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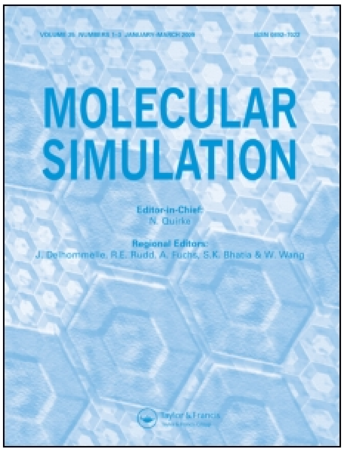

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Computer Simulation of the Structures and Cross Correlation Functions of Spherical-top Molecules in the Liquid State

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COMPUTER SIMULATION OF THE STRUCTURES AND CROSS CORRELATION FUNCTIONS OF SPHERICAL-TOP MOLECULES IN THE LIQUID STATE

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A detailed study has been made of the structural and dynamical properties of spherical-top molecules in their respective liquid phases at one bar above and below room temperature. The properties of $GeBr_4$, P_4, CBr_4 and SF_6 have been computer simulated. The structural and thermodynamical properties of each molecule have been obtained in terms of equilibrium site-site pair distribution functions and interpreted with the reference interaction site model (RISM). The single molecule dynamical properties are given by means of cross-mode correlation functions of various dynamical quantities in the laboratory and in a moving frame of reference defined by the principal molecular moments of inertia axes in each molecule. The presence of single molecule cross correlation is confirmed in this work for the spherical-top molecules. The strength of the coupling varies considerably from molecule to molecule, and reveals the sensitivity of roto-translational diffusion to details of the spherical top molecular geometry and pair interaction potential. This kind of single molecule behavior is probably at the root of cooperative phenomena observable by radiation diffraction in the rotator phases of these molecules. Simple analytical theories of molecular diffusion are unable to explain these results because of the presence of laboratory and moving frame rotation–translation coupling.

KEY WORDS: Spherical-top molecules, cross correlation functions, RISM, TETRA, liquids.

I. INTRODUCTION

Recent computer simulations [1, 2] of the molecular dynamics of carbon tetrachloride in the liquid state have revealed the presence in spherical-top diffusion of cross-mode coupling on the molecular level. This appears in the laboratory frame in the form of time cross correlation functions and also in a moving frame of reference defined by the axes of the principal molecular moments of inertia. The computer simulations produce cross correlation functions that obey the fundamental symmetry rules in both frames [3–6], i.e. they exist for $t > 0$ only when symmetry-allowed in either frame. In an isotropic liquid the relevant symmetry rules in the moving frame are governed by point group theory, and in the laboratory frame by time and parity reversal symmetry and by reflection symmetry. However, some cross correlation functions that are symmetry-allowed were actually found to vanish in the simulations, and this emphasizes the fact that symmetry rules, even in an isotropic medium, are necessary but not sufficient conditions for the existence of single molecule time cross correlation functions.

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In this paper the computer simulation of single molecule cross-mode coupling in the spherical-top is extended to the condensed liquid phases of germanium tetrabromide, phosphorus, carbon tetrabromide and sulphur hexafluoride. All four have been the subject of much detailed theoretical, computational and structural investigations [7–17] particularly of cooperative dynamical propagation and mode coupling in the rotator phase. X-ray and neutron diffraction have been used recently in a detailed study of the rotator phases of carbon tetrabromide [18]. These results were interpreted by Dove *et al.* in terms of a careful computer simulation of the collective motion [15–17], but their work was completed before the existence was established of cross-mode coupling in the spherical-tops on the more fundamental, single molecule, level. These spherical-top molecules are also accessible to reference interaction site model (RISM) theory of the equilibrium structure [19, 20], usually given in terms of site–site pair distribution functions. In this paper equilibrium pair distribution functions are obtained for all four molecules in the liquid phases and interpreted with RISM theory. The single molecule time cross correlations obtained in this work establish the nature of the molecular dynamics in both frames of reference. The computer simulations for each molecule are in accord with the symmetry rules mentioned already. The results confirm the pattern of cross-mode coupling found in the recent simulation of liquid carbon tetrachloride in both frames of reference for all four spherical tops [1]. In particular the simple cross correlation function

$$\langle \omega(t) \mathbf{v}^T(0) \rangle$$

vanishes for all t in both frames of reference in all cases. Here $\mathbf{v}$ is the molecular center of mass linear velocity vector and ω is the molecular angular velocity vector at a time t later for the same molecule. This result establishes the uniqueness of spherical top dynamics because for all other symmetries off-diagonal elements of this cross correlation function exist for $t > 0$ in the moving frame of reference. Given this, however, single molecule cross-mode coupling exists in spherical-top dynamics through the appearance in both moving and laboratory frames of symmetry-allowed higher-order cross correlation functions. It is the purpose of this paper to establish the pattern of behavior among four different spherical top molecular geometries in two frames of reference.

II. COMPUTER SIMULATION METHODS

The standard methods of constant volume computer simulation [21] were employed in the study of liquid phases of each of the four spherical-tops under consideration. The computer program package TETRA used is described in detail elsewhere [22]. The Newtonian equations for the translational and rotational motions for a system consisting of N molecules enclosed in a cubic box are solved by the Verlet method [23]. Periodic boundary conditions and minimum images with a spherical cutoff of half the box size are used in the evaluation of the interaction forces and energies. A time step of 0.005 ps was used, and trajectory data were collected for later analysis of structural and dynamical properties after discarding initial 5000 to 50 000 configurations (depending on the molecule under study; for example, it was extremely difficult to reach equillibrium with $GeBr_4$). Temperature rescaling was not activated during the production runs of up to 6000 time steps. The total energy was monitored during the productions and found to be satisfactorily constant with fluctuations of less than 0.1%.

For an input molar volume and temperature the algorithm computes the mean pressure and mean rotational and translational temperatures. The sample was considered to be in the liquid state when (i) all the three orientational averages of the unit vectors in the principal axes frame vanished and (ii) the absence of any significant order in the center of mass positions. The density and temperature of the liquid state were those for a liquid state for each sample under consideration.

It is important to make sure that the molecular dynamics ensemble is in the liquid state because the single molecule time auto and cross correlation functions used to characterize the dynamics in this paper are potentially useful as a means of investigating one of the most subtle of phase changes, that from the liquid to the rotator phase just below the freezing point at normal pressure. The symmetry pattern of cross correlation functions in the laboratory and moving frames of reference now provide sufficient scope for detailed comparison of dynamical properties above and below the freezing point.

a. *Germanium Tetrabromide*

The effective pair potential was a five-by-five site-site Lennard-Jones potential, with Lorentz-Berthelot combining rules applied to cross terms as usual. The Lennard-Jones parameters are:

$$\varepsilon/k(\mathrm{Ge\text{-}Ge}) = 64.0\,K; \qquad \sigma(\mathrm{Ge\text{-}Ge}) = 3.83\,\text{Å}$$

$$\varepsilon/k(Br\text{-}Br) = 218.0\,K; \qquad \sigma(Br\text{-}Br) = 3.90\,\text{Å}$$

with a Ge–Br bond length of 2.29 Å. At a literature liquid input molar volume of 129.6 cm^3/mole at 333 K [8], this potential provided the following thermodynamic averages over a segment of 2000 configurations of 108 molecules each: mean pressure, 2360 bar; mean translational temperature, 338.0 K; mean rotational temperature, 343.1 K; mean potential energy, −60.2 kJ/mole; mean total energy, −51.7 kJ/mole; virial, −84.490 kJ/mol. These values were obtained after melting from a face centered cubic lattice, a process that proved to be difficult for germanium tetrabromide, probably because of its close packing capability in the solid f.c.c. configuration and because of its mass. Frequent jamming of the configurations occurred, but eventually the lattice melted completely into the liquid state, as monitored by the orientational and translational averages coded for this purpose. After complete melting had occurred the pair distribution functions and time correlation functions were computed over segments of 2000 configurations each with no temperature rescaling.

