

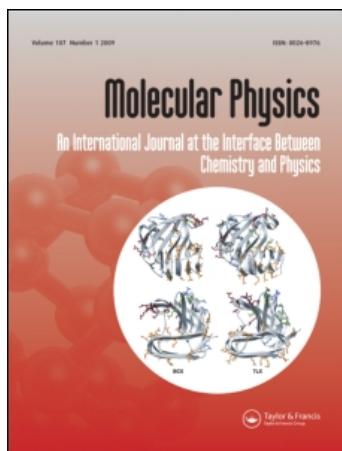
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Th. Dorfmüller^a; J. Samios^a

^a Universität Bielefeld, Fakultät für Chemie, Bielefeld, F.R. Germany

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A molecular dynamics simulation of interaction-induced dipole correlation functions in liquid CS₂

by TH. DORFMÜLLER and J. SAMIOS

Universität Bielefeld, Fakultät für Chemie,
D-4800 Bielefeld, Postfach 8640, F.R. Germany

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The interaction-induced dipole correlation function for liquid CS₂ was calculated by molecular dynamics simulation. This correlation function was separated into components parallel and normal to the molecular symmetry axis, and the shape of these, as well as of the tensorial P_2 orientational correlation function, were calculated and compared. The discussion shows that we can obtain information on the environment anisotropy fluctuations contributing to the time dependence of the induced dipoles. The comparative discussion of several of these correlation functions can be useful in obtaining a differentiated, but still partial picture of the molecular dynamics in liquid CS₂.

1. INTRODUCTION

Molecular dynamics (MD) computer simulation has provided useful information on the structural and the dynamical properties of model liquids. The value of MD simulation and, at the same time its limitation, lie in the simplified character of the objects which are simulated and which are but very distant replicas of material molecules. As a consequence of this, we are not able to simulate a liquid in all its features, but we can and must make a deliberate choice of what we think is most relevant. On the other hand, the necessary simplification will keep the input and the output of the simulation conceptually transparent, thus helping us to obtain a tractable image of what is essentially going on at the molecular level.

The object of this study is to describe the dynamical correlation of a simple linear molecule in the liquid state with its environment. The observable quantities which are extremely sensitive to the intermolecular correlations at relatively short distances are intermolecular spectral data. For this reason, the present MD simulation is mainly concerned with a particular kind of intermolecular spectroscopy: interaction-induced far infrared absorption. The situation with which we have to deal in this kind of spectroscopy is the appearance of several spectral effects in the same frequency range and which are physically coupled to each other. Such processes are, for example, single molecule rotational, translational and collective motions which may additionally depend on static correlations of neighbouring molecules.

It is well established that the source of the far infrared (FIR) absorption spectrum in nonpolar liquids are interaction-induced time-dependent dipole

moments. These result from the induction of a dipole $\boldsymbol{\mu}(t)$ in a polarizable reference molecule under the influence of the molecules within a certain range. The time dependence of the intermolecular distances and relative orientations within this interaction range determines in a very complex way the time dependence of the induced dipoles. Accordingly, we have used the following relation to calculate this moment:

$$\boldsymbol{\mu}_i(t) = \sum_j \boldsymbol{\mu}_{ij}(t). \quad (1)$$

The quantities $\boldsymbol{\mu}_{ij}(t)$ are the partial dipoles induced on the reference molecule i by the molecules j , the summation extending over a physically plausible range around the reference molecule. The dynamical variable $\boldsymbol{\mu}_i(t)$ incorporates the information about the relative motion of the reference molecule to its neighbours, its reorientation in a laboratory frame of reference and the configurational fluctuations of the environment. A quantitative description of the time evolution of this quantity is given by the following normalized dipole autocorrelation function:

$$C_s(t) = \langle \boldsymbol{\mu}_i(0) \cdot \boldsymbol{\mu}_i(t) \rangle / \langle \boldsymbol{\mu}_i(0) \cdot \boldsymbol{\mu}_i(0) \rangle. \quad (2)$$

Two other correlation functions which are important in this context are:

- (a) The reorientation correlation function of the second order Legendre polynomial

$$C_2(t) = P_2(\mathbf{u}_i(0) \cdot \mathbf{u}_i(t)), \quad (3)$$

where $\mathbf{u}_i(t)$ is the unit vector at the time t located along the molecular axis of the reference molecule i .

