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Collective contributions to the dielectric relaxation of hydrogen-bonded liquids

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Dielectric relaxation times are often interpreted in terms of the reorientation of dipolar species or aggregates. The relevant time correlation function contains, however, cross terms between dipole moments of different particles. In the static case, these cross terms are accounted for by the Kirkwood factor g_K. Theories and molecular dynamics simulations suggest that such cross correlations may also affect the time-dependent properties, as reflected in the dielectric spectra. We present an experimental method for detecting effects of such cross correlations in dielectric spectra by a comparative analysis of dielectric and magnetic relaxation data. We demonstrate that such collective contributions can substantially affect dielectric relaxation. Experiments for *n*-pentanol ($g_K = 3.06$ at 298 K) and 2,2-dimethyl-3-ethyl-pentane-3-ol ($g_K = 0.59$) and their solutions in carbon tetrachloride show that in systems with $g_K > 1$, the cross correlations slow down dielectric relaxation. In systems with $g_K < 1$, dielectric relaxation is enhanced. The results conform to theoretical predictions by Madden and Kivelson [Adv. Chem. Phys. **56**, 467 (1984)] and to results of molecular dynamics simulations. The relaxation enhancement by cross terms in the case of $g_K < 1$ is difficult to rationalize by conventional models of dielectric relaxation. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1751392]

I. INTRODUCTION

Dielectric relaxation provides information on molecular reorientation processes in liquids.[1,2] The molecular processes driving dielectric relaxation are described by the time correlation function $\Phi(t)$ of the total electric dipole moment $\mathbf{M}(t)$ of the sample[1,2]

$$\Phi(t) = \frac{\langle \mathbf{M}(t) \cdot \mathbf{M}(0) \rangle}{\langle |\mathbf{M}(0)|^2 \rangle}, \tag{1}$$

where $\mathbf{M}(t)$ is summed over the molecular dipole moments $\boldsymbol{\mu}(t)$ of the N particles

$$\mathbf{M}(t) = \sum_{\alpha=1}^{N} \boldsymbol{\mu}_\alpha(t). \tag{2}$$

Laplace transformation of $\Phi_M(t)$ provides the frequency-dependent complex permittivity $\epsilon^*(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$, with the real part $\epsilon'(\omega)$ (dielectric dispersion) and imaginary part $\epsilon''(\omega)$ (dielectric loss). Much of the complexity of dielectric theory arises from the fact that $\Phi_M(t)$ differs from the autocorrelation function of the molecular dipole moments

$$\Phi_\mu(t) = \frac{\langle \boldsymbol{\mu}_\alpha(0) \cdot \boldsymbol{\mu}_\alpha(t) \rangle}{\langle |\boldsymbol{\mu}_\alpha(0)|^2 \rangle} \tag{3}$$

by cross terms of the form $\langle \boldsymbol{\mu}_\alpha(t) \cdot \boldsymbol{\mu}_\beta(0) \rangle$ between distinct dipoles $\alpha \neq \beta$.[2] This work aims at drawing attention to some

subtle effects associated with these cross terms, but usually ignored in data evaluation. In some cases, these effects may even be counterintuitive.

The existence of cross terms is known from the theory of the static dielectric constant, in which the Kirkwood correlation factor[1-3]

$$g_K = \frac{\langle \mathbf{M}(0) \cdot \mathbf{M}(0) \rangle}{N \langle \boldsymbol{\mu}(0) \cdot \boldsymbol{\mu}(0) \rangle} = \frac{\langle M^2 \rangle}{N \mu^2}, \tag{4}$$

relates the mean square fluctuation $\langle M^2 \rangle$ of the total dipole moment to the dipole moments μ of the particles. For parallel dipole orientations one finds $g_K > 1$, antiparallel orientations lead to $g_K < 1$. Theory[2,4] and molecular dynamics (MD) simulations[5-9] indicate that such collective phenomena also affect time-dependent dielectric properties. A characterization of such phenomena is of large interest for understanding the collective dynamics of simple liquids,[10] and also forms an important prerequisite for assessing dielectric spectra of biomolecular systems.[11]

