# Collision effects in liquid CCl$_4$: A molecular dynamics study

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The trajectories of a Lennard-Jones system with the 18-6 potential reproducing the thermodynamic properties of liquid CCl$_4$ have been obtained by a molecular dynamics computer simulation at liquid densities. From these, the mean time between binary molecular collisions, the mean duration of a collision, and the force autocorrelation functions were calculated. The results display a marked discrepancy with respect to collision times estimated by cell model considerations. The result were shown to yield a consistent picture of the molecular dynamics of this system. The periodic component of the force autocorrelation function is shown to be connected to the maximum of the collision induced absorption specturm.

## I. INTRODUCTION

The molecular dynamics at liquid densities can be investigated experimentally by intermolecular spectroscopy such as collision induced absorption (CIA) and collision induced light scattering (CILS). The theoretical understanding of the intermolecular spectral features has improved in the last few years, especially in the case of very simple systems of liquid noble gases like argon or krypton. However, even in such apparently simple cases as these, some serious problems remain to be answered. Thus, the origin of both the high frequency and the low frequency regime in CILS ought to be describable in terms of an unified theory.[1] Some experimental results[2] seem to indicate that this is not yet possible.

In a study published elsewhere,[3] we advocate the opinion that the intermolecular spectral features of liquid argon can be understood in a first approximation, in terms of a simplified molecular dynamics scheme involving only two characteristic times the mean time between successive collision $\langle \tau_C \rangle$ and the mean duration of a collision $\langle \tau_D \rangle$. These times were obtained by molecular dynamics calculations on 256 spherical Lennard-Jones molecules. The present study is concerned with the question whether such a description is adequate for a molecular liquid with quasispherical molecules as CCl$_4$. To us, a realistic estimate of collision times and durations seemed useful insofar as it is relevant for such different physical processes as vibrational relaxation, dephasing and chemical reactivity in solutions. In a next step, we present a more complete molecular study of CCl$_4$ involving the time evolution of the intermolecular forces. The pertinent correlation functions are related to the memory functions in the Kubo–Mori formalism of molecular dynamics.

Since the most direct connection of our MD results of experimental quantities is provided by intermolecular spectral data obtained both from CILS and CIA, we have calculated the spectral function of the autocorrelation function (ACF) of the intermolecular forces. The importance of good estimates of collision times and durations is particularily evident in studies of vibrational relaxation.[4] Our knowledge on this point is still incomplete and thus, in many cases, we have to resort to the use of empirical pair correlations in order to obtain at best rough estimates of $\langle \tau_C \rangle$,[5,6] which are sometimes burdened with order-of-magnitude uncertainties.

## II. THE MOLECULAR DYNAMICS MODEL

The details of the MD model used have been published[3] elsewhere; therefore, only the essentials will be given here. The calculated values of $\langle \tau_C \rangle$ and $\langle \tau_D \rangle$ were mainly obtained from the binary encounters, since the frequency of ternary encounters amounted only to 1% of the former. Although we essentially have an isolated binary collision situation as a result of the computed trajectories, the system is not confined by the stringent restriction of a cell model since we simply counted the number of binary collisions occurring on the molecular trajectories. The use of a realistic spherical Lennard-Jones potential for liquid CCl$_4$ compelled us to give an adequate definition of a collision: For the purpose of our calculation, a collision is an event whereby two molecules approach each other to a distance $r_c$ smaller than or equal to a given fraction $\delta\sigma$ of the Lennard-Jones parameter $\sigma$ and then separate from each other again. Thus, the time $\langle \tau_C \rangle$ was calculated by means of the relation

$$\langle \tau_C \rangle = \left[ \frac{2}{N \cdot \tau} \int_0^\tau \sum_{\mu=1}^\nu \delta(t - t_\mu)\, dt \right]^{-1} , \qquad (1)$$

i.e., by summing the collision events as defined above over a time interval $\tau$ sufficiently large. The average duration of a collision $\langle \tau_D \rangle$ was obtained by calculating the number of time steps ($\Delta t = 10^{-14}$) between the time step at which the center–center distance $r$ of two molecules fulfills the inequality

$$r \leqslant \delta \cdot \sigma$$

and the time step at which this is no more the case. This is the numerical statistical solution of the equation

$$\langle \tau_D \rangle = \int dt \, [r_{ij}(t)] ,$$
$$t(r_{ij} \leqslant r_c) .$$