- (b) The velocity correlation function defined as

$$C_v(t) = \langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(t) \rangle / \langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(0) \rangle \quad (4)$$

where $\mathbf{v}_i(t)$ is the translational component of the molecular velocity at the time t .

2. THE INDUCTION MECHANISM

The complete induced dipole absorption correlation function can be expressed as follows, separating formally the self correlation and the pair correlation terms:

$$C_D(t) = \sum_i \langle \boldsymbol{\mu}_i(0) \cdot \boldsymbol{\mu}_i(t) \rangle + \sum_{i \neq j} \langle \boldsymbol{\mu}_i(0) \cdot \boldsymbol{\mu}_j(t) + \boldsymbol{\mu}_j(0) \cdot \boldsymbol{\mu}_i(t) \rangle. \quad (5)$$

On the other hand, the FIR spectrum of nonpolar liquids is shaped both by single-molecule and by collective motions. Both are contained in the self correlation function $C_s(t)$ and in the correlation functions of higher order. The separation of the single and the collective motions is, however, possible only under very restrictive assumptions.

The quantitative description of the interaction-induced effects at the molecular level has been greatly facilitated by two assumptions which, although generally used, are not without risks. Firstly, we calculate the local field at each point of the liquid due to the charge distributions of the molecular systems by means of the point multipole expansion, which is known to be exact at distances large in comparison to the charge separations. Secondly, we use the point polarizability

approximation, by which we consider the polarizable matter of the molecules as concentrated at their centre of mass. Both assumptions are urgently in need of a validity test. They have nevertheless been used in this simulation as a first approximation.

The point multipole expansion [1] gives the potential produced by a charge distribution of a given molecule j , at the centre of the reference molecule i , located at a distance R_{ij} from the centre of the molecule j , in terms of the total charge Q , the dipole moment $\boldsymbol{\mu}$, the quadrupole moment $\theta_{\alpha\beta}$ and higher moments in the form of the following expansion:

$$\phi_{ij} = \frac{Q}{R_{ij}} + \frac{\boldsymbol{\mu}_\alpha \cdot \mathbf{R}_{ij}^\alpha}{R_{ij}^3} + \frac{\theta_{\alpha\beta}}{3R_{ij}^5} \cdot [3R_{ij}^\alpha \cdot R_{ij}^\beta - R_{ij}^2 \delta_{\alpha\beta}] + \text{higher terms.} \quad (6)$$

The moments are defined as follows:

$$\begin{aligned} Q &= \sum_i e_i, \\ \mu_\alpha &= \sum_i e_i r_i^\alpha, \\ \theta_{\alpha\beta} &= \frac{1}{2} \sum_i e_i (3r_i^\alpha r_i^\beta - r_i^2 \delta_{\alpha\beta}). \end{aligned} \quad (7)$$

The indices α, β, γ indicate the coordinate axes in the laboratory frame of reference.

The field at a given location in a liquid sample is given within the frame of this expansion by the relation

$$\mathbf{F}_i^\alpha = \sum_{i \neq j} \sum_{\beta\gamma} \left[\frac{3}{R_{ij}^7} (5R_{ij}^\alpha R_{ij}^\beta R_{ij}^\gamma - R_{ij}^2 (R_{ij}^\alpha \delta_{\beta\gamma} + R_{ij}^\beta \delta_{\alpha\gamma} + R_{ij}^\gamma \delta_{\alpha\beta})) \right] \cdot {}^j\Theta_{\beta\gamma}. \quad (8)$$

The quantity $\Theta_{\beta\gamma}$ is given, in terms of the molecular quadrupole moments, by the expression

$${}^j\Theta_{\beta\gamma} = \frac{1}{2} \Theta (3\mathbf{u}_j^\beta \cdot \mathbf{u}_j^\gamma - \delta_{\beta\gamma}). \quad (9)$$

