

Computer Simulation of a Simple Model for Rotational Moment Fluctuations in an Associating Liquid

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Dedicated to Professor Dr. W. Müller-Warmuth

With regard to the interpretation of dielectric relaxation spectra of associating liquids such as alcohols, a two state model for the rotational tumbling motion of a dipole is considered: The moment (of constant magnitude) is assumed to undergo stochastic tumbling during a “free” state, alternating with an “associated” state where for a certain residence time the rotational motion can be neglected. One particle autocorrelation functions according to that model are calculated numerically. In any case, they can well be described as sum of (at most) two exponentials. The corresponding parameters are given as function of “association” probability and residence time.

Introduction

A problem by which one may be faced in various fields of spectroscopic studies is to draw conclusions from the spectral shape observed on the stochastic process by which the shape is determined, since processes of quite different, even peculiar time dependence may result in practically indistinguishable spectra [1]. The present communication deals with an aspect of that problem as arising in the dielectric relaxation spectroscopy of associating liquids.

The dielectric relaxation spectrum $\varepsilon''(\omega)$ of a polar liquid is directly related to the *macroscopic* polarization fluctuation spectrum $z(\omega)$ since $\varepsilon''(\omega) \sim \omega \cdot z(\omega)$. The latter reflects directly the *microscopic* stochastic rotational motion of polar constituents provided that the magnitude of the involved dipole moments is constant. Therefore the dynamics of special interaction effects such as association in hydrogen-bonding liquids can be elucidated by dielectric spectroscopy. Alcohols and water may be mentioned here as examples which have attracted interest since many years but nevertheless receive current attention [2]. Many more or less detailed suggestions have been discussed in order to explain the characteristics of their dielectric spectra in terms of hydrogen-bond dynamics [2–16]. From a chemical point of view one may think of models which consider the equilibrium between “free” and “associated” species, emphasizing either the one particle [17–19] or cooperative [20, 21] behaviour.

Reprint requests to Prof. M. Stockhausen.

In order to avoid overinterpretation of dielectric data, it seems advisable for a first stage of discussion to picture the microscopic fluctuation process as simply as possible. In a previous paper [19] we have considered a two state model which, however, was treated analytically for limiting cases only. This model is taken up again in the present note which now reports results of a numerical study for the whole range of model parameters.

Model Assumptions

We regard a single dipole moment of constant magnitude. It is assumed to undergo tumbling motion during a “free” state for a mean time T_f . Stochastic engagement of hydrogen-bonding, or some other interaction of equivalent effect, is assumed to lead to an “associated” state where for a mean residence time T_a the rotational motion can be neglected, supposing by this that the moment in question is associated to a large enough cluster which practically does not tumble as a whole.

Residence times are assumed to be exponentially distributed around T_a . Consequently also the duration of the “free” state is distributed exponentially.

Instead of considering the dielectric spectrum $\varepsilon''(\omega)$ or the fluctuation spectrum $z(\omega)$ of the macroscopic sample, it is sufficient to discuss the (normalized) autocorrelation function $\Psi(t)$ since the latter and $z(\omega)$ are related to each other as Fourier transforms. An exponentially decaying $\Psi(t)$ is equivalent to a Debye type

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$\varepsilon''(\omega)$ spectrum. A weighted sum of exponentials corresponds to a sum of Debye functions with the same weights.

In the present communication, cooperativity will not be modelled but we restrict ourselves to the one particle correlation function, which under that assumption corresponds to $\Psi(t)$.

For numerical treatment, the rotational motion of the x, y, z -frame representing the principal axes of inertia of a tumbling particle, carrying a permanent dipole moment, is discretized into time steps of equal duration. In the “free” state, the x, y, z -system is step by step rotated in the laboratory frame in the following manner: A rotation axis x or y or z is chosen randomly, and a rotation angle for that axis $\alpha_i (i = x, y, z)$ is chosen according to a normal distribution of angles. After each step, the rotation is stopped with probability P_a for a time taken from an exponential distribution around T_a . Thus, the model parameters are (i) the rms angles $\alpha_i(\text{rms})$, (ii) the “association” probability P_a after a “free” tumbling step, and (iii) the mean residence time T_a in the “associated” state.