b. *Liquid Phosphorus*

Phosphorus can be seen as a spherical top composed of four phosphorus atoms at the corners of a regular tetrahedron. The effective pair potential was thus constructed of a four-by-four Lennard-Jones atom–atom product with a single Lennard-Jones phosphorus parameters:

$$\varepsilon/k(P\text{-}P) = 119.8\,K; \qquad \sigma(P\text{-}P) = 3.41\,\text{Å}.$$

In contrast to germanium tetrabromide this melted very rapidly from an initial face centered cubic configuration into a liquid state at the literature input molar volume of 71.2 cm^3/mol at a temperature of 323 K [9–11]. Over an equilibrium segment of 2000 configurations for 108 molecules, the following thermodynamic averages were obtained with no temperature rescaling: mean pressure, 370 bar; mean translational temperature, 318.0 K; mean rotational temperature, 327.9 K; mean potential energy, −28.2 kJ/mole; mean total energy, −20.2 kJ/mole; virial, 40.05 kJ/mol.

As for germanium tetrabromide the pair distribution functions and time correlation functions were computed over an equilibrium configuration of 2000 time steps with no temperature rescaling. Note that the different types of spherical top geometry represented by these two molecules give very different thermodynamical behaviour in the liquid state. As we shall see this is also the case for the structural and dynamical properties.

c. *Carbon Tetrabromide*

This has been the subject of a recent detailed investigation in the rotator phase using over 4096 molecules [15–17]. The large sample used in this simulation was necessitated by the nature of the collective structural and dynamical correlations under investigation. A much smaller sample of 108 molecules is considered sufficient for single molecule cross-mode correlations. These are probably the root cause of the phenomena uncovered in the rotator phase in the work of Dove *et al.* [15–17] simply because collective cross-mode correlation and propagation of phonon modes in the rotator phase cannot occur without the single molecule elementary correlations discovered recently in the work of Evans *et al.* [1-4].

The pair potential was constructed from a five-by-five Lennard-Jones product using literature values for carbon and bromine Lennard-Jones parameters:

$$\varepsilon/k(Br\text{–}Br) = 218\,K; \qquad \sigma(Br\text{–}Br) = 3.90\,\text{Å}$$

$$\varepsilon/k(C\text{–}C) = 51.0\,K; \qquad \sigma(C\text{–}C) = 3.2\,\text{Å}$$

After melting from an initial face centered cubic lattice the following equilibrium average thermodynamical properties were obtained over 2000 configurations of 108 molecules: mean pressure, 3675 bar; mean translational temperature, 382.0 K; mean rotational temperature, 383 K; mean potential energy, −56.060 kJ/mol; mean total energy, −46.528 kJ/mol; virial, −114.446 kJ/mol. These were computed at an input temperature of 373 K and molar volume of 110.0 cm^3/mole taken from the literature for the liquid state of carbon tetrabromide [13, 14]. Time correlation functions and atom–atom pair distribution functions were computed over the same number of configurations and molecules.

d. *Sulphur Hexafluoride*

This is an O_h symmetry spherical-top and therefore slightly higher in point group type than the T_d symmetry examples cited already. This is known to have a profound effect on the nature of the rotator phases. The purpose of including SF_6 in the present investigation is to monitor the effect of increasing the spherical symmetry on cross-mode correlations on the single molecule level in the liquid state.

The effective pair potential was a seven-by-seven site–site interaction potential. These were made up of the sulphur and fluorine Lennard-Jones terms:

$$\varepsilon/k(S\text{–}S) = 190.0\,K; \qquad \sigma(S\text{–}S) = 3.80\,\text{Å}$$

$$\varepsilon/k(F\text{–}F) = 54.9\,K; \qquad \sigma(F\text{–}F) = 3.10\,\text{Å}$$

with Lorentz–Berthelot combining rules. After equilibration from a face centered cubic lattice the following equilibrium averages were obtained over a 2000 time step segment of 108 molecules: mean pressure, 78.8 bar; mean translational temperature, 258 K; mean rotational temperature, 285 K; mean potential energy, -6.45 kJ/mole; mean total energy, -0.323 kJ/mole; mean virial, 4.58 kJ/mol. These were computed from a literature input molar volume of 75.6 cm^3/mole at temperature of 222 K in the liquid state of sulphur hexafluoride [15–17].

III. RESULTS AND DISCUSSION

The molecular dynamics results are given in terms of time auto and cross correlation functions between various dynamical quantities, and the structural results in terms of atom–atom pair distribution functions. The existence of laboratory frame cross correlation functions in spherical-top molecules was first reported recently in liquid carbon tetrachloride, and in this paper we confirm these results in four more spherical-top molecules. The time dependence and normalized amplitude of these cross correlation functions are seen to vary according to the structure and mass distribution in the molecule, and they thus depend on the point group symmetry. In this paper, the point group symmetry of sulphur hexafluoride is $\mathbf{O}_\mathrm{h}$ and that of the other three molecules is $\mathbf{T}_\mathrm{d}$.

a. *Germanium Tetrabromide Dynamics*

The molecular dynamics of liquid germanium tetrabromide are analyzed in this section in terms of auto and cross correlation functions of time, both in the laboratory frame of reference and in the moving frame defined by the three principal molecular moments of inertia of the molecule. If a dynamical quantity A is defined with respect to x, y, and z in the laboratory frame, then it can be transformed into the moving frame (1, 2, 3) by the frame transformation relations:

$$\begin{aligned} A_1 &= A_x e_{1x} + A_y e_{1y} + A_z e_{1z} \\ A_2 &= A_x e_{2x} + A_y e_{2y} + A_z e_{2z} \\ A_3 &= A_x e_{3x} + A_z e_{3y} + A_z e_{3z} \end{aligned}$$

For the spherical top the normalized auto correlation function in both frames has the same time dependence for any vector quantity **A**. However, for time cross correlation functions of the general type

$$\langle \mathbf{A}(t)\mathbf{B}^T(0)\rangle$$

this is no longer true. Such cross correlation functions may exist in the moving frame (1, 2, 3) and vanish in the laboratory frame (x, y, z) and vice versa. Of particular interest in the context of spherical top diffusion are cross correlations between dynamical quantities involving translational velocity **v** and molecular angular velocity

ω, and between net center of mass force **F** and net torque $\mathbf{T}_q$. These establish that diffusion in the spherical top molecule is neither exclusively rotational nor translational. The two fundamental modes of motion are linked ineluctably. This should always be borne in mind when using the Debye theory of rotational diffusion, which, despite its manifest elegance, is incomplete.