In the particular case of the CS₂ molecule, whose lowest order multipole is a quadrupole, we can assume that, at least for intermolecular distances which are not too small, the contribution of this term will be dominant. We thus neglect the higher order terms in a first approximation, keeping in mind that any discrepancies between the simulation and experimental results might be traced back, among others, to this simplification. The local field, due to the surrounding molecular quadrupoles, is analyzed into a component parallel to the axis of the reference molecule \mathbf{F}_i^\parallel and a component normal to it \mathbf{F}_i^\perp as follows:

$$\mathbf{F}_i = \mathbf{F}_i^\parallel + \mathbf{F}_i^\perp, \quad (10 a)$$

$$\mathbf{F}_i^\parallel = [\mathbf{F}_i \cdot \mathbf{u}_i] \mathbf{u}_i, \quad (10 b)$$

$$\mathbf{F}_i^\perp = \mathbf{F}_i - \mathbf{F}_i^\parallel. \quad (10 c)$$

These field components are used to calculate the corresponding components of the induced dipole moment on the reference molecule

$$\boldsymbol{\mu}_i^\parallel = \alpha^\parallel \cdot \mathbf{F}_i^\parallel, \quad (11 a)$$

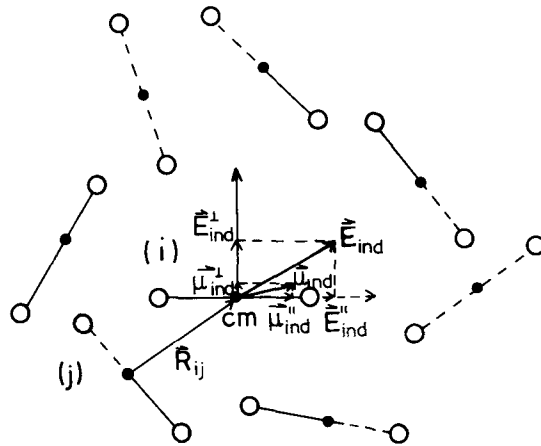


Figure 1. Representation of the analysis of the inducing field and of the induced dipoles into components parallel and normal to the molecule axis. The reference molecule is i and the centres of the surrounding molecules are located at distances R_{ij} from the centre of i . \circ , centres of the sulphur atoms, \bullet , centres of the carbon atoms.

$$\mu_i^\perp = \alpha^\perp \cdot \mathbf{F}_i^\perp, \quad (11 b)$$

$$\mu_i = \mu_i^\parallel + \mu_i^\perp. \quad (11 c)$$

The values of the two components of the polarizability tensor parallel to the molecular axis α^\parallel and normal to it α^\perp are taken from experimental data [2].

The procedure used to calculate the induced dipole moment on a given reference molecule is illustrated in figure 1. The configurational space of the liquid is defined by the distances R_{ij} of the reference molecule i to the other molecules of the system and the three cartesian components of the unit vector \mathbf{u}_i on the molecular axis with respect to the laboratory reference system. The total dipole correlation function $C_s(t)$ is analyzed into a parallel $C_s^\parallel(t)$, a normal component $C_s^\perp(t)$ and a cross correlation $C_s^+(t)$, according to whether we calculate the auto-correlation of the parallel, the normal dipole component, or the cross correlation between them

$$C_s(t) = C_s^\parallel(t) + C_s^\perp(t) + C_s^+(t), \quad (12 a)$$

$$C_s^\parallel(t) = \langle \mu_i^\parallel(0) \cdot \mu_i^\parallel(t) \rangle / \langle \mu_i(0) \cdot \mu_i(0) \rangle, \quad (12 b)$$

$$C_s^\perp(t) = \langle \mu_i^\perp(0) \cdot \mu_i^\perp(t) \rangle / \langle \mu_i(0) \cdot \mu_i(0) \rangle, \quad (12 c)$$

$$C_s^+(t) = \langle \mu_i^\parallel(0) \cdot \mu_i^\perp(t) + \mu_i^\perp(0) \cdot \mu_i^\parallel(t) \rangle / \langle \mu_i(0) \cdot \mu_i(0) \rangle. \quad (12 d)$$