To simulate the one particle correlation function, a unit vector \mathbf{u} , representing the moment direction, is fixed in the x, y, z -frame and its autocorrelation function (ACF) $\Psi(t)$, where “time” t corresponds to the number of steps, is calculated according to

$$\Psi(t) = \langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle$$

by averaging over a sufficiently large number N of runs. Each run is initialized for a time large in comparison to T_a . Then the starting position of \mathbf{u} is put the same for all runs, so that

$$\Psi(t) = \mathbf{u}(0) \cdot \langle \mathbf{u}(t) \rangle.$$

For $P_a = 0$, viz. only free tumbling, the simulation results with a high degree of accuracy in an exponential function $\Psi(t)$. Thus we have a suitable though simple model of a motional process leading to Debye type relaxation.

To illustrate the general case including “free” and “associated” states, Fig. 1a shows the time dependence of one component u_z of \mathbf{u} from an arbitrarily selected single run, and Fig. 1b gives the corresponding ACF as obtained by averaging over $N = 5 \cdot 10^5$ runs. The simulated $\Psi(t)$ is subsequently fitted by the sum $\Psi_{\text{fit}}(t)$ of two exponentials, the slopes of which are indicated in Figure 1b. The fit quality is very good; on average, the relative difference of Ψ and Ψ_{fit} is

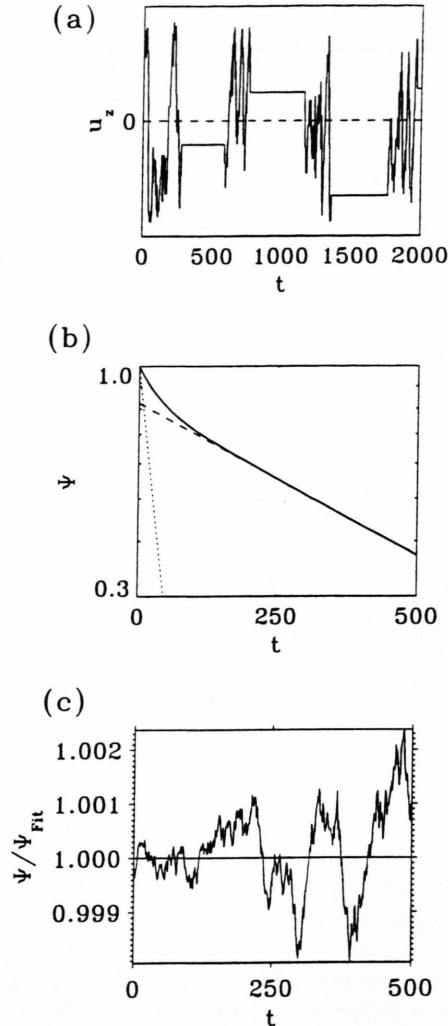


Fig. 1. Simulation and fit example for $P_a = 0.005$ and $T_a = 500$. – (a) Fluctuation of a vector component u_z vs. “time” t (single run). – (b) Autocorrelation function $\Psi(t)$ (log scale) as resulting from averaging over $N = 5 \cdot 10^5$ runs, and fit of $\Psi(t)$ by the sum of two exponentials (this is undistinguishable from $\Psi(t)$ on the scale used; the straight lines indicate the slopes of the two exponentials). – (c) Ratio Ψ/Ψ_{fit} of simulated and fitted function.

$< 2 \cdot 10^{-3}$ as to be seen from the ratio Ψ/Ψ_{fit} shown in Figure 1c.

Results

In the present paper we consider only the case of isotropic rotational motion. The examples regarded in

