Rotational Dynamics of Chiral Molecules

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A theory of the rotation (R) - translational (T) motion of chiral molecules is developed, and various RT and orientational correlation functions are calculated. It is demonstrated that the difference between the RT dynamics of enantiomer and racemic mixtures is a direct manifestation of the combined effect of the RT coupling and violation of the parity invariance.

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1 Introduction

Chiral molecules have no center of inversion and exist as mirror-image pairs, known as enantiomers. An equimolar mixture of these enantiomers is a racemic mixture. It has been known for a long time that physical properties of some enantiomer liquids and racemic solutions differ considerably. For instance, racemic lactic acid melts at 291K, the enantiomers at 326K (see, e.g., [1]). It was however demonstrated more recently, both via computer simulations [1, 2, 3, 4, 5, 6, 7, 8] and spectroscopic polarization experiments on optically active molecules [6, 7], that rotational dynamics of racemic mixtures differed from that of pure liquids of left and right enantiomers. To our knowledge, there has been no theory of rotational and orientational relaxation of chiral molecules explaining this phenomenon. The point is that such a theory, as it has been emphasized elsewhere [1, 2, 3, 4, 5, 6, 7, 8] and will become evident further, must simultaneously and correctly treat both rotational (R) and translational (T) motions, and also their coupling. On the other hand, the majority of the contemporary theories of rotational relaxation in gases and liquids relies upon the assumption, that R and T motions can be considered separately [9, 10]. Of course, there exists a large amount of literature devoted to the combined RT diffusion (see, e.g., [11, 12] and references cited therein). However these approaches are valid in the hindered rotation limit and completely ignore relaxation of linear and angular velocities. In addition, these theories are concentrated on calculations of the grand RT diffusion tensors for some specific molecular shapes (ellipsoids, long rods, arbitrary rigid N-bead species, etc.) but do not explicitly address the problem of the difference of RT relaxation in enantiomer and racemic liquids. The only theoretical approach available for describing RT relaxation of chiral molecules is that based on the generalized Enskog theory [13]. However the explicit calculations in [13] were limited to a few simplest correlation functions (CFs) for chiral "rough screwballs" and "partially rough spheres", and no further efforts in this direction were reported. The aim of the present work is to outline the way for constructing such a theory. In order to simplify the presentation, we restrict ourselves to chiral species having spherical inertial symmetry. Although such molecules look somewhat artificially, one should note that a fundamental chiral molecule, CHBrClF (bromochlorofluoromethane), has tetrahedral symmetry. Also, as it has been pointed out in [14], the RT coupling in a fluid of spherical molecules can considerably be greater than that, e.g., in a fluid of planar asymmetric tops. Moreover, the consideration of spherical tops allows us to derive simple analytical formulas for various CFs of interest, and a good deal
of these formulas is also correct for symmetric tops. Generalization of our approach to asymmetric top molecules is quite straightforward.

Note that dimensionless variables are used throughout the article. Velocity $V$ is measured in units of $\sqrt{kT/m}$, angular momentum in units of $\sqrt{I/kT}$, and time in units of $\sqrt{I/(kT)}$. Here $m$ and $I$ are, respectively, the mass and the main moment of inertia of the molecule, and $k$ is the Boltzmann constant. In these variables, the R and T equilibrium Boltzmann distributions are written as follows:

$$\rho_{eq}(V) = (2\pi)^{-3/2} \exp\{-V^2/2\},$$  \hspace{1cm} (1)

$$\rho_{eq}(J) = (2\pi)^{-3/2} \exp\{-J^2/2\}. $$  \hspace{1cm} (2)