3. THE MD SIMULATION

We have used an ensemble of 256 rigid linear triatomics with atom-atom Lennard-Jones interactions. This model potential is of the form

$$\phi(\mathbf{R}_{ij}, \mathbf{u}_i, \mathbf{u}_j) = \sum U_{ij}(\mathbf{r}_{ab}), \quad (13)$$

$$U_{ij}(\mathbf{r}_{ab}) = 4\varepsilon_{\alpha\beta} \cdot \left[\left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}} \right)^6 \right], \quad (14)$$

where r_{ab} are the distances between one atom of the molecule i and one atom of the molecule j . The parameters of the L – J potential were identical to those used in a previous simulation of liquid CS₂ [3]

$$\begin{aligned}\sigma_{\text{SS}} &= 3.52 \text{ \AA}, & \varepsilon_{\text{SS}}/k &= 183 \text{ K}, \\ \sigma_{\text{CC}} &= 3.35 \text{ \AA}, & \varepsilon_{\text{CC}}/k &= 51.2 \text{ K}, \\ \sigma_{\text{CS}} &= 3.44 \text{ \AA}, & \varepsilon_{\text{CS}}/k &= 96.8 \text{ K}.\end{aligned}$$

The time step used was 10^{-15} s. The bond length CS was 1.56 Å [4] and the potential cutoff was set at half the box length $L/2 = 11.05$ Å. The initial configuration used in the simulation was a FCC lattice with a density of $d = 1.26 \text{ g cm}^{-3}$ and an initial temperature of 298 K. We have used the Verlet [5] and Singer [6] algorithms to simulate the translational and the rotational motions respectively. Our simulation differs from previously reported CS₂ simulations in the particular combination of the potential parameters and the procedure by which the equations of motion were solved [3, 7]. The average internal energy of the system (-24.9 kJ/mol) is in good agreement with experiment (-25 kJ/mol). The observed fluctuation of the average total temperature (299.6 K) was ± 8 K. A first run of approximately 12 ps was necessary to equilibrate the system. Most of the runs were performed by starting from this configuration and, after a change of parameters like the temperature, letting the system equilibrate again for approximately 6 ps. A subsequent run of 40 ps was started from the last configuration to calculate the correlation functions.

4. RESULTS AND DISCUSSION

Figure 2 displays the decay of the total and the three component dipole correlation functions. The intercepts at $t = 0$ show that the contributions to the induced moment of the parallel and the normal components in the static limit $t \rightarrow 0$ extrapolate to the ratio 2.3 : 1, which is a factor of 3.4 smaller than the value of the square of the corresponding components of the static polarizability $(\alpha^{\parallel}/\alpha^{\perp})^2 = 7.8$. As expected, there is no cross correlation between the two components in the static limit, i.e. $C_s^+(0) = 0$. We can also easily calculate the average value of the ratio of the parallel to the normal component of the local electric field at the centre of the reference molecule

$$\langle |\mathbf{F}^{\parallel}(0)| \rangle = 0.54 \langle |\mathbf{F}^{\perp}(0)| \rangle. \quad (15)$$

The value of the proportionality factor, which differs significantly from the value 0.71 expected in the case of an isotropic field, illustrates the effect of the static translational and orientational correlations of the molecules within the interaction range of the reference molecule. This result is qualitatively consistent with the values of the orientational correlation parameter g_2 calculated recently by MD simulation in liquid CS₂ by Impey *et al.* [3]. The information conveyed by this and our results is, however, different since the local field anisotropy reflects both the orientational correlation of the surrounding molecules as well as the anisotropy in the distribution of the centres of mass. The average translational structure of CS₂ will be significantly affected by energetically favourable configurations involving pair configurations like the normal nonplanar and the parallel shifted by one CS bond length.