This equation defines the time $\langle \tau_D \rangle$ as an ensemble average of a path integral of the time over that part of the trajectory where the collision configuration $r_{ij} \leqslant r_c$ is the case. The integrand is parametrized with $r_{ij}$ as a parameter. Actually, due to the finite length of the

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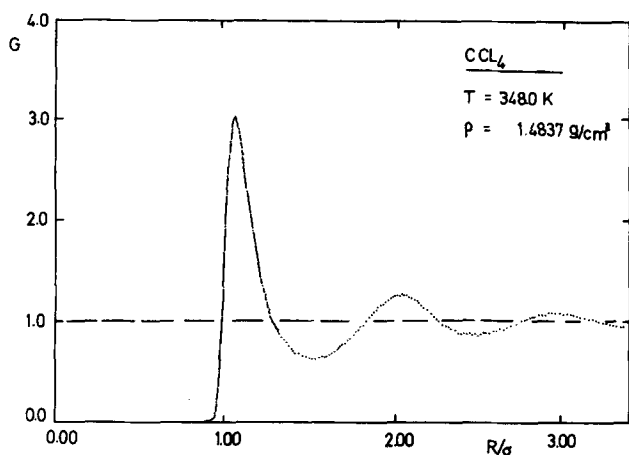[a]Author to whom requests for reprints should be addressed.

FIG. 1. Pair correlation function $g(r)$ of liquid CCl₄ at 348 K and at a density of 1.4837 g/cm³.

time steps, the integral is substituted by a summation of the time steps along the collision configuration trajectory.

Both times are parametrically dependent upon and were studied as functions of δ. The fluctuations of the intermolecular forces were studied by using the following ACF's:

$$C_{FM}(t) = \frac{\langle |F(0)| \cdot |F(t)| \rangle}{\langle |F(0)|^2 \rangle} \quad , \tag{2a}$$

$$C_{FU}(t) = \frac{\langle F_0(0) \cdot F_0(t) \rangle}{\langle F_0(0)^2 \rangle} \quad , \tag{2b}$$

$$C_{FV}(t) = \frac{\langle F(0) \cdot F(t) \rangle}{\langle F(0)^2 \rangle} \quad . \tag{2c}$$

The ACF $C_{FM}(t)$ describes the autocorrelation of the magnitude of the resultant force $|F(t)|$ exerted on a given molecule by its neighbors. In a similar way, the symbols $C_{FU}(t)$ and $C_{FV}(t)$ are used to represent the ACF of the unit vector $F_0(t)$ along the resultant force and of the total vector $F(t)$, along the resultant force, respectively. The products involved in the definitions are scalar products. These ACF's were calculated from approximately 6000 MD configurations after equilibrium of the system. The potential used was[7]

$$U(r) = \frac{n}{n-6} \cdot \epsilon \cdot \left(\frac{n}{6}\right)^{6/(n-6)} \left[ \left(\frac{\sigma}{r}\right)^n - \left(\frac{\sigma}{r}\right)^6 \right] \quad ,$$

with

$\epsilon/k = 320$ K ,

$\sigma = 5.25 \ 10^{-10}$ m ,

$n = 18$ .

The 18-6 potential which we used for computations reproduced the thermodynamic properties of liquid CCl₄ in the temperature range between 300 and 350 and at liquid densities of 1.4 to 1.6 g/cm³. These results were in perfect agreement with values obtained by a method due to Redlich and Kwong.[8-11] This is not the case for a 12-6 potential which is also commonly used and which we thus rejected.