The computer simulation results show that linear and angular motions are statistically interdependent through cross correlation functions both in the laboratory and in moving frames of reference. They are not decoupled, as assumed in the overwhelming majority of papers on diffusional motion for the spherical-top. The clue to their inter-dependence is given by the existence in the laboratory frame of the so-called "pseudo" accelerations, for example the centripetal acceleration [1–3] and the Coriolis acceleration. These are molecular accelerations that involve simultaneously the position, **r**, the center of mass linear velocity, **v**, and the molecular angular velocity, ω. Their existence for the spherical-top implies the need to extend the available theories of molecular diffusion. The symmetry constraints on the existence of cross correlation functions allow a finite time dependence for certain patterns as described elsewhere [1–3]. Figure 1a illustrates the three diagonal elements of the cross correlation function in the moving frame

$$\mathbf{C}_1^{ij}(t) = \frac{\langle[\mathbf{v}(t) \times \omega(0)]_i \mathbf{v}_j(t)\rangle}{\langle[\mathbf{v}(0) \times \omega(0)]_i^2\rangle^{1/2}\langle \mathbf{v}_j^2(0)\rangle^{1/2}}$$

which is seen to exist above the noise level as a positive peak near the origin. Group theory [1] in frame (1, 2, 3) shows that each peak in the $\mathrm{T_d}$ symmetry spherical-top should be equal in amplitude. The residual differences in Figure 1a are due to noise. Similarly Figures 1b and 1c illustrate the diagonal elements of the cross corrlelation functions.

$$\mathbf{C}_2^{ij}(t) = \frac{\langle[\mathbf{r}(t) \times \omega(t) \times \omega(t)]_i[\mathbf{r}(0) \times \omega(0)]_j\rangle}{\langle[\mathbf{r}(0) \times \omega(0) \times \omega(0)]_i^2\rangle^{1/2}\langle[\mathbf{r}(0) \times \omega(0)]_j^2\rangle^{1/2}}$$

and

$$\mathbf{C}_3^{ij}(t) = \frac{\langle[\mathbf{r}(t) \times \omega(t)]_i \mathbf{r}_j(0)\rangle}{\langle[\mathbf{r}(0) \times \omega(0)]_i^2\rangle^{1/2}\langle \mathbf{r}_j^2(0)\rangle^{1/2}}$$

in the moving frame (1, 2, 3). Here the center of mass position vector **r** is defined in frame (1, 2, 3) through the transformation relations. In these figures the first peak is positive and exists above the background noise level. Figures 1a–1c provide clear evidence for the interrelation of modes of motion in the diffusing spherical-top on the fundamental level. They are examples of the general class of single molecule cross-mode correlations. Their existence poses a problem for the analytical theory of molecular diffusion, but they can be determined "experimentally" by simulation.

Recent work has revealed the existence of a theoretically infinite number of laboratory frame cross-mode correlations involving the set of non-inertial accelerations and time derivatives thereof. Some members of the set are forbidden by parity reversal and reflection symmetry, and by "hidden" symmetries analogous to those in quantum mechanical wave functions. However, some members of the set survive these symmetry constraints and are present for the spherical-top directly in frame (x, y, z). Two of these are illustrated for liquid $\mathrm{GeBr_4}$ in Figures 2a and 2b, and are

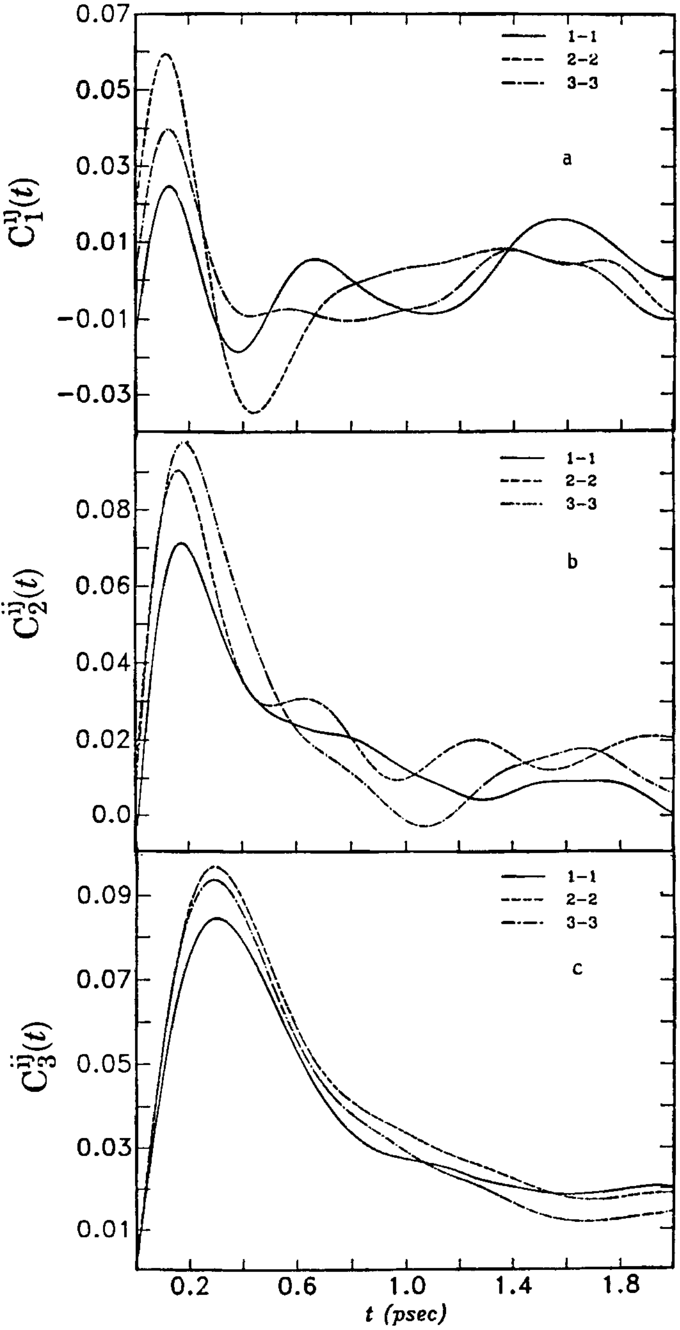

Figure 1 (a) (1,1), (2,2) and (3,3) elements of $C_1(t)$; (b) (1,1) (2,2) and (3,3) elements of $C_2(t)$; (c) (1,1), (2,2) and (3,3) elements of $C_3(t)$ for $GeBr_4$.

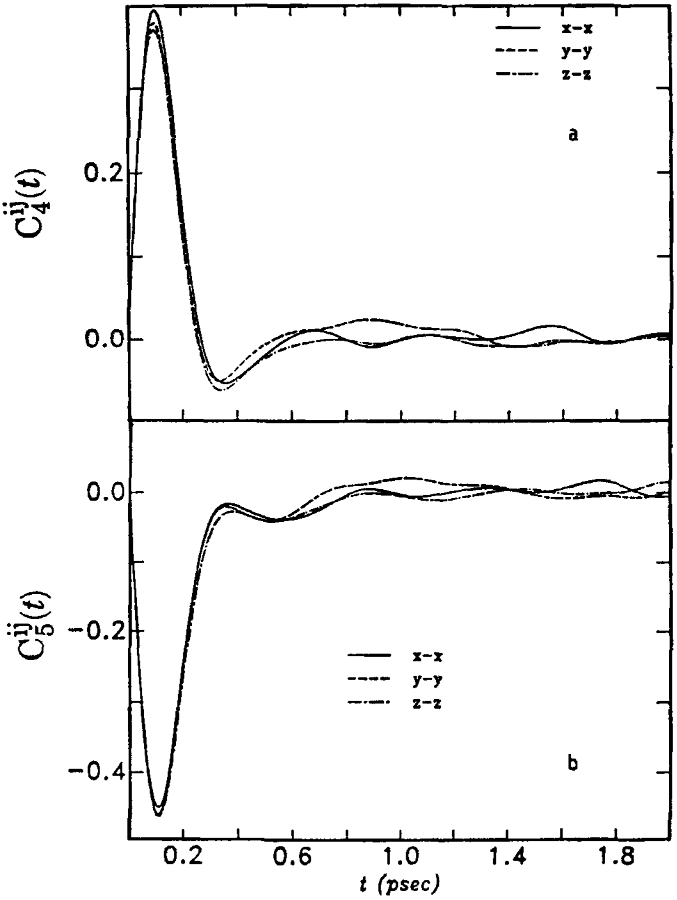

Figure 2 (a) (x, x), (y, y) and (z, z) elements of $C_4(t)$; (b) (x, x), (y, y) and (z, z) elements of $C_5(t)$ for $GeBr_4$.