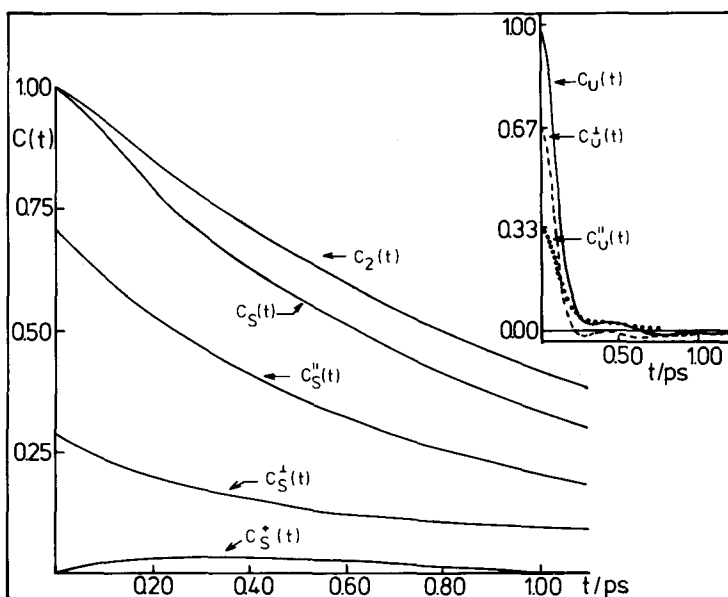


Figure 2. Comparison of the dipole autocorrelation function defined in equation (2), the components defined in equations 12 (a)–12 (d), and the reorientation correlation function defined in equation (3). The insert displays the velocity correlation function and its components [7].

The components of the velocity correlation function calculated by Steinhauser [7] have been included in the insert of figure 2, because they are very instructive in completing the picture of the anisotropy in liquid CS_2 . The translation normal to the molecular axis appears to have a more oscillatory character than the motion parallel to the axis. The parallel motion is qualitatively better described by a succession of correlated jumps from site to site, whereas the normal motion is better approximated by a damped oscillation.

Another feature of some interest is the shape of the parallel-normal cross correlation function $C_s^+(t)$ displayed in figure 2. The zero time limit of this function $C_s^+(0) = 0$ results from the random distribution of the inducing field. This is a static effect and is expected, if the simulation is free from artifacts. At non-zero time shifts, however, we observe a small, but significant value of $C_s^+(t)$ reflecting a dynamic correlation between the two components. The exact significance of this effect is, at this point, difficult to assess, however, it seems to indicate a slightly non-random relative reorientation of the molecules, probably as a consequence of the preference of energetically favourable alignments. At large time shifts this correlation decays to zero as all the other correlations do.

As the long time evolution of the correlations in liquids is more or less diffusive, a logarithmic plot of the correlation functions is instructive. In figure 3 we compare the orientational correlation function $C_2(t)$ with the parallel component of the interaction-induced dipole correlation function $C_s^{\parallel}(t)$. The former reflects a tensor rotation of the molecular symmetry axis with respect to the laboratory frame of reference and the latter the changes of the induced molecular dipole moments due to relative motions of the molecules. These relative motions of the molecules can be described as resulting both from the collective effect of fluctua-

