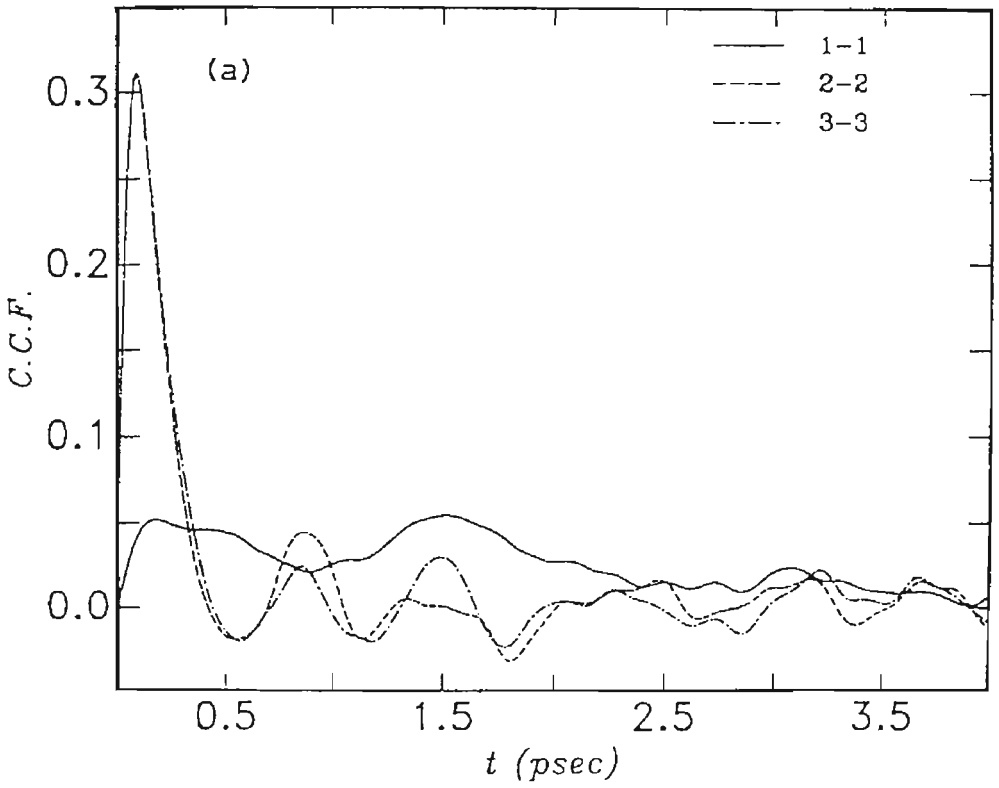
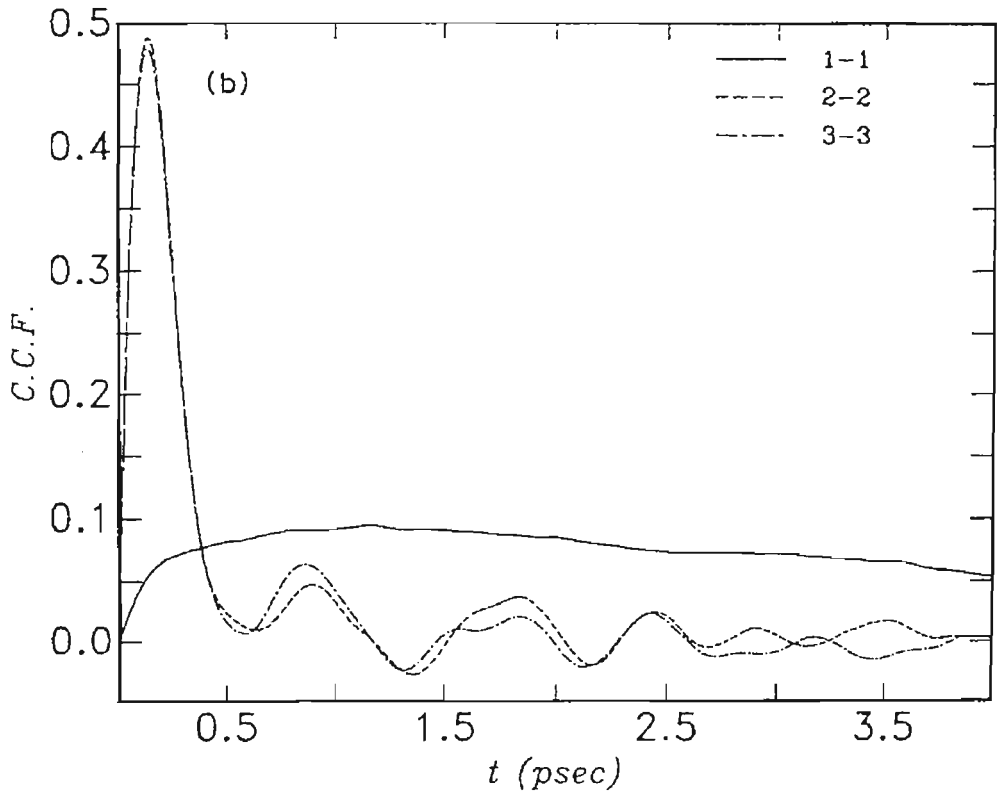


Figure 17. As for fig (9), liquid.