Theories often consider the diffusive limit, referred to as Debye behavior, for which the correlation functions decay exponentially and can be described by a single relaxation time. Interest then focuses on the relation between the observed Debye dielectric relaxation time τ_M and the "single-particle" relaxation time τ_μ of the molecular dipole moment. A theory of Madden and Kivelson[2,4] predicts that

$$\tau_M = f \frac{g_K}{g'} \tau_\mu, \tag{5}$$

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where f stands for an internal field correction and g' is a dynamical correlation factor. Several MD simulations[6–9] confirm the Kivelson–Madden relation in the simpler form

$$\tau_M = g_K \tau_\mu, \tag{6}$$

with the bare Kirkwood factor as the coupling factor.

From the experimental perspective, the challenge is to find ways to estimate the dipolar relaxation time τ_μ. As $\Phi_\mu(t)$ reflects fluctuations of molecular dipoles due to reorientation,[1,2] our strategy is to estimate τ_μ from nuclear magnetic relaxation data, which monitor single-particle orientational dynamics.[12] A similar approach has been used[13] to study collective contributions to depolarized light scattering.[14] Based on data for some simple liquids,[15] and on a pilot study for mixtures of n-butanol with CCl_4,[16] such an approach seems indeed an adequate way to study collective contributions to reorientational dynamics.

An experimental test of the Kivelson–Madden relation is most promising for systems with Kirkwood factors largely different from unity. This directs attention to some hydrogen-bonded liquids such as alcohols. Near room temperature, the lower normal alcohols exhibit high Kirkwood factors, $g_K \cong 3$, due to preferred parallel dipole correlations.[1] On the other hand, some branched alcohols show g_K values substantially lower than unity.[1] In such cases, sterical hindrance enables the formation of small aggregates with antiparallel orientations or even of dimers only.[17] Here, we consider n-pentanol ($g_K = 3.09$ at 298.15 K) and 2,2-dimethyl-3-ethyl-pentan-3-ol (DMEP) ($g_K = 0.59$) as prototypical examples for systems with Kirkwood factors deviating from unity in opposite directions. Moreover, we consider their mixtures with CCl_4, in which dilution eventually results in isolated dipoles, so that g_K approaches unity.

II. THEORY

We restrict the subsequent discussion to pure liquids. The expressions are easily generalized to solutions in apolar solvents such as CCl_4, because apolar solvents do not contribute to orientational relaxation. Following Guàrdia and co-workers,[6] we decompose the correlation function $\Phi_M(t)$ into the dipole moment autocorrelation function $\Phi_\mu(t)$ and a distinct correlation function $\Phi_d(t)$ for correlations between different molecular dipoles. Noting that the amount μ of the dipole moment vector $\boldsymbol{\mu}(t)$ does not depend on time, while its direction fluctuates due to molecular reorientation, Eq. (3) can be rewritten as

$$\Phi_\mu(t) = \langle \mathbf{u}_\alpha(t) \cdot \mathbf{u}_\alpha(0) \rangle, \tag{7}$$

where $\mathbf{u}_\alpha(t)$ is the unit vector along the dipole axis of molecule α. The (normalized) distinct correlation function then takes the form

$$\Phi^d(t) = \frac{\langle \boldsymbol{\mu}_\alpha(t) \cdot \boldsymbol{\mu}_\beta(0) \rangle}{\langle \boldsymbol{\mu}_\alpha(0) \cdot \boldsymbol{\mu}_\beta(0) \rangle} = \frac{\langle \mathbf{u}_\alpha(t) \cdot \mathbf{u}_\beta(0) \rangle}{\langle \mathbf{u}_\alpha(0) \cdot \mathbf{u}_\beta(0) \rangle}. \tag{8}$$