## 2 Kinetic equations for chiral molecules

It is the conventional practice to describe R and T relaxation in terms of kinetic equations [9, 10]. In paper [15], we proposed a RT generalization of the Keilson-Storer (KS) collision kernel, which allowed us to describe the RT coupling. The kernel reads

$$T_\pm(V, J|V', J') = (2\pi)^{-3} \exp\{-\frac{s^2(J - \gamma_J J')^2}{2(1 - \gamma_J)}\}$$

$$- \frac{c^2(V - \gamma_J V')}{2(1 - \gamma_J^*)} + 2sc((\gamma_J - \gamma_J)J)(V - \gamma_J V')$$

$$- \frac{c^2(\gamma_J - \gamma_J)J^2 + s^2(\gamma_J - \gamma_J)J^2}{2(1 - \gamma_J^*)}$$

$$\pm 2sc(\gamma_J - \gamma_J)J((V - \gamma_J V')^2) \right\}.$$  \hspace{1cm} (3)

It is the conditional probability density function that the molecule possesses the velocity $V$ and the angular momentum $J$ just after an instantaneous collision, provided these variables just before the collision were $V'$ and $J'$ (the meaning of the label $\pm$ will become clear a bit later). This kernel obeys normalization

$$\int dV dJ T_{\pm}(V, J|V', J') = 1$$  \hspace{1cm} (4)

and detailed balance

$$T_\pm(V, J|V', J')\rho_{eq}(V')\rho_{eq}(J) =$$

$$T_\pm(V', J'|V, J)\rho_{eq}(V)\rho_{eq}(J).$$  \hspace{1cm} (5)

Kernel (3) contains three basic parameters: $-1 \leq \gamma_J \leq 1$, $-1 \leq \gamma_V \leq 1$, and $-1 \leq c \leq 1 (s^2 + c^2 = 1)$. The parameters are responsible, correspondingly, for the rate of the angular momentum change, the rate of the velocity change, and the RT coupling. Any collision kernel, suitable for describing the RT relaxation of non-chiral molecules, must be invariant under the time and parity reversal [8]. The former requirement reads as $V \rightarrow -V$, $J \rightarrow -J$. It leaves Eq. (3) unchanged. However the latter transformation $V \rightarrow -V$, $J \rightarrow J$ frustrates the invariance: the so-obtained kernel differs with that given by Eq. (3) by the substitution $\pm \rightarrow \mp$. In order to conform the kernel for parity invariance, we proposed to use its symmetrized form [15]. One should however realize that the parity invariance is violated for chiral molecules. So, kernel (3) does describe collisions of chiral molecules. This immediately becomes evident, if one calculates the averaged values of the velocity and angular momentum just after a collision:

$$< J > = (s^2\gamma_V + c^2\gamma_J)J' \pm sc(\gamma_J - \gamma_V)V',$$  \hspace{1cm} (6)

$$< V > = (s^2\gamma_V + c^2\gamma_J)V' \pm sc(\gamma_J - \gamma_V)J'.$$  \hspace{1cm} (7)

Therefore, the signs $\pm$ in Eq. (3) correspond to the left and right enantiomers. It is to be remarked that it is tacitly assumed in writing Eq. (3) that the collision efficiencies $(\gamma_J, \gamma_V, c)$ are the same for "+" and "−" enantiomers. There exists a possibility of the so-called chiral discrimination, that the dynamic parameters can slightly (within 0.1 %) be different, e.g., for "++" and "+-" colliding enantiomers [6]. This effect is however too small to explain actual differences that are observed in enantiomer and racemic mixtures, and it is not taken into account at the present investigation.

Let us further introduce the quantities $\sigma_{\pm}$, which are the relative numbers of $\pm$ enantiomers in the solution, so that $\sigma_+ + \sigma_- = 1$. The racemic mixture is recovered when $\sigma_+ = \sigma_- = 1/2$. Such a
situation directly corresponds to the symmetrized collision kernel studied in [15]. Since the probability of a collision of the molecule under study with the \( \pm \) buffer enantiomer is proportional to \( \sigma_\pm \), the kinetic equation governing the RT relaxation can be written as follows:

\[
\partial_t \rho(V, J, t) = -z_c \rho(V, J, t) + z_c \int dV' dJ' \left\{ \sigma_+ T_+(V, J|V', J') + \sigma_- T_-(V, J|V', J') \right\} \rho(V', J', t)
\]

This is the equation which will be used in all the subsequent calculations.