The MD calculation of the pair distribution functions

$g(r)$ at various temperatures (300–350 K), Fig. 1 show the usual behavior of Lennard-Jones liquids. The "first neighbor shell" calculated from the MD pair distribution functions give us satisfactory coordination numbers $Z \simeq 12 - 9$ as compared to experimental values.[12-14] This good agreement permits us to use our $g(r)$ values for the calculation of the collision times by means of the equation[15]

$$\langle \tau_c^{-1} \rangle = \sqrt{2\pi r^2 (N_A/V)} \langle v \rangle g(r) \quad , \tag{3}$$

where $N_A$ and $V$ are the Avogadro number and the molar volume of the liquid and $\langle v \rangle$ is the mean molecular velocity. The pair correlation function in this equation corrects the underlying simple kinetic model for the deviation of the actual first-neighbor number density from the thermodynamic limit $N_A/V$. Equation (3) can yield meaningful results when $g(r)$ has been calculated with a sufficient accuracy at small values of $r$ between $r = \sigma$ and $r = 0.90\sigma$. Our earlier work on argon[3] confirmed the identity of the collision times by this method and the MD trajectory method when the potential used for both is good enough.

## III. RESULTS

The IBC model has been used in the form of a cell model of the liquid structure to evaluate collision times. This procedure is currently used to interpret vibrational relaxation data in the form of a somewhat refined version, in which the simultaneous motion of a given molecule and of its neighbors was taken into account.[16] In spite of the success of this model in predicting the order of magnitude of vibrational relaxation times, a significant discrepancy has to be explained, and a basic doubt as to the adequacy of a collision model founded upon a hard sphere potential has to be posted.[4] In order to shed some light into this, a comparison of collision frequencies calculated by trajectory simulations by the use of Eq. (3), and by the IBC models both with static and movable walls is given in Fig. 2. One can see that at $r_c \simeq \sigma$ the collision frequencies obtained from trajectory simulations and from the cell model with movable walls are very similar in magnitude. The cell model with fixed walls gives collision frequencies which are too low by a factor of 2 for all values of $r_c$, admitting that the molecular trajectory values are the most appropriate picture of what is going on at the molecular level.

However, the most serious discrepancy occurs in hard energetic collisions with low collision radii. In this situation, the cell model overestimates the collision frequency by more than an order of magnitude. This result is easily understood in terms of the Boltzmann distribution of the translational energy, which is needed to overcome the repulsive energy in an energetic collision. The cell model with fixed walls fails completely in describing this situation, except for a fortuitous coincidence at $r_c \simeq 0.97\sigma$. The difference between the molecular trajectory results and the values obtained by Eq. (3) is related to the quality of the intermolecular potential used in the calculation.

A second equally important quantity characteristic of the interaction between molecules in the liquid phase is
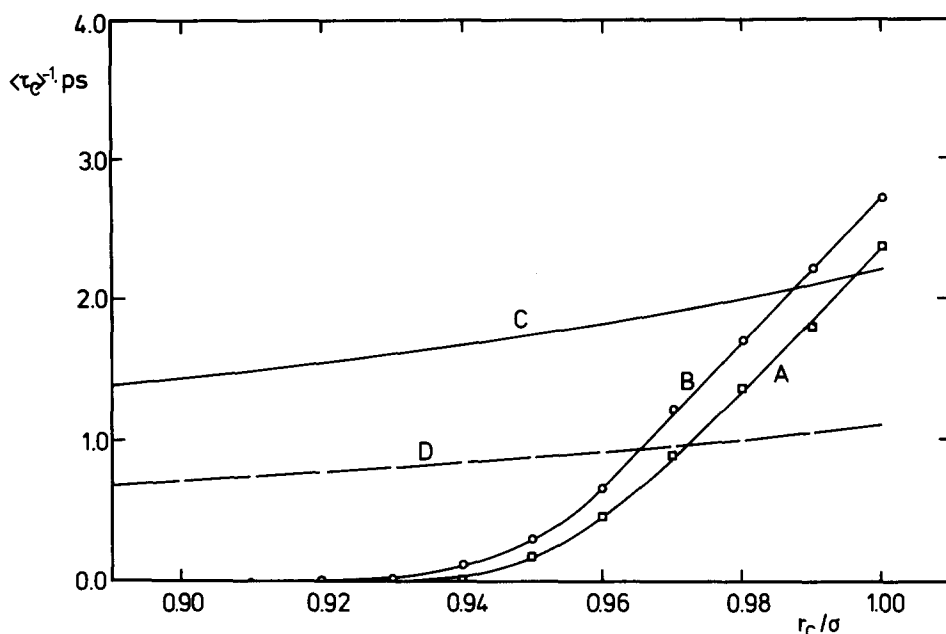
FIG. 2. Mean collision rates as a function of the reduced collision radius $r_C/\sigma$ at 300 K: (A) MD calculation based upon Eq. (3), (B) MD calculation based upon Eq. (1), (C) cell model with movable walls, (D) cell model with fixed walls.

