Application of the mode matching model to V-T relaxation in liquid CCl₄

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Application of the mode matching model to $V-T$ relaxation in liquid $\text{CCl}_4$

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The mode coupling approach has been used to calculate the energy transition probability between vibrational and translational modes of colliding molecules in liquid $\text{CCl}_4$. This calculation is used to interpret Brillouin scattering and molecular dynamics simulation results in terms of the angle of approach of colliding molecules. By this approach we rationalize the dependence of vibrational relaxation times upon the symmetry of the modes involved and upon the temperature.

1. INTRODUCTION

Our knowledge of the details leading to inelastic collisions in liquids of the form $V'\rightarrow V$ and $V\rightarrow T$ where $V'$, $V$ designate vibrational energy levels of two molecules and $T$ the translational reservoir is still incomplete. This is due to the random character of the pertinent events in liquids in time and in configuration space. As a consequence of this, the experimental facts at our disposition are essentially statistic in that sense that they represent ensemble averages of a system of strongly interacting molecules. This intrinsic smearing of states and hence of the processes entails a risk of an overinterpretation of the experimental data by overestimating their actual resolving power with respect to the models used. In the field of energy relaxation in liquids we are now in a position to study the dependence of transition probabilities of different molecules by means of time resolved spectroscopy [1] and by Brillouin spectroscopy [2, 3]. On the other hand, the theoretical models [4–6] commonly used have been mainly restricted to collinear collisions [7, 8] of diatomics or to collisions with molecules whose vibration is described by the breathing sphere model [9, 10]. The use of such models although representing the gross features of the experimental data is unrealistic for most polyatomic liquids since the actual symmetry of the relevant vibration is completely neglected. This situation has been remedied to a certain extent by the development of the mode-matching model (MM) [11, 12] which avoids the stringent assumption underlying the breathing sphere model and yields a mode-specific reduction of the transition probabilities. This theory opens the door to a more specific description of intermolecular collisions since the symmetry of the mode whose relaxation is monitored experimentally is directly connected to the geometry of approach of the colliding molecules.

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2. THEORY

Vibrational relaxation is usually treated by separating the experimental relaxation time $\tau$ in a product of the collision rate $Z$ and the transition probability $P_{ab}$, where $a$ and $b$ stand for the vibrational modes of the two colliding molecules.

$$\tau^{-1} = P_{ab} \cdot Z \cdot \theta_{ab} \tag{1}$$

$\theta_{ab}$ takes care of the population of the modes and is given by

$$\theta_{ab} = 1 - \exp \left(-\frac{h\nu_a}{k_B T}\right)$$

where $\nu_a$ is the frequency of the initial mode $a$.

The separability assumption underlying equation (1) can be questioned on the ground that the separation of molecular trajectories in the liquid in such a fashion as to obtain distinct independent collisions amounts to using features of a gas model for the liquid state. This objection is essentially justified for the case of events such as phase relaxation [13] occurring at 'soft' collisions and less for vibrational relaxation [14] requiring hard, hence less frequent, collisions of much shorter durations and which thus are more separated from each other.

The transition probability between the two modes $a$ and $b$ of the two colliding molecules $A$ and $B$ lead to the simultaneous changes in the quantum state $i \rightarrow j$ and $k \rightarrow l$. The transition probability $P_{k-l}^{i-j}(a, b)$ thus specified is again separated into a product of steric factors $P_0(a), P_0(b)$; vibrational factors $V_a, V_b$, characterizing the specific vibration levels involved and an energetic factor which depends upon the intermolecular energy parameters $\phi_0, r_0$, the reduced mass, $\mu$, and the exoenergeticity, $\Delta E$, of the quantum levels with respect to the translational reservoir

$$P_{k-l}^{i-j}(a, b) = P_0(a)P_0(b)V_a^2 V_b^2 \exp \left(\frac{\Delta E}{kT}\right) \int_0^{\infty} f(u) \, du, \tag{2}$$

$f(u)$ is the distribution of the relative velocity of approach $u$ of the molecules $A$ and $B$ illustrated in figure 1. $f(u)$ is given by

$$f(u) = \left(u/\alpha^4\right)(r_C/r_0)^2 \exp \left(-\frac{\mu u^2}{2kT}\right) \left[\frac{\exp \left(\frac{l-l'}{2}\right)}{1-\exp \left(\frac{l-l'}{2}\right)}\right], \tag{3}$$

with

$$l = 4\pi^2 \frac{\mu u}{\alpha h}, \quad l' = 4\pi^2 \frac{\mu \nu}{\alpha h},$$

$\nu$ is the relative velocity after the collision, $\alpha$ is an exponential repulsion parameter and $(r_C/r_0)$ is a reference factor relating the distance of closest approach, $r_C$, and the distance at the energy zero, $r_0$.