$$C_4^{ij}(t) = \frac{\langle [\mathbf{v}(t) \times \omega(t)]_i [\mathbf{T}_q(0) \times \mathbf{v}(0)]_j^T \rangle}{\langle [\mathbf{v}(0) \times \omega(0)]_i^2 \rangle^{1/2} \langle [\mathbf{T}_q(0) \times \mathbf{v}(0)]_j^2 \rangle^{1/2}}$$

and

$$C_5^{ij}(t) = \frac{\langle [\mathbf{v}(t) \times \omega(t)]_i [\mathbf{F}(0) \times \omega(0)]_j \rangle}{\langle [\mathbf{v}(0) \times \omega(0)]_i^2 \rangle^{1/2} \langle [\mathbf{F}(0) \times \omega(0)]_j^2 \rangle^{1/2}}$$

respectively. These are characterized by a sharp peak near the time origin, $t = 0$, which attains nearly the same normalized amplitude for each diagonal element of the tensors $C_4(t)$ and $C_5(t)$. This reflects the isotropy of the sample. The peak is positive in Figure 2a and negative in Figure 2b. The amplitude of these peaks is so large that

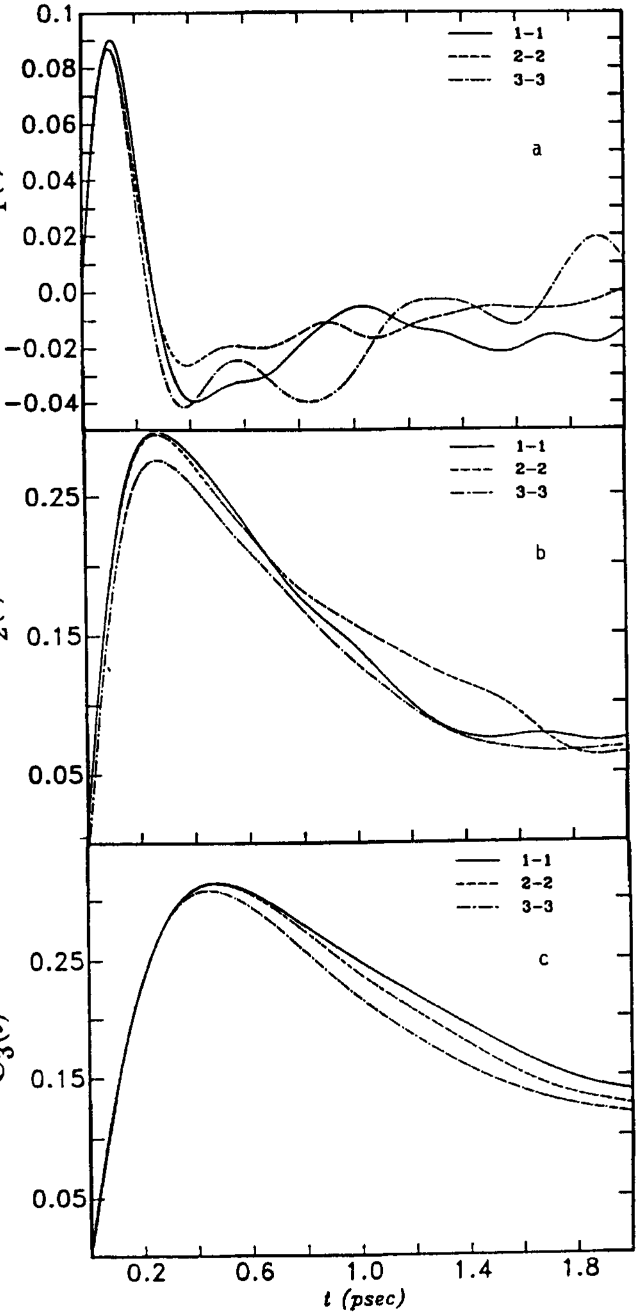

Figure 3 Same as Figure 1, but for CBr_4.

there is no means of reasonably approximating them with any theory of decoupled rotational and translational diffusion, even in the spherical-top. This conclusion is valid for all four spherical-tops investigated in this work, indicating the need for a fundamentally new approach to the theory of molecular diffusion.

b. *Carbon Tetrabromide Dynamics*

The broad pattern of results in Figures 3a–3c, 4a and 4b is similar to those for $GeBr_4$, indicating again the complete breakdown of the Debye theory of rotational diffusion, or for that matter any theory that relies on the statistical decorrelation of fundamental modes of diffusion on the single molecule level in the liquid state. It is clear that computer simulation methods are well in advance of analytical theory and also serve as good approximations to actual experimental results – as discussed in a later section on liquid structure by radiation diffraction – for these spherical-tops. There is still a

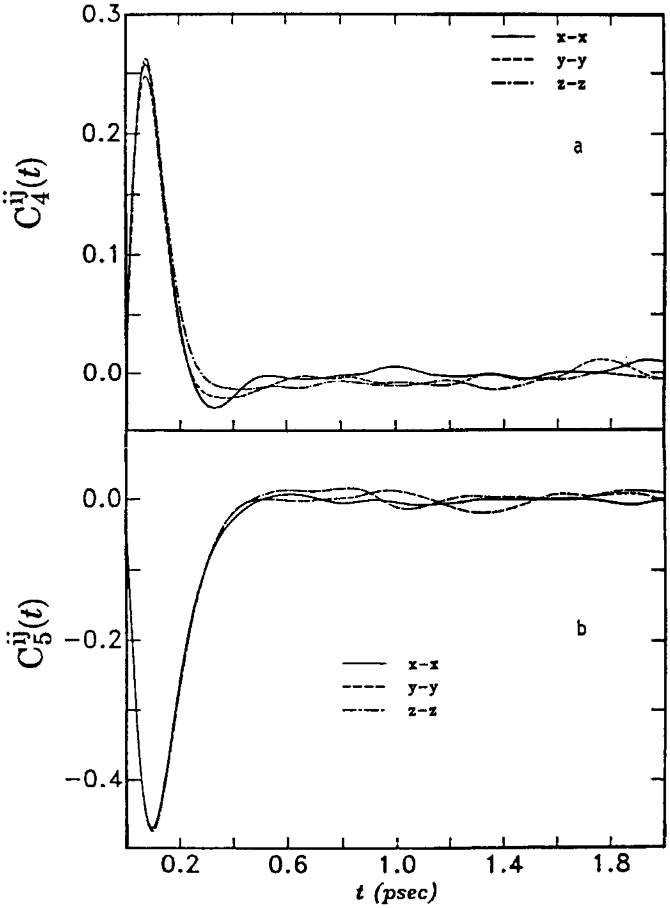

Figure 4 Same as Figure 2, but for CBr_4.

lack of meaningful dynamical experimental data from the range of spectroscopies that could be applied simultaneously to the problem. The dynamical results in Figures 3a–3c, 4a and 4b serve to complement the recent results of Dove *et al.* in the rotator phase of CBr_4 where new types of multi molecule cross mode coupling were discovered by simulation and analyzed using Mori theory [15–17]. The single molecule cross-mode correlations discovered in this work would also exist in the rotator phases formed by all four spherical-tops, and it would be valuable to use constant pressure methods to look at their time dependence for comparison with that in the liquid.

c. *Liquid Phosphorus Dynamics*

There are virtually no useful dynamical data, and reliance is therefore put on the computer simulation results of Figures 5a–5c, 6a and 6b for information on the diffusional properties of tetrameric phosphorus in the liquid state. These figures are probably good first approximations to true experimental data.