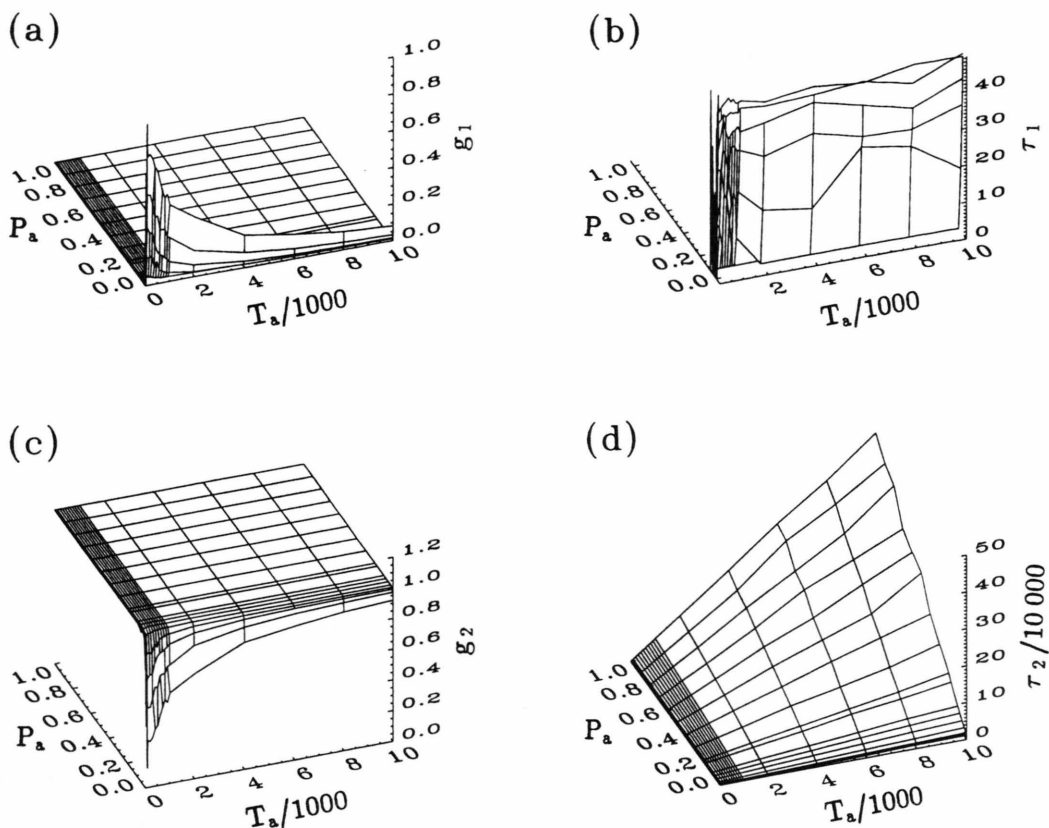


Fig. 2. Fit parameters g_i and τ_i as dependent on model parameters $P_a (=0 \dots 1)$ and $T_a (=2 \dots 10\,000)$. – (a) g_1 ; (b) τ_1 ; (c) g_2 ; (d) τ_2 .

the following are simulated for $\alpha_i(\text{rms}) = 20^\circ$. If $P_a = 0$, one obtains $\tau_f^* = 49.2$ as “uninterrupted free tumbling” correlation time.

ACF's were simulated for the whole range of “association” probabilities $P_a = 0 \dots 1$ and for mean residence times $T_a = 2 \dots 10\,000$, thus including the limits of $T_a \ll \tau_f^*$ as well as $T_a \gg \tau_f^*$, which can be treated analytically. It is a noteworthy result that in all cases it was possible to fit the simulated $\Psi(t)$ very well by a sum of (at most) two exponentials, as for the example depicted above (Figure 1b,c). This is in accord with the predictions of the Anderson model [17] which is similar to ours and is found also for the two state case of models which are treated in more general manner [2]. The results will therefore be given in terms of the two fitted exponentials,

$$\Psi_{\text{fit}}(t) = \sum_{i=1,2} g_i \exp(-t/\tau_i), \quad g_1 + g_2 = 1,$$

by displaying the fit parameters $g_{1,2}$ and $\tau_{1,2}$ (indexed such that $\tau_1 < \tau_2$) as dependent on model parameters P_a and T_a .

Figure 2 gives an overview. A first glance shows, as a remarkable feature, that *two* components occur only in the case of rather small “association” probabilities P_a (roughly $P_a < 0.1$), that is a fast one with τ_1 varying relatively little within the range $\tau_1 \lesssim \tau_f^*$, and a slow one with a correlation time τ_2 which increases considerably as P_a and T_a increase. For the most part of the P_a range, i.e. roughly $P_a > 0.1$, the ACF consists of *one* (“slow”) term only while the fast one vanishes, $g_1 \rightarrow 0$. In that region, the “slow” correlation time τ_2 is approximately proportional to P_a and to T_a (note that analytically $\tau_2 = \tau_f^* P_a T_a$ for $P_a \rightarrow 1$, $T_a \rightarrow \infty$ [19]).

To display more details, slices for $T_a = \text{const}$ and $P_a = \text{const}$ are given in Figs. 3 and 4, respectively. As far as applicable, these figures also show the limiting behaviour derived analytically [19].