The details of the inelastic interaction of interest are contained in the vibrational factors $V_a$ and $V_b$ and in the steric factors $P_0(a)$ and $P_0(b)$. In order to underline the scope of the following calculation we write

$$P_{k-l}^{i-j}(a, b) = V_a^2 V_b^2 F_{tr} \tag{4}$$

where $V_a^2 = P_0(a)P_0(b)V_a^2 V_b^2$ and $F_{tr}$ is the energetic factor which has been explicitly calculated with the Schwartz, Slawsky, Herzfeld, Tanczos (SSHT) formalism by using a 18-6 Lennard-Jones potential [15] ($\epsilon_0 = 325$ K, $r_0 = 5-25$ Å).
and which will not be further analysed in this context. The main point at this stage of our calculation is to specify the way to handle the interaction of two polyatomic molecules. One can thus assume that $A$ and $B$ interact via pairs of surface atoms $s_a$ and $s_b$ and one can use the following form for this interaction

$$V = V_0 \exp \left[ \alpha \left( -r + \sum_a \Delta r_{sa}(a) + \sum_b \Delta r_{sb}(b) \right) \right].$$  

(5)

$\Delta r_{sa}$ and $\Delta r_{sb}$ are the lengths of the cartesian displacements of the two surface atoms from their equilibrium positions due to the normal vibrations $Q_a$ and $Q_b$. The two sums are over all normal vibrations of the two molecules. The vibrational factors are then calculated by calculating the average over the transition probabilities of all surface atoms. Under these assumptions we obtain

$$V_{sa}^2 = P_0(a) \left( \frac{i + \frac{1}{2} \pm \frac{1}{2}}{2\gamma a} \right) \left( v_a^2 / N_s \right) \sum A_{sa}^2,$$

where $N_s$ is the number of surface atoms and $\gamma_a = 4\pi v_a / h$. The quantities $A_{sa}$ are the internal motion coefficients derived by means of the normal coordinate analysis [16–18]. The breathing sphere model assumes the displacements $\Delta r$ to be collinear to the direction of approach. Since this cannot be the case for all kind of modes, the steric factors $P_0(a)$ and $P_0(b)$ are introduced to compensate for the mode mismatching. Since our concern in this paper is centred around collision-induced $T-V$ transitions we have to consider the mode mismatch between the mode, whose activation/deactivation is experimentally observed and the relative translational motion of the colliding molecules. This mismatch is excluded from the calculation of the vibrational factors in the breathing sphere model because that model assumes the cartesian displacements $\Delta r$ to be collinear with the line of approach.

In the MM model the angular relations between the line of approach and the normal-mode displacements of the atoms involved in the contact are taken explicitly into account. This leads to an interaction of the form

$$V = V_0 \exp \left[ -\alpha \left( r - \sum_a n \cdot x_{sa} - \sum_b n \cdot x_{sb} \right) \right].$$  

(6)
This relation reduces to the form (5) if the unit vector on the line of approach \( \mathbf{n} \) is parallel to the cartesian displacement vector \( \mathbf{x}_s(a) \). Introducing the normal coordinates and calculating the pertinent matrix elements in the same approximation as previously and carrying out the averaging over the surface atoms \( s \) and \( s' \) and over the directions \( \Omega \) one obtains for \( V_g \) the following expression

\[
V_{gab}^2 = \frac{(ia + \frac{1}{2} \pm \frac{1}{2}) (ib + \frac{1}{2} \pm \frac{1}{2})}{2\gamma a} \left[ \sum \frac{1}{\Omega_{0b}} \int_\Omega u_{sa} u_{sb} u_{sa} u_{sb} d\Omega \right].
\]

In this expression \( \Omega_{0b} \) is the solid angle (figure 2) in which the direction vector must lie so that an atom–atom collision be sterically possible. The integration is extended over this solid angle to include all collision events of the two surface atoms \( s \) and \( s' \). The integrand contains the expansion coefficients \( u_{sa}(n) \) of the projection \( \mathbf{x} \cdot \mathbf{n} \) of the cartesian displacements \( \mathbf{x} \) on the line of approach in terms of normal modes

\[
\mathbf{x} \cdot \mathbf{n} = \sum_a u_{sa}(n) Q_a.
\]

The use of this model has led to the calculation of transition probabilities for the \( \nu_6-\nu_3 \) transition [19] in \( \text{CH}_3\text{Cl}-X(X=\text{He, Ne, Ar, Kr, Xe}) \) collision which represent a substantial improvement over the breathing sphere results.