There are some differences from the tetrabromides, for example in the auto correlation function of rotational velocity (not shown), which remains positive and approximately exponential. Were it not for the information on cross-mode correlation in P_4 given in this section, this could be an almost flawless example of the angular velocity autocorrelation function given by "rotational" diffusion theory, corrected for inertia, as for example given by Lewis, McConnell and Scaife a decade ago [24]. It cannot be too strongly emphasized, however, that this theory is mathematically self-consistent but is completely unable to account for any of the new results in Figures 5a–5c, 6a and 6b. Similarly, the theory of "translational" diffusion is able to give a rough approximation, but unable to proceed further, either in frame (1, 2, 3) or (x, y, z). An analytical remedy has been suggested by Evans in terms of linked Langevin equations [25], but these equations are intricately and inextricably nonlinear, and so far remain unsolved. Once again computer simulation is the only method capable of giving realistic results for molecular diffusion.

The cross correlation functions in Figures 5a–5c, 6a and 6b reveal sharp, high amplitude peaks for liquid phosphorus. Clearly an approximately exponential angular velocity auto correlation function is a completely misleading sign of the efficacy of rotational diffusion, even in the spherical-top. Naturally there is no hope for the Debye theory in the asymmetric top, and least of all in elongated liquid crystalline molecules. The amplitudes of the moving and laboratory frame cross correlation functions in liquid phosphorus are often higher than in the tetrabromides, indicating that the more nearly we approach the conditions laid down by the analytical theories of uncoupled diffusion, the less likely they are to work. It seems that they must be either abandoned in favor of simulation or radically improved at the fundamental level.

d. *Sulphur Hexafluoride Dynamics*

The symmetry of the SF_6 molecule is $\mathbf{O}_h$, and higher than $\mathbf{T}_d$. It is not possible to obtain a more spherical simple molecule because of fundamental valence rules, although nearly perfect spheres can be synthesized with modern methods of organic and inorganic chemistry. These molecules are higher in symmetry than $\mathbf{O}_h$ but too big for routine computer simulation at present. In the present work SF_6 is taken as an accessible example of $\mathbf{O}_h$ symmetry. Despite its higher symmetry, the diffusional

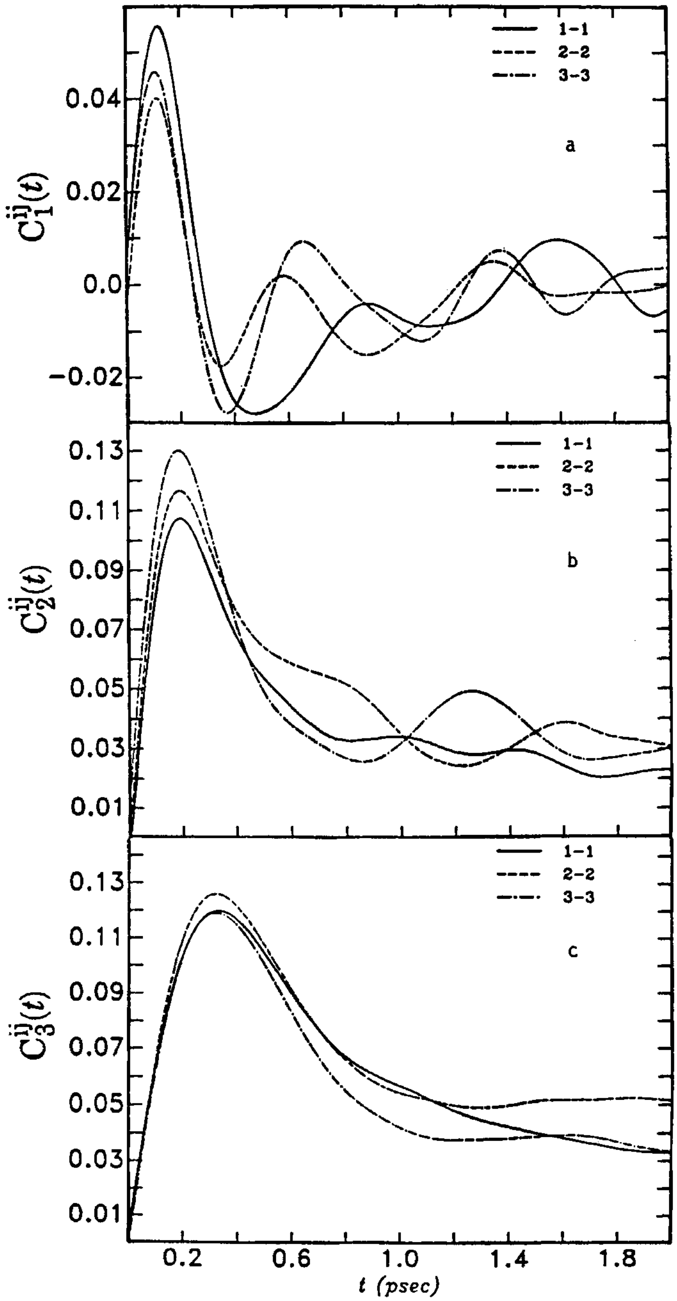

Figure 5 Same as Figure 1, but for phosphorus.

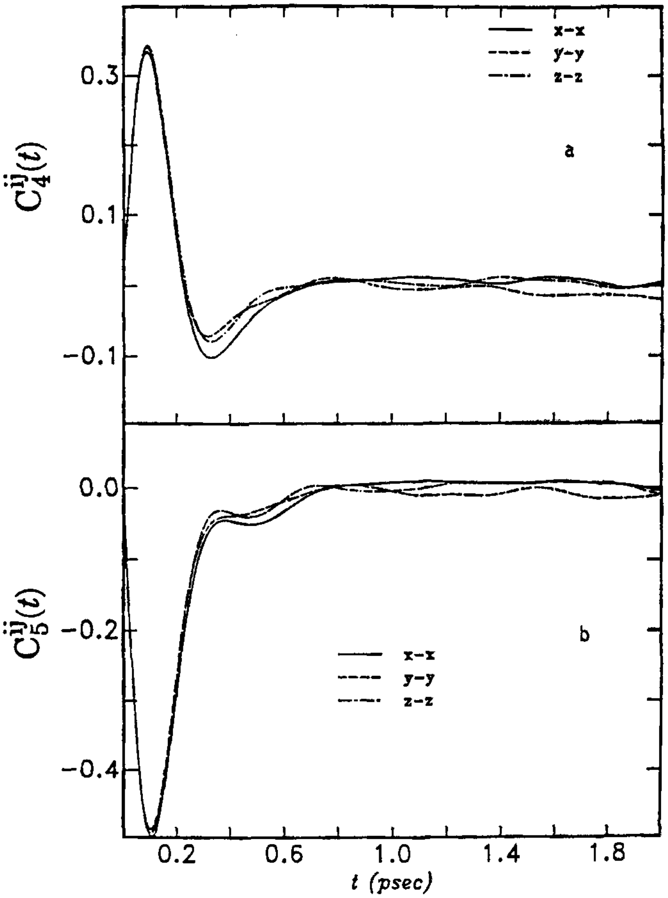

Figure 6 Same as Figure 2, but for phosphorus.