3 Rotational relaxation

Starting from Eq. (8), one can analytically calculate various RT CFs. To do this, one might multiply Eq. (8) by quantities like \( J \) and \( V \) and perform integrations over \( J \) and \( V \). This procedure reduces the task to the solution of the system of linear differential equations. As the result, one arrives at the following explicit expressions for CFs of angular momenta, linear velocities and mixed RT CFs:

\[
C_J(t) = \frac{\nu_V}{\nu_V - s_2/s_1} \exp\{-s_1 t\} - \frac{\nu_J}{\nu_J - s_2/s_1} \exp\{-s_2 t\}, \quad (9)
\]

\[
C_V(t) = \frac{\nu_J}{\nu_J - s_2/s_1} \exp\{-s_1 t\} - \frac{\nu_V}{\nu_V - s_2/s_1} \exp\{-s_2 t\}, \quad (10)
\]

\[
C_{JV}(t) = \frac{\nu_J}{\nu_J - s_2/s_1} \exp\{-s_1 t\} - \frac{\nu_V}{\nu_V - s_2/s_1} \exp\{-s_2 t\}, \quad (11)
\]

Here

\[
s_{1,2} = [\nu_J + \nu_J \pm \sqrt{(\nu_J - \nu_V)^2 + 4\lambda^2}]/2; \quad (12)
\]

\[
\nu_J = z_c(1-s^2\gamma_V-c^2\gamma_J), \quad \nu_V = z_c(1-c^2\gamma_V-s^2\gamma_J),
\]

\[
\lambda = z_c sc(\sigma_+ - \sigma_-)(\gamma_J - \gamma_V). \quad (13)
\]

In the pure liquid of "+" or "-" enantiomers (\( \sigma_+ = 1, \sigma_- = 0 \) or \( \sigma_+ = 0, \sigma_- = 1 \)) CFs (9) and (10) are biexponential and identical for \( \pm \) enantiomers, but mixed CFs (11) are of different signs. This behaviour was revealed via computer simulations [1, 2, 3, 4, 5, 6, 7, 8]. It was automatically reproduced in our model. In the racemic mixture (\( \sigma_+ = \sigma_- = 1/2, \lambda = 0 \)) the angular momentum (9) and linear velocity (10) CFs decay strictly exponentially, with the corresponding relaxation frequencies \( \nu_J \) and \( \nu_V \), and mixed RT CF (11) is identically zero. The latter observation is a direct consequence of the fact that, in the racemic mixture, "+" and "-" contributions into CF (11), being of different signs, reconcile each other yielding zero. This must be so according to the simple parity invariance arguments [8]. One can immediately get the expressions for the integral relaxation times of these CFs:

\[
\tau_J = \int_0^\infty dt <\frac{J(0)J(t)}{J^2}> = \frac{\nu_V}{\nu_J \nu_V - \lambda^2}; \quad (14)
\]

\[
\tau_V = \int_0^\infty dt <\frac{V(0)V(t)}{V^2}> = \frac{\nu_J}{\nu_J \nu_V - \lambda^2}; \quad (15)
\]

\[
\tau_{JV} = \int_0^\infty dt <\frac{J(0)V(t)}{\sqrt{J^2 V^2}> = \frac{\lambda}{\nu_J \nu_V - \lambda^2}. \quad (16)
\]

