A Remark on the Two-State Model of Dielectric Relaxation

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The two state model with exchange between the tumbling modes of the relaxing molecules is treated by computer simulation. Some results are given in dependence on the reorientational angular steps characterizing the respective states, which compare well with recent literature results obtained analytically.

The dielectric relaxation spectrum of associating liquids reflects the dynamics of the association process. Aiming at a guiding line for the interpretation of experimental spectra, we have previously dealt with a simple model [1] which resembles that suggested by Anderson [2]. It is based on the assumption that each molecule can experience just two states, termed "free (f)" and "associated (a)". Association dynamics enter the model *via* a certain probability P_a to change from the "f" to the "a" state. The residence time in the "a" state is presupposed to be exponentially distributed around T_a, so the probability to change from "a" to "f" is $P_f = 1/T_a$. In both states the molecule may undergo rotational tumbling motion. To allow for quite arbitrary assumptions on that process, we have treated the model by computer simulation in discretized steps counted as "time" t. In [1], the one-particle autocorrelation function (ACF) $\Psi(t)$ was considered for the special case that the molecule stays motionless in the "a" state but rotates isotropically in the "f" state with discrete rotation angles according to a binomial distribution characterized by α_f(rms). The numerical results could well be fitted by two exponentials,

$$\psi(t) = \sum_{1,2} g_i \exp(-t/\tau_i), \quad g_1 + g_2 = 1, \qquad (1)$$

the fit parameters g_i, τ_i depending on the model parameters α_f(rms), P_a and T_a.

In this note we consider the somewhat more general case that *both* states allow for molecular tumbling motion. The respective motions are defined as in [1] and are characterized by the correlation times which would result in the limiting case of their uninterrupted continuation (no exchange between "f" and "a" states); these are denoted by τ_f^* and τ_a^*, repectively. An equivalent model has recently been treated analytically by Stannarius, Kremer, and Arndt [3]. It seems worthwhile to compare the results of the numerical and the analytical treatment.

The results given in [3] for the symmetrical case $P_a = P_f$, written with the above-mentioned model parameters, read:

$$g_{1,2} = \frac{1}{2}\left(1 \mp \frac{1}{T_a q}\right), \qquad (2)$$

$$\frac{1}{\tau_{1,2}} = \frac{1}{T_a} + \frac{1}{2}\left(\frac{1}{\tau_f^*} + \frac{1}{\tau_a^*}\right) \pm q, \qquad (3)$$

where

$$q = \left(\frac{1}{T_a^2} + \frac{1}{4}\left(\frac{1}{\tau_f^*} - \frac{1}{\tau_a^*}\right)^2\right)^{1/2}.$$

Simulations of uninterrupted runs ($P_a = P_f = 0$) for varying rotation angles α (rms) (which afterwards may be assigned to either "f" or "a") yield purely exponential correlation functions $\psi(t)$. The τ_f^* and τ_a^* values to be introduced in (2) and (3) are obtained from those ACFs in dependence upon $\alpha_{f,a}$(rms). The simulation is continued with exchange "switched on", keeping P_a and T_a at fixed values but varying α_f and/or α_a. The resulting ACFs can again be fitted with high accuracy according to (1), *viz.* by two exponentials.

As an example, Fig. 1 shows the parameters $g_{1,2}$ and $\tau_{1,2}$, obtained for $T_a = 1000$ and α_f(rms) = 20°, as functions of α_a(rms). The results from the direct simulation and those from the application of (2) and (3) are fairly consistent. This is because the model assumptions made about the uninterrupted tumbling motion lead to a one exponential ACF [1] which, on the other hand, is the basic presupposition for the analytical treatment [3].

Qualitatively, three regions of tumbling angles α_a (in relation to $\alpha_f = 20°$) can be distinguished in Figure 1. (i) For $\alpha_a \lesssim 2°$ the situation is still as in case of the motionless "a" state [1]: The fast relaxation is determined by τ_f^* (447 for the present α_f), the slow relaxation by the lifetime in the associated state, T_a (= 1000). (ii) A transition region around α_f extends