dynamics of SF_6, measured in Figure 7a–7c, 8a and 8b in analogy with the three other spherical-tops, are as intricately inter-correlated. The amplitudes of the cross correlation function components in both frames are comparable with their counterparts in the T_d spherical tops. There are negative overshoots in the auto correlation-functions of linear and angular velocity for SF_6 (not illustrated). It is well known that there is a long negative tail for the center of mass linear velocity auto correlation functin in liquid argon (first simulated 23 years ago by Rahman), which when discovered went against the conventional wisdom of "classical" diffusion theory. Our results, for a high-symmetry molecule, allow the further conclusion to be drawn that "classical" diffusion theory is wholly inapplicable to the description of diffusional motion once translation (as in an atom) is supplemented by rotation (as in a molecule). Both conclusions, from Rahman [26] and from the present work, were obtained from simulation; neither was predicted analytically.

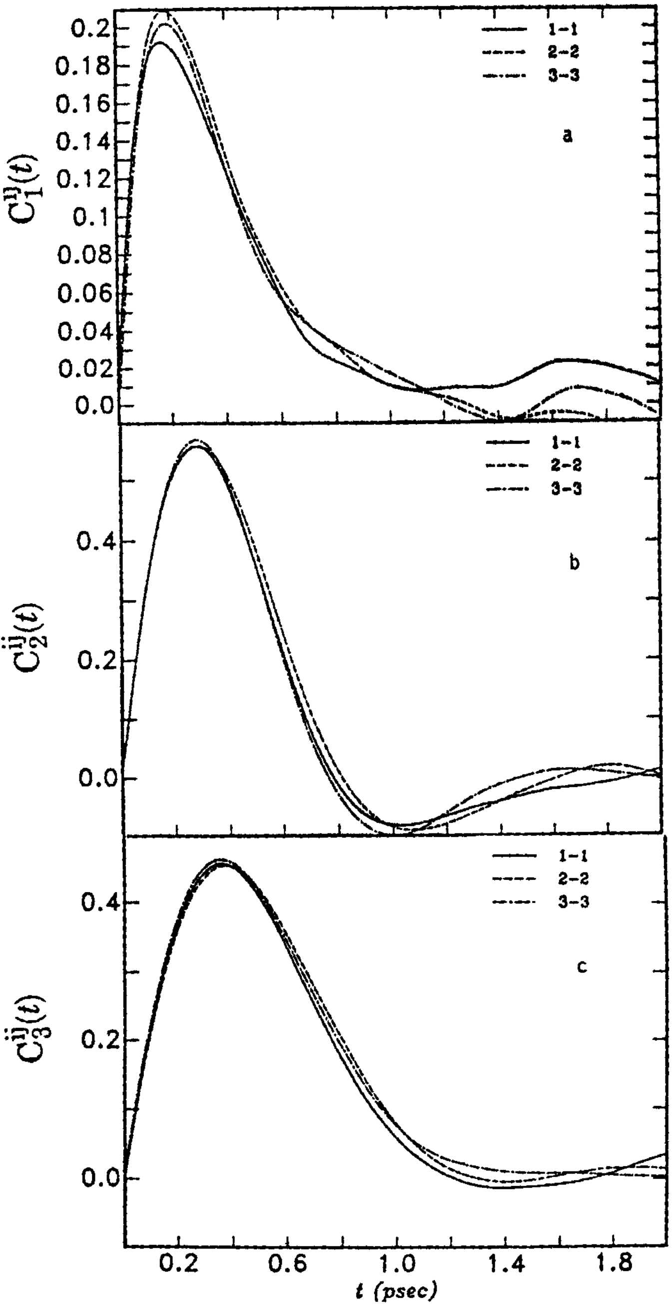

Figure 7 Same as Figure 1, but for SF_6.

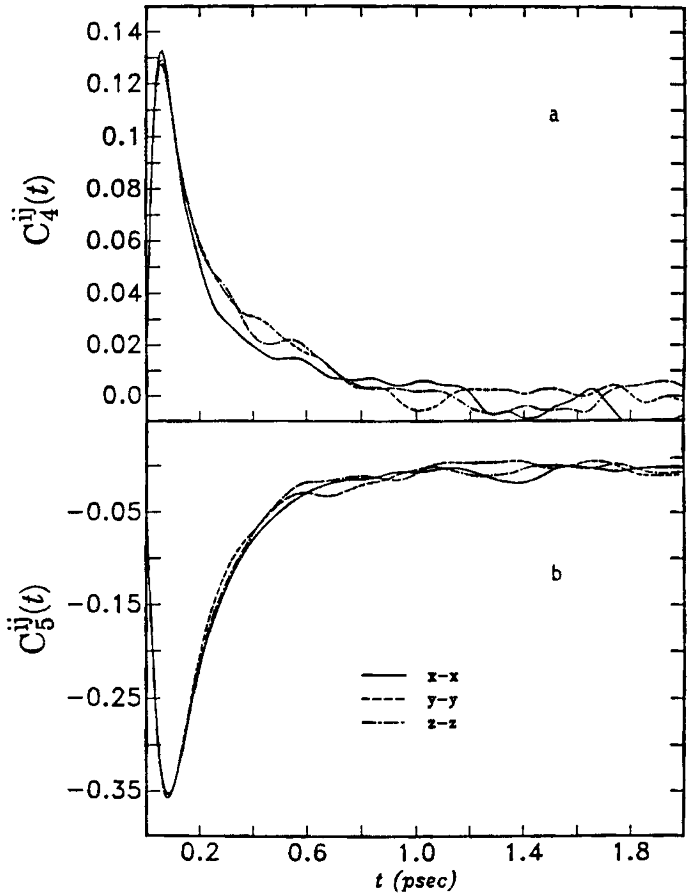

Figure 8 Same as Figure 2, but for SF_6.

e. *Equilibrium Partial Radial Distribution Functions*

From the simulation results we have calculated the partial radial distribution functions for all the liquids simulated. Further, in the case of $GeBr_4$ and P_4, the partial distribtuion functions are computed with the reference interaction site model (RISM) of Chandler *et al.* [19, 20]. For $GeBr_4$ the RISM equations were solved by Swamy and Bhuiyan utilizing a sphere diameter of 2.44 Å for Ge and 3.4 Å for Br atoms [12]. The Ge–Ge, Ge–Br and Br–Br distribution functions are shown in Figure 9. The Br–Br distribution function shows a maximum at 4.1 Å. That for Ge–Ge has its main peak at 6.49 Å, while the RISM theory predicts a peak at 6.1 Å. For Ge–Br, the simulation predicts two peaks for $r < 7.0$ Å occurring at 4.95 Å and 6.04 Å, while the RISM theory predicts a single peak at 5.3 Å. In the case of P_4, the RISM equations were solved by Granada and Dore with a phosphorous diameter of 3.2 Å [10]. The RISM results along with the simulation and the experimental results for the P–P distribution