In the racemic mixture, \( \tau_J = 1/\nu_J, \tau_V = 1/\nu_V, \tau_{JV} = 0 \). By comparing the RT dynamics of molecules in chiral solutions and racemic mixtures one might take into account the following. Let us consider two mixtures that differ by the concentration of "+" and "-" enantiomers, but otherwise are the same. Keeping in mind that parameters \( \nu_J \) and \( \nu_V \) are entirely determined by the collision dynamics, one concludes that these are identical for the two hypothetical mixtures. So, the difference in the RT dynamics stems entirely from parameter \( \lambda \). If one of our liquids is racemic and other is enantiomer, one immediately concludes from Eqs. (9, 10) and (14-16) that

\[
C_J^{rac}(t) < C_J^{enant}(t), \quad C_V^{rac}(t) < C_V^{enant}(t); \quad (17)
\]
where the superscripts ”rac” and ”enant” stand for racemic and enantiomer mixtures. To put it differently, rotational relaxation in a racemic mixture runs faster than that in a chiral one. This conclusion is totally supported by the results of computer simulations of liquid 1,1-chlorofluoroethane (1,1-C₂H₄FCl), 3-methylcyclohexane, and bromochlorofluoromethane (CHBrClF) [1, 2, 3, 4]. It is apparent from Eq. (12) that the roots $s_{1,2}$ are real and positive. So, one arrives at the important conclusion: CFs (9-11) never exhibit an oscillatory behaviour, which is predicted by stochastic equations with cross RT terms [8, 16, 17]. So, the RT coupling is not a reason for oscillations of the angular momentum CF (OCF) of two spherical molecules, these look like as follows:

\[
\tau^{\text{rac}}_J < \tau^{\text{enant}}_J, \quad \tau^{\text{rac}}_V < \tau^{\text{enant}}_V,
\]  

(18)

According to the Greene-Kubo formulas, the diffusion coefficient

\[
D \equiv \tau_J.
\]  

(22)

Eq. (21) is also easily derivable from Eq. (19). The so-called Hubard relation for the orientational relaxation time $\tau^{\Omega,j}$ is immediately derived from Eqs. (20-22) [9, 10, 20]:

\[
\tau^{\Omega,j} \equiv \int_0^t dt \delta^{\Omega,j}_J(t) = \frac{1}{j(j+1)\tau_J}.
\]  

(23)

Now we are in the position to specialize the above general results to the orientational relaxation of chiral molecules in the hindered rotation limit. It is a direct consequence of Eq. (20) that the quicker is rotational relaxation (i.e., the smaller is CF $C_J(t)$), the slower is orientational relaxation (i.e. the greater is OCF (19)). In conjunction with Eqs. (17) and (18) this allows one to arrive at the conclusion that orientational relaxation, as distinct from rotational relaxation, runs more slowly in racemic mixtures than in enantiomer ones:

\[
G^{\text{rac}}_J(t) > G^{\text{enant}}_J(t).
\]  

(24)

In terms of orientaional relaxation times (23) this statement can be written as follows:

\[
\tau^{\text{rac}}_J > \tau^{\text{enant}}_J.
\]  

(25)

On trying to verify predictions (24) and (25) against simulation results one reliably notifies that these hold true for 3-methylcyclohexane [1]. However, the opposite inequality $G^{\text{rac}}_J(t) < G^{\text{enant}}_J(t)$ was obtained for liquid 1,1-chlorofluoroethane [2, 3]. This is quite surprising. The point is that Eqs. (24) and (25) directly originate from Eqs. (17) and (18), respectively, with an additional assumption that the first cumulant (19) or diffusion (20) equations describe orientational relaxation adequately. Provided Eqs. (17) and (18) are the case for liquid 1,1-chlorofluoroethane, one has to conclude that simplified diffusion and/or first cumulant formulas are too crude for treating orientational relaxation in this liquid. However, as a rule, Eqs. (19) and (20) are

4 Oriental relaxation

Let $\vec{\mu}_1$ and $\vec{\mu}_2$ be two arbitrary unit vectors fixed in a molecule. It is the standard and very general result [9, 10, 20] that orientational CF (OCF) of two irreducible tensors of rank $j$

\[
< P_J(\vec{\mu}_1(t)\vec{\mu}_2(t)) > \equiv \sum_{k,m=-j}^j D^{j}_{km}(\vec{\mu}_1(t))D^{j}_{m0}(\vec{\mu}_2) (21)
\]  

(19)