Moreover, we rewrite the Kirkwood factor in Eq. (4) in terms of these unit vectors, finding

$$g_K = 1 + (N-1)\langle \mathbf{u}_\alpha(0) \cdot \mathbf{u}_\beta(0) \rangle, \quad \alpha \neq \beta. \tag{9}$$

A combination of Eqs. (7)–(9) then yields the time correlation function

$$\Phi_M(t) = \frac{1}{g_K} \Phi_\mu(t) + \left(1 - \frac{1}{g_K}\right) \Phi_d(t). \tag{10}$$

For $g_K \to 1$, the contribution of the cross terms $\Phi_d(t)$ to $\Phi_M(t)$ vanishes.

The present work aims at studying collective reorientational dynamics by a comparative analysis of dielectric and magnetic relaxation data. Single-particle molecular reorientation in liquids is usually analyzed through a series of correlation functions $C_l^s(t)$,[10] associated with spherical harmonics of order l. In terms of these correlation functions, Eq. (7) is equal to the $l = 1$ reorientational correlation function of the dipoles; that is, $\Phi_\mu(t) \equiv C_1^s(t)$. The common method to obtain information on single-particle reorientational dynamics is nuclear magnetic relaxation, which monitors processes associated with the $l = 2$ autocorrelation function[12]

$$C_2^s(t) = \langle \tfrac{3}{} [\mathbf{u}_\alpha(0) \cdot \mathbf{u}_\alpha(t)]^2 - 1 \rangle. \tag{11}$$

For a Debye liquid, $C_1^s(t)$ and $C_2^s(t)$ decay exponentially; that is,

$$C_l^s(t) = \exp(-t/\tau_l^s), \quad l = 1,2, \tag{12}$$

and the two time constants are interrelated by[10]

$$\tau_1^s = 3\tau_2^s. \tag{13}$$

For real liquids such as the n-alcohols,[18] the correlation functions decay nonexponentially, and Debye behavior is limited to their long-time tails. Magnetic relaxation experiments on fluid systems are, however, conducted at the condition $\omega \ll 1/\tau_2^s$, where only an integral correlation time[12]

$$\bar{\tau}_2^s = \int_0^\infty C_2^s(t) dt \tag{14}$$

is obtained. MD data for ethanol[19] show that this integral correlation time may differ from the Debye correlation time of the long-time tail by a factor of 2. Thus, it seems more appropriate to compare $\bar{\tau}_2^s$ with integral dielectric relaxation times defined by

$$\bar{\tau}_M = \int_0^\infty \Phi_M(t) dt, \tag{15a}$$

$$\bar{\tau}_\mu = \int_0^\infty \Phi_\mu(t) dt. \tag{15b}$$

According to MD data for ethanol,[19] the relation $\tau_1^s = 3\tau_2^s$ is also a good approximation for these integral quantities. However, it may be difficult to design NMR experiments with regard to motions of the dipole axis in the molecule. Thus, in converting NMR to dielectric relaxation data, anisotropic molecular reorientation has to be taken into account. Ignoring at this instance effects of anisotropic reorientation, the previous considerations suggest testing the Kivelson–Madden relation for real liquids by setting $\bar{\tau}_\mu \cong \bar{\tau}_1^s \cong 3\bar{\tau}_2^s$. Thus, we compare the integral relaxation time $\bar{\tau}_M$ calculated from the dielectric spectrum with the quantity $3\bar{\tau}_2^s$ deduced
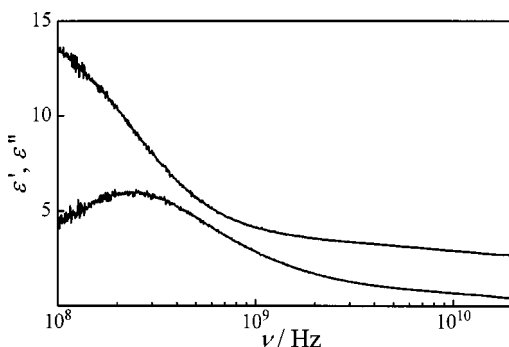
FIG. 1. Real and imaginary part of the complex dielectric spectrum of *n*-pentanol at 298.15 K.

from magnetic relaxation data. Uncertainties caused by reorientational anisotropy will be considered later.