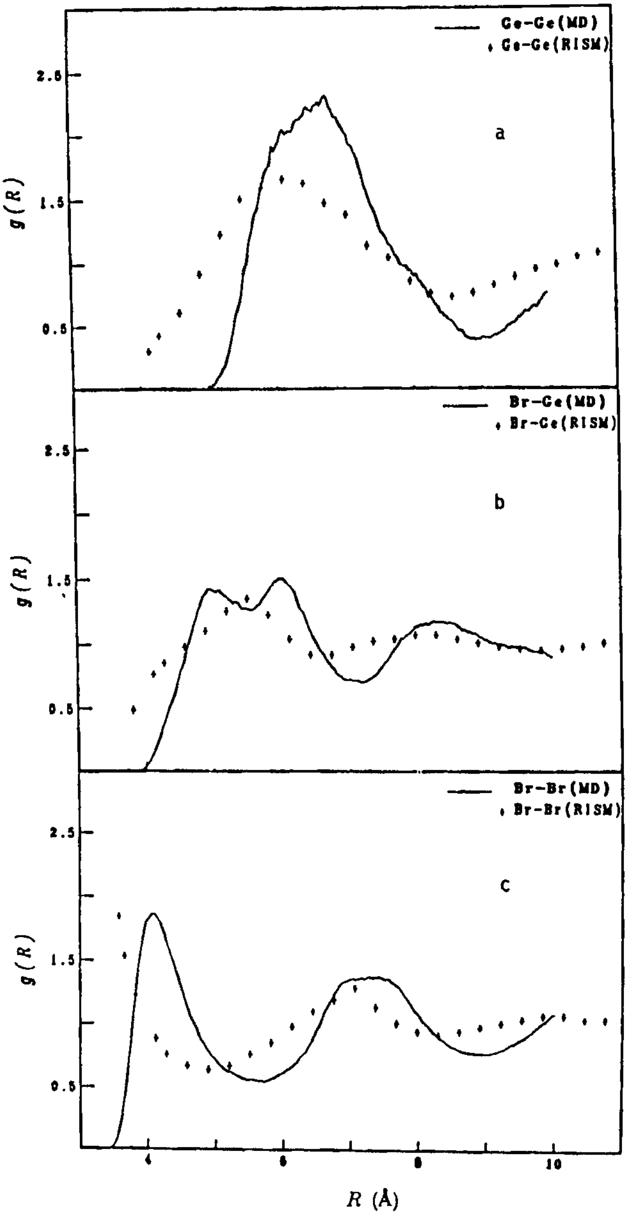

Figure 9 Partial radial distribution functions for $GeBr_4$. The simulation resutls are compared with RISM results.

functions are shown in Figure 10. The simulation prediction of the peak positions are in excellent agreement with the experiment. The RISM theory results are similar to those for $GeBr_4$, the peak positions differing from the experiment. The simulations

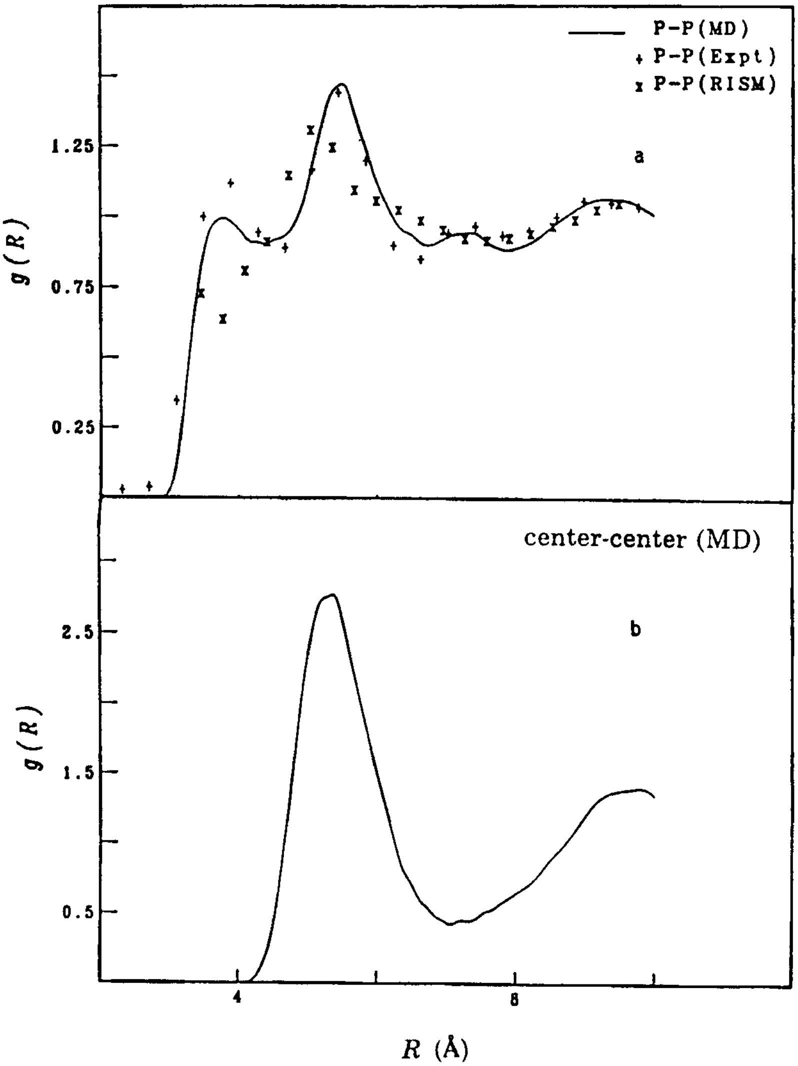

Figure 10 (a) P–P and (b) center–center distribution functions for liquid phosphorous. The P–P distribution functions are compared with the RISM and with experimental results

also predicts a small peak around 7.0 Å in agreement with the experimental results of Granada and Dore [10]. The structure of the distribution function implies a strong orientational correlation between neighboring molecules and the peak at 7.0 Å suggests strong correlations extending to the next shell of neighbors. In this respect these results are similar to those for amorpohous arsenic [27]. The center–center correlation function for liquid P_4 is plotted in Figure 10. In this case the first peak appears at r = 5.5 Å. The S–F, S–S and F–F partial distribution functions for liquid SF_6 are