$P_J(\vec{\mu}_1\vec{\mu}_2)$ is the Legendre polynomial, $D^{j}_{m0}(\vec{\mu}_1)$ is the Wigner function) is described in the hindered rotation limit by the first cumulant formulas. For spherical molecules, these look like as follows

\[
G^{j}_{km}(t) = G^{j}(t)\delta^{j}_{km},
\]  

(19)

\[
G^{j}(t) = \exp\{-j(j+1)\int_0^t dt' C_J(t')\}.  
\]  

(20)

Here $C_J(t)$ is the angular momentum CF. At a long enough time interval $t \gg \tau_J$, Eq. (19) reduces to the simple exponential diffusion [9, 10, 20]

\[
G^{j}(t) = \exp\{-Dj(j+1)t\}.  
\]  

(21)
roughly correct in reproducing molecular reorientation in liquids [9, 10, 20]. It is our opinion that more probable explanation for \( G_{\text{rac}}^J(t) < G_{\text{enant}}^J(t) \) is the following. In liquid 1,1-chlorofluoroethane, \( C_J(t) \) exhibits pronounced oscillatory sign-alternating behaviour and persists for a long enough time interval. This makes an accurate evaluation of the angular momentum relaxation time \( \tau_J \) problematic.

Computer simulations for 1,1-chlorofluoroethane revealed that Eqs. (17) were correct at short enough times (\( \leq 1 \text{ps} \)). It is not unrealistic to assume that this is not so at longer times, at which inequalities (17) and (18) reverse their signs. The conjecture is also collaborated by the observation that, for liquid 3-methylcyclohexanone, CFs \( C_J(t) \) are more or less exponential [1], so that Eqs. (17), (18), (24) and (25) are unambiguously correct.

5 Conclusion

In the present article, the theory of the RT relaxation of chiral molecules is sketched. It predicts that RT dynamics in racemic mixtures and in chiral solutions is different. This is embodied in the predictions that are summarized in Eqs. (17), (18), (24), and (25). Of course, the approach developed here is semi-empirical in nature, since it does not allow one to evaluate the RT coupling parameter \( c \) from the first principles. Actually, simulations revealed that the RT coupling depends strongly on geometry of molecules and peculiarities of their mutual interactions. It can be quite pronounced (1,1-chlorofluoroethane [2, 3]) or rather small (3-methylcyclohexanone [1]). However, the collision efficiencies \( \gamma_J, \gamma_V, c \) can explicitly be calculated in the framework of Enskog theory for specific collision models, like chiral “rough screwballs” and “partially rough spheres” [13].

It is essential for understanding RT relaxation of enantiomer and racemic liquids that CFs \( C_J(t), C_V(t), \) and \( G^J(t) \), that are of fundamental importance for spectroscopy and molecular dynamics, are identically the same both for “+” and “-” enantiomers. However mixed RT CFs \( C_{JV}(t) \) (11) have the same magnitude but different sign for “+” and “-” enantiomers. In addition, if the collision rates of the angular momentum and velocity are the same (\( \gamma_J = \gamma_V \)), the RT variables decouple irrespective of the value of parameter \( c \), which is primarily responsible for the RT mixing. In this case, kernel (3) is parity invariant and \( \lambda = 0 \)(see Eq. 13). To put it by other words, the liquid under study behaves like a racemic mixture, even when \( \sigma_+ \neq \sigma_- \). So, namely the RT coupling is responsible for the difference in rotational relaxation of enantiomer and racemic mixtures. We would like to emphasize that the RT coupling effects illustrated here for chiral molecules by all means exist in normal gases and liquids consisting of non-chiral species. However for such normal gases and liquids conventional laboratory spectroscopic experiments would hardly allow one to get knowledge about statistical correlation between molecular rotation and center-of-mass translation. On the contrary, experiments on enantiomer and racemic solutions would make these effects more evident and transparent. As a final remark we note that the difference between enantiomer and racemic mixtures is considerably amplified by the application of external fields, and new kinds of RT CFs arise in this case [5, 21, 22, 23, 24].

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References