III. METHODS

Samples. *n*-pentanol, 2,2-dimethyl-3-ethyl-pentan-3-ol (DMEP) and CCl_4 of the highest purity (Aldrich) were used without further purification. Deuteration of DMEP at its hydroxyl groups was performed by ^2H exchange with heavy water. Binary mixtures with CCl_4 were prepared by weight.

Dielectric relaxation. We have used dielectric reflection spectroscopy in the frequency range 200 MHz$\leq \nu = \omega/2\pi \leq$ 20 GHz to determine the real part $\epsilon'(\omega)$ (dielectric dispersion) and imaginary part $\epsilon''(\omega)$ (dielectric absorption or loss) of the complex permittivity $\epsilon^*(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$ of *n*-pentanol and DMEP. Experimental details are described elsewhere.[16] All experiments were performed at (298.15 $\pm$0.1) K. Figure 1 shows as an example the measured spectrum of *n*-pentanol.

Following Barthel and Buchner,[18] we have parameterized the spectra by three Debye-type modes with amplitudes $S^{(k)}$ an relaxation times $\tau_1^{(k)}$

$$\epsilon^*(\omega) = \epsilon_\infty + \sum_{k=1}^{3} \frac{S^{(k)}}{1 + i\omega\tau_1^{(k)}}, \qquad (16)$$

numbering the modes from low to high frequency, ϵ_∞ is the high-frequency limit due to optical and vibrational processes. For *n*-pentanol and its mixtures, the full equation (16) was used, with ϵ_∞ fixed by the usual approximation $\epsilon_\infty \cong 1.05 \, n^2$, where *n* is the optical refractive index.[1] To reduce the number of adjustable parameters, we fixed the high-frequency mode at $\tau^{(3)} = 3$ ps, estimated from data for lower alcohols.[18] In the case of DMEP, the processes were less well separated in frequency, and we considered two terms only, accounting for the third process by an adjustable value of $\epsilon_\infty > 1.05 \, n^2$. The parameterization is summarized in Table I. x_1 is the mole fraction of the alcohol. The fitted static dielectric constants (ϵ_S) given by the sums of the amplitudes $S^{(k)}$ plus ϵ_∞, agree within uncertainty with more direct determinations by a Wayne–Kerr bridge operating at 1 kHz (Table I).

Kirkwood factors were then calculated from ϵ_S by the standard relation of Kirkwood–Fröhlich theory.[20] For a pure liquid, the relevant expression is

$$g_K\mu^2 = \frac{9k_B T\epsilon_0}{(N/V)} \frac{(\epsilon_S - \epsilon_\infty)(2\epsilon_S + \epsilon_\infty)}{\epsilon_S(\epsilon_\infty + 2)^2}, \qquad (17)$$

where ϵ_0 is the permittivity of the vacuum, k_B the Boltzmann constant, N/V the number density of the dipoles, and $\mu = 1.70$ D $(1D = 3.335 \times 10^{-30}$ C m) the dipole moment of the isolated alcohol molecules. The extension to binary mixtures relies on approximations, and different expressions were used in the literature.[1] In mixtures of apolar solvents such as CCl_4, Eq. (17) is, however, more easily generalized, because apolar solvents do only contribute to the nuclear and electronic polarization, but not to orientational polarization.