3. Calculations for the Vibrational Relaxation of \( \text{CCl}_4 \)

We have been able in a previous study [20–22] to correlate unambiguously the vibrational relaxation observed in the dispersion of the Brillouin linewidth in liquid \( \text{CCl}_4 \) to the transition between the \( \nu_2 \) mode of this molecule and the translational reservoir. In this experiment we have obtained the relaxation times \( \tau \) of this transition as a function of temperature. We have furthermore

\[\text{Figure 2. Collision geometry of two tetrahedral molecules.}\]
V–T relaxation in CCl₄

Table 1. Comparison of relaxation and collision rates in CCl₄.

<table>
<thead>
<tr>
<th>T/°C</th>
<th>τ⁻¹/ps⁻¹ × 10⁻²</th>
<th>Z/10⁻¹²</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.53</td>
<td>0.94</td>
</tr>
<tr>
<td>25</td>
<td>0.62</td>
<td>1.11</td>
</tr>
<tr>
<td>45</td>
<td>0.67</td>
<td>1.70</td>
</tr>
<tr>
<td>65</td>
<td>0.65</td>
<td>1.93</td>
</tr>
</tbody>
</table>

Relative change 23 per cent 100 per cent

calculated by a molecular dynamics simulation [23, 24] the collision rates Z in liquid CCl₄ as a function of the temperature. This calculation was performed with the same 18-6 Lennard-Jones potential mentioned above and by defining the collisions as the events in which two molecules approach to a distance equal or smaller to the equilibrium distance $r_0 = 1.089 \, r_0$. Table 1 lists the experimental relaxation rates $\tau$ and the collision rates $Z$ obtained by the simulation at four temperatures. In this table we see that whereas the relaxation rate increases by little more than 20 per cent between 5 and 65°C the collision rate decreases by more than 10 per cent in this range indicating a significant increase of the transition probability with increasing temperature. The theoretical transition probabilities should then conform to this temperature dependence. Under the simplified conditions of a V–T transition of a single normal mode of one molecule, the collision partner changing only its translational energy, the factor $V_g$ takes the form

$V_g^2 = P_d(a) V_a^2$.

Table 2. Relaxation data obtained by calculation by means of the breathing sphere and the mode matching models.

<table>
<thead>
<tr>
<th>T/°C</th>
<th>$F_{tr}$</th>
<th>$\theta_a$</th>
<th>$V_{a(b)}^2$</th>
<th>$V_{a(b)}^2 \times 10^{-10}$</th>
<th>$\tau_{a(exp)}^{-1} \times 10^{-10}$</th>
<th>$\delta / \text{grad}$</th>
<th>$V_{a(exp)}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.041</td>
<td>0.68</td>
<td>0.017</td>
<td>0.29</td>
<td>0.53</td>
<td>50.7</td>
<td>0.030</td>
</tr>
<tr>
<td>25</td>
<td>0.060</td>
<td>0.65</td>
<td>0.016</td>
<td>0.36</td>
<td>0.62</td>
<td>47.4</td>
<td>0.027</td>
</tr>
<tr>
<td>45</td>
<td>0.085</td>
<td>0.63</td>
<td>0.016</td>
<td>0.48</td>
<td>0.67</td>
<td>42.9</td>
<td>0.022</td>
</tr>
<tr>
<td>65</td>
<td>0.12</td>
<td>0.60</td>
<td>0.016</td>
<td>0.62</td>
<td>0.65</td>
<td>32.2</td>
<td>0.017</td>
</tr>
</tbody>
</table>

We first calculate $V_a^2$ in the breathing sphere model. The results for four temperatures are given in table 2 (4th column). Obviously the temperature dependence is very weak. The calculation of the translational factor $F_{tr}$ and of the population factor $\theta_a$ are straightforward and the results are displayed in columns 2 and 3 of table 2. We thus can calculate, by means of the equation

$\tau^{-1} = Z F_{tr} \theta_a V_g^2$, (8)

the relaxation rates in the breathing sphere model (neglecting the steric factor). The result, which is displayed in column 5 of table 2 is of the right order of magnitude but displays a much stronger increase with temperature than the experimental values given in the next column. Our suggestion is that this
can be remedied by using the more realistic mode-matching model which yields values of \( V_{g2} \) which depend upon the mean angle of approach.