the duration of a collision. The assumption that this latter quantity is much smaller than $\langle \tau_C \rangle$ has been frequently made[17,18] and the idea of an instantaneous collision whereby molecular velocities, rotational frequencies, and reorientations change at an infinite rate seemed to be an acceptable simplification. The situation, as viewed from the molecular dynamics viewpoint, is illustrated in Fig. 3. The duration of the collisions decrease with decreasing $r_C$ at approximately linear rate, whereas the times between collisions increase rapidly especially for small values of $r_C$. Thus, the relation $\tau_C/\tau_D$ increases from 3 to 250 in the interval $r_C/\sigma = 1$ to $r_C/\sigma = 0.94$, as indicated in the figure. This result restricts the validity of the approximation $\tau_D \ll \tau_C$ to the hard collisions with $r_\sigma/\sigma < 0.95$, where $\tau_C/\tau_D < 100$.

The idea of two characteristic times describing roughly the intermolecular dynamics is a simplification of the rather complex situation in a liquid and the next degree of sophistication requires to consider the perti-
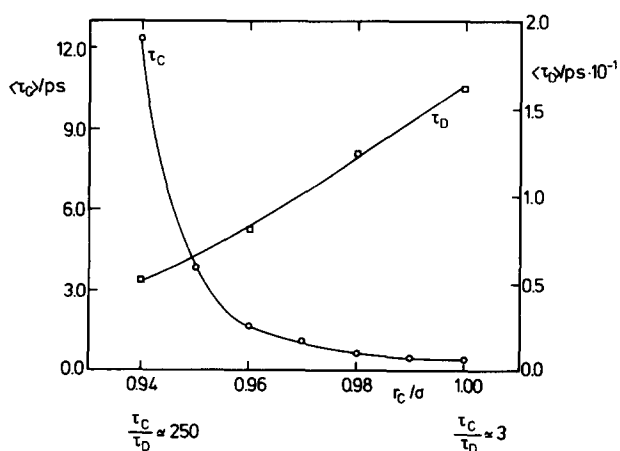
nent time correlation functions. Figure 4 shows the three force autocorrelation functions $C_{FM}(t)$, $C_{FU}(t)$, and $C_{FV}(t)$ defined in Eqs. (2a)–(2c). A remarkable feature illustrated by this figure is the fast decay of $C_{FM}(t)$ between 0 and 0.1 ps and the extremely slow decay thereafter. This is a good illustration of the slowly varying mean field upon which a fast varying collision induced force is superimposed. The shape of $C_{FU}(t)$ reflects the relative "rotation" of molecules, with respect to their environment. The quotation marks underline the situation in which central forces acting on a spherical molecule result in a rotation of a force vector which might give observable depolarization effects in polarizable molecules. The effect thus described is obviously a collective one caused by the fluctuations of the translational symmetry of the next neighbors to a given molecule. The correlation function connected to
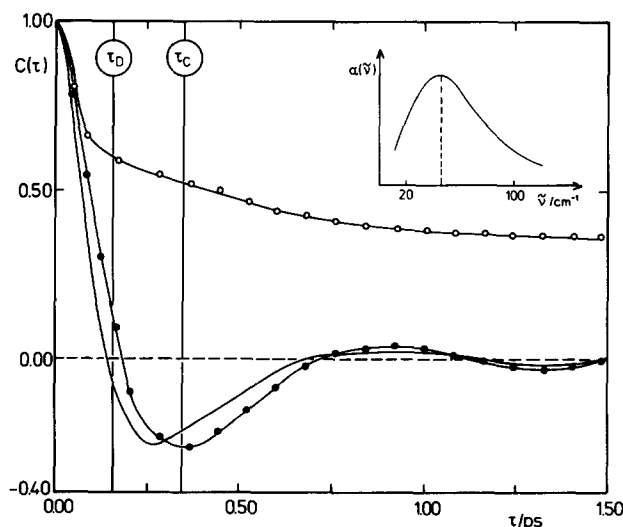


FIG. 3. Mean collision times and mean collision duration as a function of the reduced collision radius $r_C/\sigma$ of CCl₄ at 300 K.