TABLE I. Parameterization of dielectric spectra of mixtures of *n*-pentanol and DMEP with CCl_4 at 298.15 K.

x_1	d (g cm^{-3})	$S^{(1)}$	$\tau^{(1)}$ (ps)	$S^{(2)}$	$\tau^{(2)}$ (ps)	$S^{(3)}$	$\tau^{(3)}$ (ps)	ϵ_∞	1.05 n^2	ϵ_S (fit)	ϵ_S (1 kHz)	g_K
					n-Pentanol–CCl_4							
0.1	1.4780	0,11	61,8	0.29	9.1	0.01	3.0	2.20	2.21	2.61	2.49	0.85
0.2	1.4115	0.25	119.4	0.32	17.4	0.20	3.0	2.20	2.20	2.97	2.88	0.93
0.4	1.2551	1.58	352.6	0.49	32.0	0.41	3.0	2.18	2.17	4.66	4.72	1.58
0.5	1.1728	3.17	462.8	0.55	36.2	0.49	3.0	2.18	2.15	6.39	5.69	1.92
0.6	1.1077	4.63	536.9	0.59	38.3	0.54	3.0	2.17	2.14	7.93	8.08	2.33
0.7	1.0063	6.9	606.4	0.58	39.7	0.63	3.0	2.16	2.13	10.27	10.03	2.71
0.8	0.9478	8.25	639.4	0.61	40.3	0.66	3.0	2.16	2.11	11.68	11.86	2.86
0.9	0.8861	10.02	672.5	0.62	42.6	0.72	3.0	2.15	2.10	13.51	13.58	2.97
1.0	0.8105	11.64	672.2	0.65	44.5	0.77	3.0	2.15	2.08	15.21	15.09	3.06
					DMEP–CCl_4							
0.21	1.346	0.23	13.9	0.38	5.7			2.15	2.22	2.78	2.73	0.79
0.31	1.247	0.20	15.1	0.48	5.8			2.15	2.21	2.85		
0.41	1.167	0.22	18.8	0.65	6.3			2.15	2.21	3.03	3.02	0.73
0.51	1.102	0.18	22.2	0.79	6.3			2.15	2.20	3.13		
0.61	1.040	0.18	26.8	0.89	6.5			2.15	2.20	3.21	3.25	0.67
0.71	0.978	0.14	30.7	0.97	7.0			2.15	2.19	3.24		
0.81	0.928	0.12	36.9	1.05	7.4			2.15	2.19	3.28	3.39	0.66
1.00	0.872	0.21	38.7	1.16	7.5			2.15	2.18	3.48	3.49	0.59

TABLE II. Experimental deuteron relaxation times $(T_1)_D$, measured hydroxyl proton chemical shifts δ_{OH}, calculated deuteron quadrupole coupling constants χ_D, and rotational correlation times for the O–H vector of DMEP in mixtures with CCl_4 at 298.15 K.

x_1	T_1 (s^{-1})	δ_{OH} (ppm)	χ (kHz)	$\bar{\tau}_{NMR}$ (ps)
0.005	1.186	0.401	298.75	0.898
0.03	1.504	0.524	296.86	1.153
0.05	1.807	0.582	296.04	1.393
0.10	2.492	0.729	293.67	1.952
0.20	4.133	0.918	290.78	3.300
0.40	10.338	1.218	286.16	8.530
0.60	15.025	1.352	284.09	12.58
0.80	18.903	1.429	283.06	15.94
1.00	22.318	1.510	281.35	19.04

FIG. 2. Kirkwood factors g_K in mixtures of n-pentanol with CCl_4 (squares) at 298.15 K compared with the quantity $g^* = \bar{\tau}_M / \bar{\tau}_\mu$ (circles), as estimated by $\bar{\tau}_\mu \cong 3\bar{\tau}_{OH}$. x_1 is the mole fraction of n-pentanol.