In order to apply the MM model we start with equation (7) which can be specified for a tetrahedral molecule whose orientational parameters are illustrated in figure 2. We obtain

\[
V_{g2} = \left( \frac{h}{8\pi^2} \right) \left( \alpha_{g2}^2 / N_n \right) \left( 1 / \Omega_{0n} \right) \sum_{i=1}^{4} \left[ \pi (A_{x_i}^2 + A_{y_i}^2) \right. \\
\left. \times \left( \frac{1}{18} \cos 3\theta - \frac{3}{4} \cos \theta + \frac{3}{4} \right) - (2\pi/3)A_{z_i}^2 (1 - \cos \theta) \right].
\]

(9)

Thus the equation given by the mode matching model is cast into a form enabling us to obtain \( V_{g2} \) as a function of the angle \( \theta \). The internal motion coefficients \( A_{x_i}, A_{y_i}, \) and \( A_{z_i} \) are obtained by a transformation in a cartesian system with the \( Z \) axis in the direction of the intermolecular centre-to-centre line, \( i \) being the surface atom index.

In order to fit the experimental data to the MM model, we calculate for each temperature the angle \( \bar{\theta} \) which satisfies equations (8) and (9) by using the experimental values for the relaxation rate \( \tau^{-1} \). We thus obtain \( V_{g2} \) and hence an angle \( \bar{\theta} \) as a function of temperature as displayed in table 2. In this table we see that now \( V_{g2} \) is a strongly decreasing function of the temperature and that this entails a decrease of \( \bar{\theta} \) by almost 40 per cent between 5 and 65°C. The other factors in (9) being only weakly temperature dependent we can conclude that the vibration factor decreases at higher temperatures mainly as a consequence of the decrease of \( \bar{\theta} \). The angle \( \bar{\theta}(T) \) is the angle of collision under which most of the transitions takes place. The collision rate as a function of the angle of approach \( \bar{\theta} \) depends, (a) on the probability density of collision \( P(\bar{\theta}) \) for a given angle and (b) on the efficiency of the collision \( Q(\bar{\theta}) \) under a given angle. The factor \( V_{g2}^{(\text{exp})} \) describes quantitatively the collision efficiency whose dependence on the angle of approach is given between 0 and 90° by figure 3. As we see, \( V_{g2}^{(\text{exp})} \) is zero at \( \bar{\theta} = 0 \) and has a maximum at \( \bar{\theta} = 90° \). The probability function \( P(\bar{\theta}) \) on the other hand is expected to have a maximum at \( \bar{\theta} = 0 \) and to decrease at larger \( \bar{\theta} \). Thus the overall collision rate will be maximal for some angle \( \bar{\theta} \) given by the values in table 2.

Finally we must rationalize the temperature dependence of \( \bar{\theta} \). Within the framework of the model, \( V_{g2}^{(\text{exp})} \) is only weakly temperature dependent via \( \alpha_{g2}^2 \) which changes by 2 per cent in the temperature range considered. Thus the main temperature dependence in the relaxation rate \( \tau^{-1} \) should come

![Figure 3](https://example.com/figure3.png)

**Figure 3.** Angular dependence of the vibrational factor \( V_{g2} \) of the \( \nu_2 \) mode.
from the term $P(\theta)$ and can be traced back to the change of configuration of 
the liquid with temperature. Our result might imply that at low temperatures 
the interlocked parallel configuration is more probable leading to a broader 
shape of $P(\theta)$. With increasing temperature the molecules are less fixed into 
the parallel position thus increasing the chance of collisions in which the C–Cl 
axis is oriented along $n$ leading to a more pronounced peak around $\theta = 0$ in 
$P(\theta)$. Thus the angle $\theta$ under which most of the transitions occur is shifted 
toward smaller values.

In concluding we want to underline that the present interpretation of our 
vibrational relaxation data based upon the MM model gives us some insight 
into the influence of the configuration of the liquid on the $V$–$T$ relaxation of a 
specific vibrational mode i.e. the $v_3$ mode with the $E$ character. The vibrational 
factors as calculated on this basis are strongly mode-specific and thus the 
activation/deactivation of a given mode depends upon the mean geometry of 
approach. Our calculation explains the observed temperature dependence 
of $\tau^{-1}$ in terms of this concept instead of attempting to correct the temperature 
dependence of the translational factor.

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References

Gases and Liquids (J. Wiley).