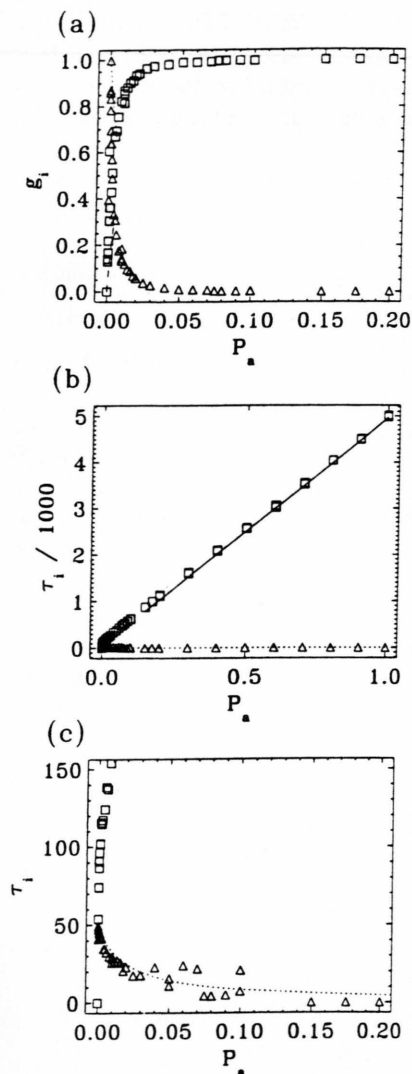


Fig. 3. Fit parameters g_i and τ_i as function of "association" probability P_a for constant mean residence time $T_a = 100$. Symbols: Δ $i = 1$; \square $i = 2$. Limiting analytical results are also indicated: Solid line for the single exponential case ($T_a \ll \tau_f^*$, $P_a \gg 1/\tau_f^*$), dashed and dotted lines for the two exponentials case ($T_a \gg \tau_f^*$, $P_a \ll 1/\tau_f^*$). – (a) $g_{1,2}$; (b) $\tau_{1,2}$ for the full range of P_a ; (c) $\tau_{1,2}$, lower left detail of (b).

Conclusions

Without going into details, it may be emphasized that the model is suited to understand the features of the dielectric spectra of alcohols on a qualitative level. In the "classical" relaxation region (say, below 100 GHz), their spectrum is usually broadened in

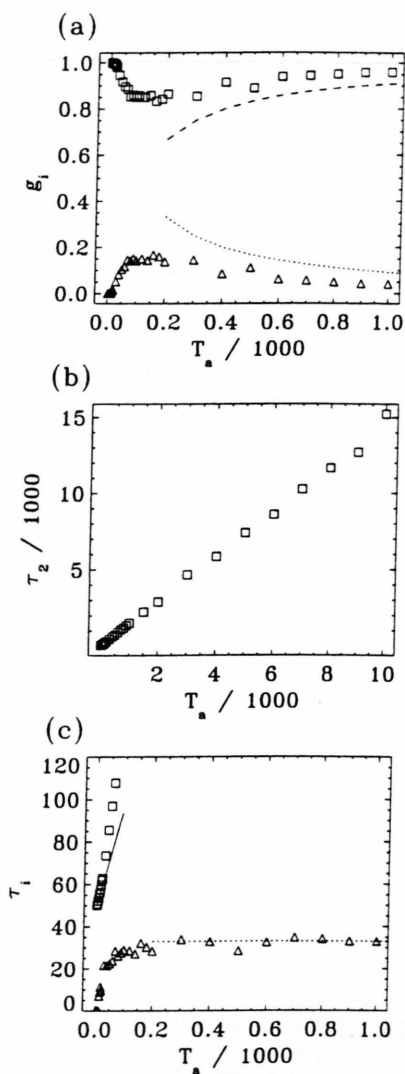


Fig. 4. Fit parameters g_i and τ_i as function of mean residence time T_a for constant probability $P_a = 0.01$. Meaning of symbols and lines as Figure 3. – (a) $g_{1,2}$; (b) τ_2 (τ_1 not representable in that scale); (c) $\tau_{1,2}$, lower left detail of (b).

comparison to a Debye type spectrum and can often roughly be approximated by (at least) two more or less resolvable Debye components. From the viewpoint of the model, this fact is indicative of a relatively low association probability P_a . The "slow" contribution is found to be the dominating one for pure alcohols and for solutions of high concentration ($g_2 > g_1$), but it

vanishes on decreasing concentration ($g_2 \rightarrow 0$). This can reasonably be understood as a further decrease of P_a on dilution. The model suggests to interpret the relaxation time found for the slow contribution as reflecting the residence time of a molecule in its asso-

ciated state. On the other hand, if Debye type dielectric spectra are found for *associating* liquids such as water, this fact may according to the model be regarded as hint at a comparatively large association probability.

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