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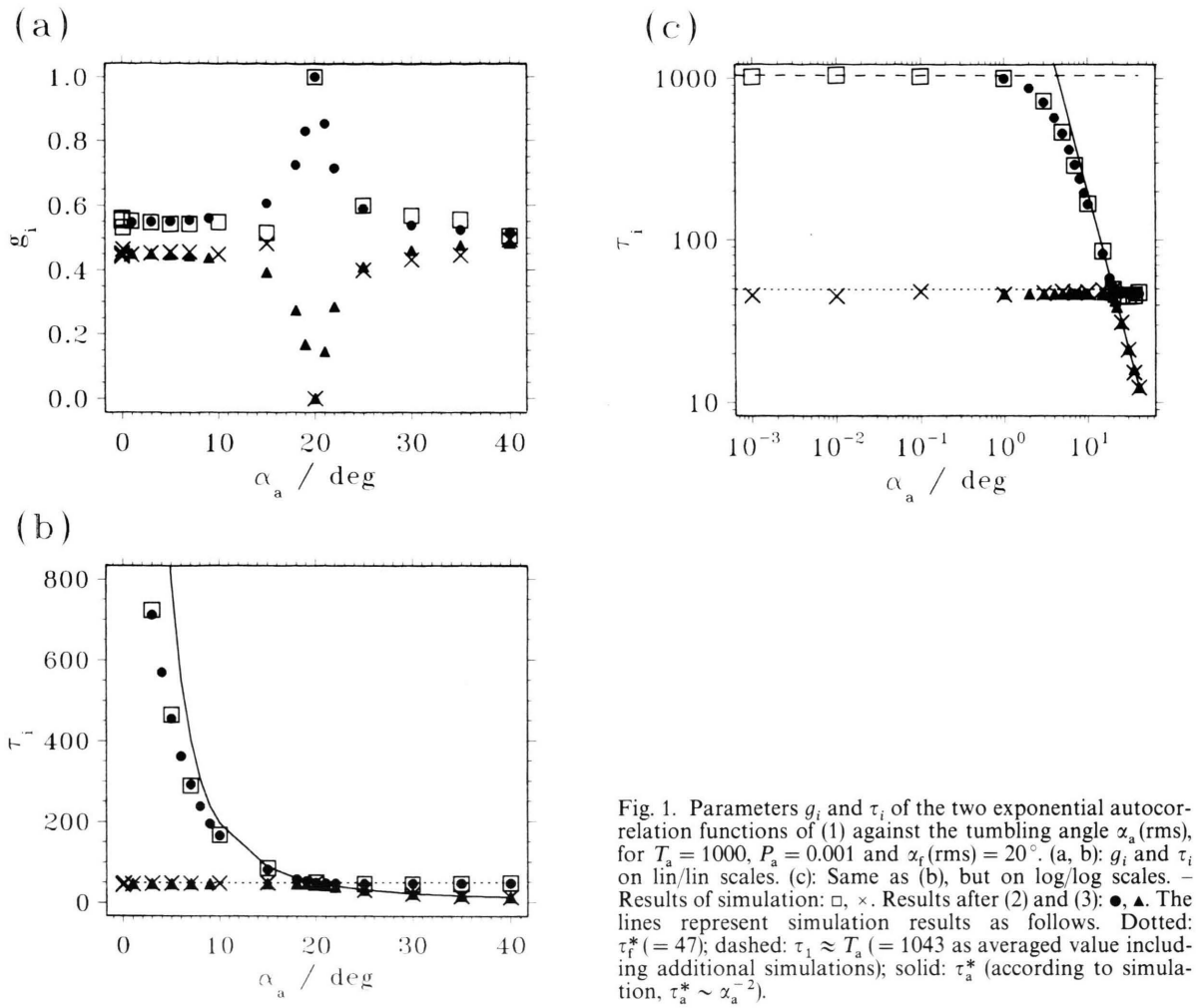

Fig. 1. Parameters g_i and τ_i of the two exponential autocorrelation functions of (1) against the tumbling angle α_a(rms), for $T_a = 1000$, $P_a = 0.001$ and α_f(rms) = 20°. (a, b): g_i and τ_i on lin/lin scales. (c): Same as (b), but on log/log scales. – Results of simulation: □, ×. Results after (2) and (3): ●, ▲. The lines represent simulation results as follows. Dotted: τ_f^* (= 47); dashed: $\tau_1 \approx T_a$ (= 1043 as averaged value including additional simulations); solid: τ_a^* (according to simulation, $\tau_a^* \sim \alpha_a^{-2}$).

over a range of about $2° \lesssim \alpha_a \lesssim 25°$. Naturally, only one exponential appears for $\alpha_a = \alpha_f = 20°$. (iii) For larger $\alpha_a \gtrsim 25°$, there remains the τ_f^* process as before, but since in fact "a" is now the state of *faster* relaxation, the second term is characterized by τ_a^*, which by simulation is found to depend on α_a as $\tau_a \sim \alpha_a^{-2}$.

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