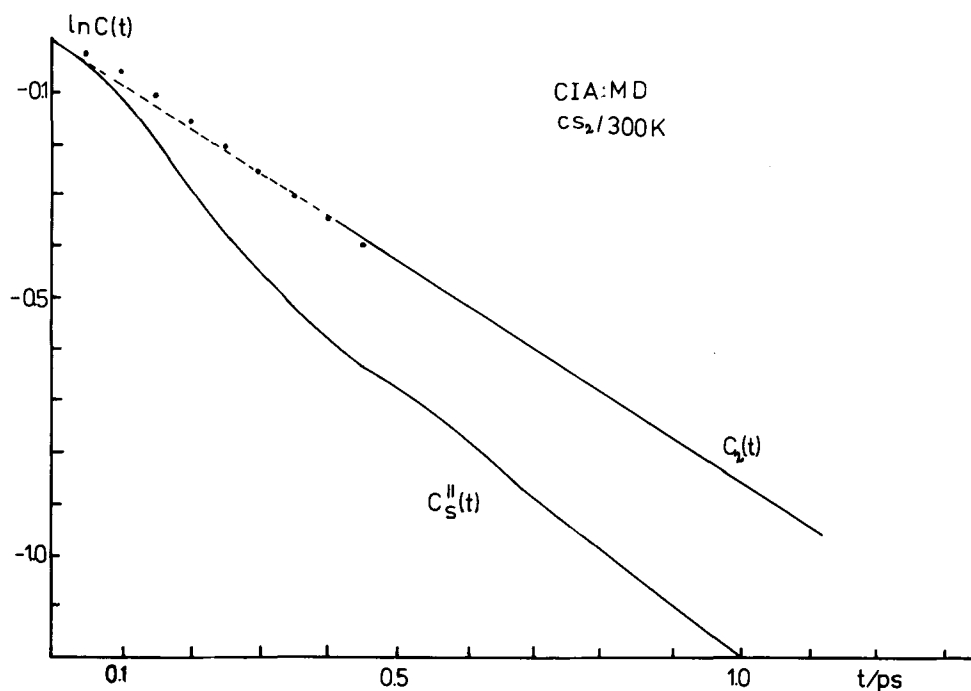


Figure 3. A logarithmic plot of the orientational correlation function $C_2(t)$ and the parallel component of the dipole correlation function $C_s^{\parallel}(t)$. The first reflects the tensorial P_2 reorientations of the molecular symmetry axis in a laboratory frame of reference, and the latter the concerted effect of reorientation and environment anisotropy fluctuations with respect to the same axis.

tions of the 'molecular cage' itself on the one hand and from changes of the position of the reference molecule within the cage on the other. The concept of a molecular cage in which the molecules are constrained to move for some time is certainly not without problems. The problems come from the difficulty in defining properly the molecules forming the cage and from the lifetime of the cage which must be long compared to the time scale of the molecular motions studied, if the concept of a cage is to be a useful one. In our case, we assume that the interaction-induced effect stems from all the molecules within the simulation box which we thus consider to form the cage. The fluctuations of the cage configuration results in a fluctuation of the inducing field at the location of the reference molecule and this leads to the changes in the induced dipoles. The purpose of the comparison in figure 3 is to bring forth the difference between the reorientation of the reference molecule which can be expressed by the first-order or by the second-order Legendre polynomial correlation functions and the collective property reflected in $C_s^{\parallel}(t)$. What is actually compared in this figure are the two following correlation functions:

$$C_2(t) = P_2(\mathbf{u}(0) \cdot \mathbf{u}(t)), \quad (16)$$

$$C_s^{\parallel}(t) \cong (\alpha^{\parallel})^2 \langle \mathbf{u}_i(0) \cdot \mathbf{u}_i(t) \rangle \cdot \langle (\mathbf{F}_i(0) \cdot \mathbf{u}_i(0)) \cdot (\mathbf{F}_i(t) \cdot \mathbf{u}_i(t)) \rangle. \quad (17)$$

The second expression shows that the correlation function $C_s^{\parallel}(t)$ depends both upon the single molecule reorientation via the vector $\mathbf{u}_i(t)$ and upon the collective