FIG. 4. Force ACF's of CCl₄ at 300 K: o-o-o: $C_{FM}(t)$, ●-●-●: $C_{FU}(t)$, —: $C_{FV}(t)$. The two dynamical times $\langle \tau_C \rangle$ and $\langle \tau_D \rangle$ are marked on the $t$ axis. The insert illustrates the CIA spectrum of CCl₄ under the same conditions.

this is manifested in the depolarized light scattering spectrum of liquid CCl$_4$.[19,20] The total force ACF $C_{FV}(t)$ results from the superposition of the decays of the two components.

In Fig. 4 we have indicated the two times $\langle\tau_D\rangle$ and $\langle\tau_C\rangle$ for a collision radius $r_C = \sigma$. The consistency of the force ACF's with the values of $\langle\tau_C\rangle$ and $\langle\tau_D\rangle$ is evident: The time between collisions $\langle\tau_C\rangle$ is seen to be equivalent to the time at which the direction of the force vector is reversed, whereas the total force ACF has decayed to 0 after the time $\langle\tau_D\rangle$ has elapsed. This coincidence shows that the events responsible for the decay of the resultant force and the reversal of its direction are mainly the soft collisions with $r_C = \sigma$. The latter i.e., the quasiperiodic behavior of $C_{FV}(t)$ is a direct illustration of the cage effect in liquids and solutions. Actually, the molecule will leave its cage after a number of quasi-oscillations only in a collective motion in which several molecules are involved. The times characteristic for such collective motions seem to be long as compared to $\tau_C$. A lower limit of 1.5 to 2 ps can be estimated from the envelope of the $C_{FV}(t)$ curve to CCl$_4$.

In concluding, a thought should be given to the question whether the two characteristic dynamical times are consistent with the gross features of collision induced spectra. This aspect of our calculation is related to the well known fact, that the width of CIA and CILS spectra are associated with the length of time during which the induced dipoles have an appreciable value.[21] The linewidths at half-height of both spectra are related in principle by simple relations.[22,23] This time can be calculated analytically in principle for the case of gases from the range of the induced dipole responsible for the spectrum and the molecular velocity. However, we can obtain a fairly good estimate time at liquid densities from MD values for $\langle\tau_D\rangle$. The second spectral feature which can be estimated from our calculations is the position of the maximum $\bar{\nu}_M$ of the collision induced spectrum. The insert in Fig. 4 gives the CIA spectrum of CCl$_4$[24] at 300 K with $\bar{\nu}_M \simeq 45$ cm$^{-1}$ and a width $\Delta\bar{\nu} = 70$. The oscillation period as visualized in the periodic component of $C_{FV}(t)$ with a period of $T_C \simeq 0.75$ ps is in good agreement with $\bar{\nu}_M$. The spectral width is determined by the time dependence of the octopole induced dipole. As far as the translational component of this quantity is concerned, and under the assumption of the validity of the multipole expansion for such small distances occurring at molecular collision configurations, we expect the ACF of a $r^{-5}$ interaction to be the adequate description. The values of $\langle\tau_D\rangle$ given here are mainly determined by the repulsive $r^{-18}$ interaction and are clearly too short for the description of CIA spectra. Collision durations for the $r^{-5}$ interaction based ACF have been calculated in the same manner and are extensively discussed elsewhere.[25]

The conclusion which can be drawn from our calculations can be summarized briefly as follows: The dy-

namical times $\langle\tau_D\rangle$ and $\langle\tau_C\rangle$ give a simplified albeit a meaningful description of the molecular dynamics of liquid CCl$_4$. However, the calculated values of these quantities depend very sensitively upon the quality of the potential used. The force ACF's obtained by MD are related in an intuitively obvious way to $\langle\tau_D\rangle$ and $\langle\tau_C\rangle$. The values obtained for $\langle\tau_C\rangle$ were shown to be consistent with CIA spectral information and thus to have a sound physical basis. A spherical interaction seems to be sufficient to reproduce the collision times and eventually the collision durations for tetrahedral nonpolar molecules such as CCl$_4$.

## ACKNOWLEDGMENTS

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