(a)
1-1
2-2
3-3
0.3
0.2
0.1
0.0
C.C.F.
0.5
1.5
2.5
3.5
t (psec)


(b)
1-1
2-2
3-3
0.5
0.4
0.3
0.2
0.1
0.0
C.C.F.
0.5
1.5
2.5
3.5
t (psec)

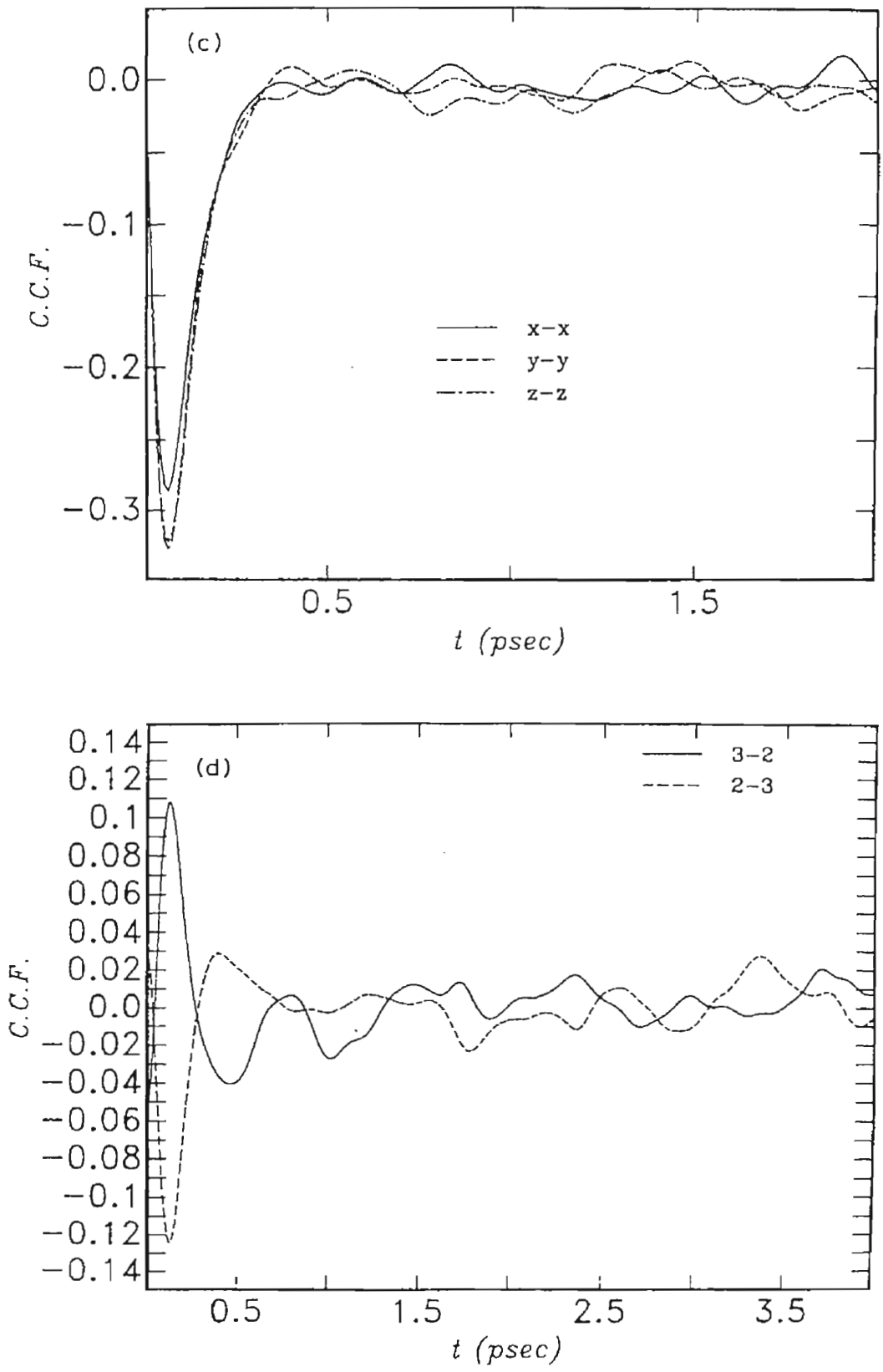


Figure 18. As for fig (10), liquid.

intensity due to the decreased effect of Coriolis acceleration on the molecule's own linear velocity. The lab frame c.c.f. of Fig. (10c) is again characterized by a peak at short times followed by a relatively long tail, but the intensity of the peak is this time greater in the lab. frame for the liquid than for the compressed gas. This is the opposite to the effect of the phase change on the moving frame c.c.f.'s of Figs. (10a) and (10b). In Fig. (10d) it is observed that the effect on the simple c.c.f. of the moving frame is to increase the peak intensity of the (2,3) and (3,2) elements from almost nothing in the compressed gas to about 0.1 in the liquid. The elements are mirror images by C_{3v} symmetry.

Conclusions

The simulation shows that the diffusion in the compressed gas and liquid of a long, rigid, molecule such as methyl hexa-tri-yne is an intricate process involving several types of fundamental time cross correlation, linked ineluctably. The power of the IBM Kingston ICAP1 supercomputer allows details to be resolved which are unaccounted for in contemporary theories of hard rod diffusion.

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