rearrangement of the cage molecules via the vector $\mathbf{F}_i(t)$. A separation of the two components is possible under the assumption that the two motions are statistically independent and that the time scales of $\mathbf{F}_i(t)$ and $\mathbf{u}_i(t)$ are quite different. Both are poor assumptions for a simple liquid like CS_2 . The comparison of $C_s^{\parallel}(t)$ with $C_2(t)$ rather than with $C_1(t)$ can be justified by the form of equation (17) which shows that this expression is invariant under a reorientation of the vector $\mathbf{u}(t)$ by an angle of π in analogy to the second rather than to the first Legendre polynomial. One feature of figure 3 is that, whereas the single molecule P_2 tensor reorientation proceeds according to a diffusive law in most of the time range, i.e. from 0.2 to 4 ps, the induced dipole correlation is diffusive only after approximately 0.5 ps, displaying a shape reminiscent of a 'free' rotation at times shorter than that. Furthermore, the two relaxation times, obtained from the slopes of the linear sections, are different. The relaxation times corresponding to the tensor reorientation on one hand and the dipole component parallel to the molecular symmetry axis on the other are $\tau_2 = 1.2$ and $\tau_s^{\parallel} = 0.9$ ps. This result, i.e. that the decay of the parallel induced dipole correlation is faster than the decay of the single molecule orientation correlation, is not unexpected, since the former has both a single-molecule and a collective component. In other words, the time dependence of the induced dipole moment along the molecular axis, as observed by the absorption of radiation, reflects the orientational motion of each single molecule as well as the relative motions of the cage. The exponential parts of the three correlation functions $C_1(t)$ [8], $C_2(t)$ and $C_s(t)$ give relaxation times equal to $\tau_1 = 4$ ps, $\tau_2 = 1.2$ ps and $\tau_s^{\parallel} = 0.9$ ps respectively. Assuming that $C_s^{\parallel}(t)$ is the result of the two parallel decay channels described by $C_2(t)$ and by the collective process we find for the latter a relaxation time of $\tau_{\text{coll}} = 3.6$ ps. This is considerably slower than the single molecule relaxation time. Since τ_{coll} contains rotational and translational components of the motion of the cage molecules relative to each other and relative to the reference molecule an interpretation of this quantity presupposes a more detailed analysis of the dynamics of liquid CS_2 .

Another aspect of the molecular dynamics is also reflected in the shape of the parallel and the normal components of the dipole correlation function. These are plotted on a logarithmic scale in figure 4. The short time dynamics of both components, reflecting a rotation less hindered by random interactions, are very similar. After 0.5 ps the diffusive regime sets in and the two correlation functions decay at different rates. The relaxation times calculated from the two linear sections are $\tau_s^{\parallel} = 0.9$ ps and $\tau_s^{\perp} = 1.4$ ps. This difference can be rationalized easily, if we look more closely at the motion of the model molecules in configurational space. The induced dipole vector will change its orientation by interaction with the other molecules via two different mechanisms:

- (a) Collision-like interactions which, by producing a torque about a molecular axis, will reorient the reference molecule i by some angle around this axis.
- (b) Reorientation and/or translational rearrangements of the surrounding molecules which change the inducing field at the location of the symmetry axis of the molecule.

Both mechanisms will affect the parallel as well as the normal component of $C_s(t)$, however, due to the absence of torques around the molecular axis in the model, no reorientations about this axis will be observed in the model liquid. Thus the

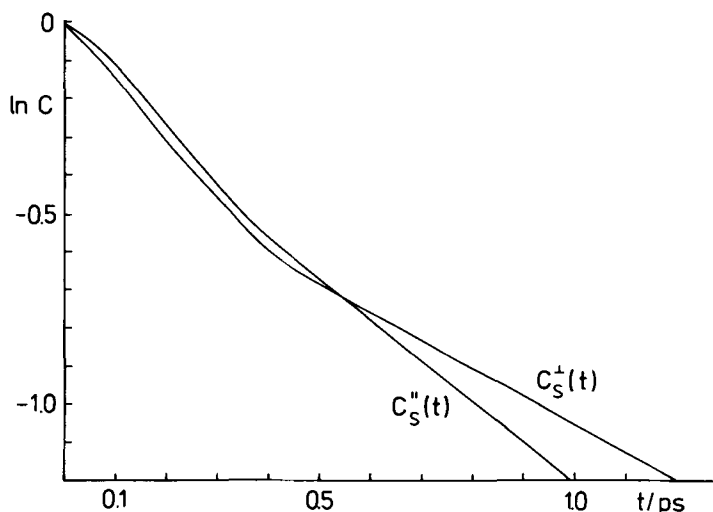


Figure 4. A logarithmic plot illustrating the anisotropy of the reference molecule reorientation as well as the environment anisotropy fluctuations.