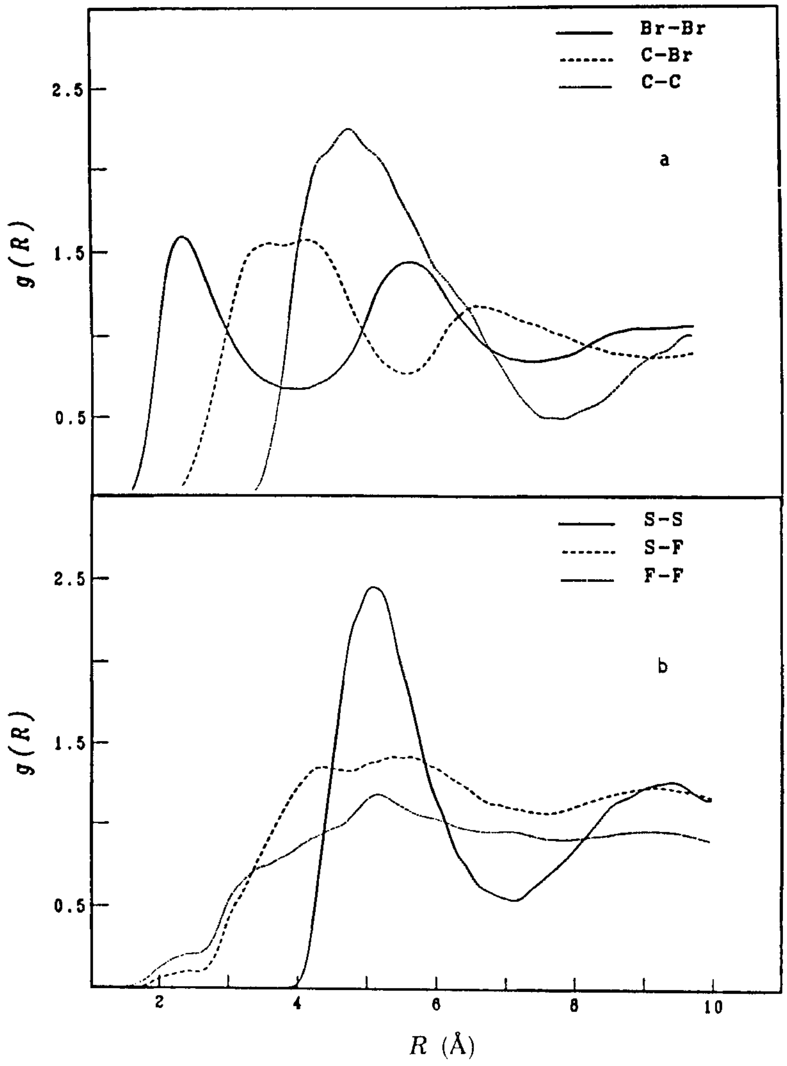

Figure 11 Partial radial distribution functions for (a) CBr_4 and (b) SF_6.

shown in Figure 11a and the C–Br, C–C, and Br–Br partial distribution functions for liquid CBr_4 are shown in Figure 11b.

IV. CONCLUSIONS

The behavior of spherical top molecules is dynamically and structurally more intricate than simple theories allow. Dynamically the existence of various hitherto unsuspected cross correlation functions in both frames of reference points to the need for a diffusion theory that embraces both types of motion self-consistently. Structurally, the RISM theory is not an apt description of the pair distribution functions obtained either by simulation or, as in the case of phosphorus, by radiation diffraction data. Excellent agreement has been obtained between the computer simulation results and the radiation diffraction data in the case of liquid phosphorus.

References

[1] M.W. Evans and G.J. Evans, "Langevin equations and computed correlation functions for a rotating and translating asymmetric top," *Phys. Rev. A*, **34**, 468 (1986).

[2] M.W. Evans, "Molecular dynamics simulation of water/carbon tetrachloride mixtures," *J. Chem. Phys.*, **86**, 4096 (1987).

[3] M.W. Evans, G.C. Lie and E. Clementi, "A molecular dynamics simulation of rotational flow induced by a left circularly polarised laser field," *Chem. Phys. Lett.*, **138**, 149 (1987).

[4] M.W. Evans, "Molecular dynamics simulation of new auto and cross correlation functions in liquid water," *J. Mol. Liq.*, **32**, 173 (1986).

[5] J.P. Ryckaert, A. Bellemans and G. Ciccotti, "The rotation–translation coupling in diatomic molecules," *Mol. Phys.*, **44**, 979 (1981).

[6] B.J. Berne and R. Pecora, *Dynamical Light Scattering with Applications to Physics, Chemistry, and Biology*, Wiley Interscience, New York, 1976, ch. 7.

[7] V.K. Agarwal, G.J. Evans and M.W. Evans, "Far-infrared and computer simulation analysis of liquid and rotator phase bromoform," *J. Chem. Soc., Faraday Trans. II*, **79**, 137 (1983).

[8] P.A. Egelstaff and D.I. Page, "Orientational correlations in molecular liquids by neutron scattering: carbon tetrachloride and germanium tetrabromide," *Mol. Phys.*, **20**, 881 (1971).

[9] C.D. Thomas and N.S. Gingrich, "The atomic distribution in the allotropic forms of phosphorous at different temperatures," *J. Chem. Phys.*, **6**, 659 (1938).

[10] J.R. Granada and J.C. Dore, "Neutron diffraction studies of phosphorous II. The super-cooled liquid and plastic crystal phases", *Mol. Phys.*, **46**, 757 (1982).

[11] J.H. Clarke, J.C. Dove, J.R. Granada, J. Reed and G. Walford, "Neutron diffraction studies of liquid phosphorous I. Reactor and pulsed neutron measurements at 50°C," *Mol. Phys.*, **42**, 861 (1981).

[12] K.N. Swamy and L.B. Bhuiyan, "The reference interaction site model and the structure of liquid germanium tetrabromide," *Phys. Chem. Liqs.*, **9**, 169 (1980).

[13] M.T. Dove, "A simulation study of the disordered phase of CBr_4: I. Single particle properties," *J. Phys. C: Solid State Phys.*, **19**, 3325 (1986).

[14] M.T. Dove and R.M. Lynden-Bell, "A simulation study of the disordered phase of CBr_4: II. Collective properties and rotation–translation coupling," *J. Phys. C: State Phys.*, **19**, 3343 (1986).

[15] M.T. Dove and G.S. Pawley, "A molecular dynamics simulation study of the plastic crystalline phawe of sulfur hexafluoride," *J. Phys. C: Solid State Phys.*, **16**, 5969 (1983).

[16] M.T. Dove and G.S. Pawley, "A molecular dynamics simulation study of the orientationally disordered phase of sulfur hexafluoride," *J. Phys. C: Solid State Phys.*, **17**, 6581 (1984).

[17] M.T. Dove, G.S. Pawley, G. Dolling and B.M. Powell, "Collective excitations in an orientationally frustrated solid: newtron scattering and computer simulation studies of SF_6," *Mol. Phys.*, **57**, 865 (1986).

[18] M. More, J. Lefebvre and B. Hennion, "Quasielastic coherent neutron scattering in the disordered phase of CBr_4: experiment evidence of local order and rotational dynamics of molecules," *J. Physics (France)*, **45**, 303 (1984).

[19] L.J. Lowden and D. Chandler, "Solution of a new integral equation for pair correlation functions in molecular liquids," *J. Chem. Phys.*, **59**, 6587 (1973).

[20] L.J. Lowden and D. Chandler, "Theory of intermolecular pair correlations for molecular liquids: applications to the liquids carbon tetrachloride, carbon disulfide, carbon diselenide and benzene," *J. Chem. Phys.*, **61**, 5228 (1974).

[21] For a useful review see D. Fincham and D.M. Heyes, "Recent advances in molecular dynamics computer simulation," in *Dynamical Processes in Condensed Matter*, M.W. Evans, ed., Wiley Interscience, New York, 1985, ch. 6.

[22] M.W. Evans, "The diffusional dynamics of liquid methanol: new cross correlation functions," *J. Chem. Soc., Faraday Trans. II*, **00**, 0000 (1987).

[23] L. Verlet, "Computer experiments on classical fluids," *Phys. Rev.*, **159**, 98 (1967).

[24] J.T. Lewis, J. McConnell and B.K.P. Scaife, "Relaxation effects in rotational Brownian motion," *Proc. Roy Irish Acad.*, **76**, 43 (1976).

[25] M.W. Evans, "New Langevin equations for a translating and simultaneousiy rotating asymmetric top," *Phys. Rev. Lett.*, **55**, 1551 (1985).

[26] A. Rahman, "Correlations in the motion of atoms in liquid argon," *Phys. Rev.*, **136**, (1964).

[27] M.F. Daniel and A.J. Leadbetter, "The structure of vapor-deposited films of molecular arsenic (As_4)," *Phil. Mag. B*, **44**, 509 (1981).