parallel component of the induced moment will change at every type-*a* interaction having a component along the *x* and *y* axes on the molecular frame of reference. The normal component, on the other hand, will change only if the intermolecular torque is directed along a normal axis such that $\boldsymbol{\mu}(t)$ has a non-vanishing component normal to it. The two values obtained for the relaxation times of the rotational diffusion about the parallel and the normal axis show that, although the described collision effect is indeed significant, the reorientation of the inducing field (type-*b* interactions) plays a non-negligible role since if this were not the case, the ratio of the two relaxation times $\tau_s^{\parallel}/\tau_s^{\perp}$ would be equal to 2 : 1. This ratio is actually 1.6 : 1, in qualitative agreement with the estimation of the collective times made previously. This is best illustrated by the expression used to calculate the normal component

$$C_s^{\perp}(t) \cong (\alpha^{\perp})^2 \cdot [\langle \mathbf{F}_i(0) \cdot \mathbf{F}_i(t) \rangle + \langle \mathbf{u}_i(0) \cdot \mathbf{u}_i(t) \rangle \cdot \langle \mathbf{F}_i(0) \cdot \mathbf{u}_i(0) \mathbf{F}_i(t) \cdot \mathbf{u}_i(t) \rangle - \langle \mathbf{F}_i(0) \cdot \mathbf{u}_i(t) \cdot \mathbf{F}_i(t) \cdot \mathbf{u}_i(t) \rangle - \langle \mathbf{F}_i(t) \cdot \mathbf{u}_i(0) \cdot \mathbf{F}_i(0) \cdot \mathbf{u}_i(0) \rangle]. \quad (18)$$

This model explains also the observation, illustrated in figure 4, that the onset of the diffusive regime is slightly earlier for the parallel than for the normal component.

5. CONCLUSIONS

The above discussion has shown that the interaction-induced dipole correlation functions are a convenient instrument to characterize some of the details of the molecular motion in a liquid like CS₂. In order to do this, we have separated the dynamics of the liquid into a reorientation of the reference molecules, essentially a single-molecule process, and a 'environment rearrangement', both components being defined in a way we believe to be adequate for the purpose of comparing the low frequency part of the purely interaction-induced far infrared spectra to the underlying molecular dynamics. The analysis used by us is to a

certain extent similar to that used by other authors [9, 10] in that it uses the same leading terms of the multipole expansion and a similar simulation. However, in the present calculations somewhat different correlation functions are involved, by separating the effects due to single molecule reorientation from the effects we call collective and which, for the present, are not further analysed, and mainly by calculating separately the parallel and the normal components of the induced molecular dipoles. By means of this analysis we attempt to shed light from another point of view on this complex and yet unresolved dynamical problem.

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REFERENCES

- [1] BUCKINGHAM, A. D., 1959, *Q. Rev. chem. Soc.*, **93**, 183.
- [2] BOGAARD, M. P., BUCKINGHAM, A. D., PIERENS, R. K., and WHITE, A. H., 1978, *Trans. Faraday Soc. I*, **74**, 3008.
- [3] TILDESLEY, D. J., and MADDEN, P. A., 1981, *Molec. Phys.*, **42**, 1137. IMPEY, R. W., MADDEN, P. A., and TILDESLEY, D. J., 1981, *Molec. Phys.*, **44**, 1319.
- [4] SANDLER, S. I., and NARTEN, A. H., 1976, *Molec. Phys.*, **32**, 1137.
- [5] VERLET, L., 1976, *Phys. Rev.*, **98**, 159.
- [6] SINGER, K., TAYLOR, A., and SINGER, J. V. L., 1977, *Molec. Phys.*, **33**, 1757.
- [7] STEINHAUSER, O., 1981, *Chem. Phys. Lett.*, **82**, 153.
- [8] TILDESLEY, D. J., and MADDEN, P. A., 1982, *Molec. Phys.*, **48**, 129.
- [9] MADDEN, P. A., and COX, T. I., 1981, *Molec. Phys.*, **43**, 287.
- [10] MADDEN, P. A., and TILDESLEY, D. J., 1983, *Molec. Phys.*, **49**, 193.