Dielectric theory of mixtures then yields for a system comprising a of a polar component 1 at mole fraction x_1 and apolar component 2 at mole fraction x_2

$$g_K \mu^2 = \frac{9k_B T \epsilon_0}{N_A x_1} \frac{(\epsilon_S - \epsilon_\infty)(2\epsilon_S + \epsilon_\infty)^2}{(2\epsilon_S + 1)(\epsilon_\infty + 2)^2} \times \left[\frac{\varphi(\epsilon_S - 1)}{\epsilon_S} - \frac{3x_2 M_2(\epsilon_{S,2} - 1)}{(2\epsilon_S + \epsilon_{S,2})d_2} - \frac{3x_1 M_1(\epsilon_\infty - 1)}{(2\epsilon_S + \epsilon_\infty)d_1} \right],$$ (18)

where φ is the molar volume of the mixture and the M_i, $\epsilon_{S,i}$, and d_i ($i = 1,2$) are the molar masses, dielectric constants, and densities of the pure components, respectively.[21]

Nuclear Magnetic Relaxation. Longitudinal relaxation times T_1 for the deuteron in the hydroxyl group of DMEP were measured by the inversion recovery $(180\text{-}\tau\text{-}90)$ pulse sequence at a magnetic field of 7.05 T (resonance frequency $\nu = 46.07$ MHz for ^2H). Relaxation is caused by the interaction of the electric quadrupole moment of the ^2H nucleus with the intramolecular electric field gradient at the nucleus,[12] the direction of which coincides with the OH axis of the alcohol molecules. In the limit $\omega \tau_2^s \ll 1$, the relaxation rate $1/T_1$ is given by

$$\frac{1}{T_1} = \frac{3}{2} \pi^2 \chi^2 \bar{\tau}_{OH},$$ (19)

where a correction for the asymmetry of the electric field gradient (for alcohols $< 1\%$[22]) is neglected. Following a procedure by Wendt and Farrar,[23] we have calculated the nuclear quadrupole coupling constant χ from a linear correlation between χ and the chemical shift of the OH proton, δ_{OH}, here recorded at 300.13 MHz relative to an internal tetramethylsilane reference. As discussed elsewhere,[24] a large number of alcohols obey the linear correlation χ (kHz) $= 304.94 - 15.92 \delta_{OH}$ (ppm). The results for DMEP are summarized in Table II. Correlation times for n-pentanol were taken from previous work,[22] in which a ^{17}O-induced relaxation method[22,25] was employed.

IV. RESULTS AND DISCUSSION

n-Pentanol. As a prerequisite for the subsequent discussion, we consider the behavior of the Kirkwood factor. Its value is subject to some debate, as the high-frequency extrapolation of $\epsilon'(\omega)$ provides ϵ_∞ values that deviate from the
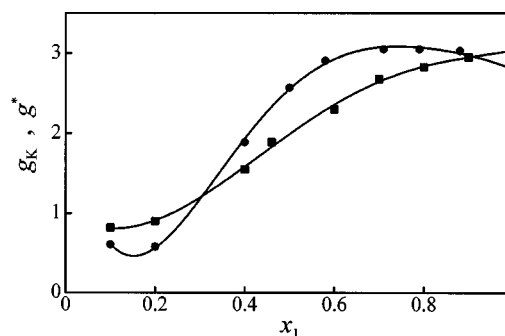
values deduced from refractive index data.[18] This indicates the presence of high-frequency processes. The relevance of these processes for the Kirkwood factor is not entirely clear. Ignoring such fine details, there is general agreement that at 298 K the pure n-alcanols exhibit unusually high Kirkwood factors, $g_K \cong 3$, which are commonly attributed to multimers with preferred parallel dipole orientations.[1]

Upon dilution of n-pentanol in CCl_4, the dipolar correlations gradually vanish (Fig. 2), and at infinite dilution g_K approaches unity, as expected for an isolated dipole. The concentration dependence shows, however, a nonmonotonic behavior with a minimum and g_K values below unity at $x_1 < 0.2$. The existence of such minima is well documented for other n-alcanols in apolar solvents.[1] A variety of association equilibria have been suggested to explain this particular shape in terms of the formation of dimers and small multimers with antiparallel dipole orientations, followed by large clusters with parallel orientations. As an illustrative example, we mention the work of Brot *et al.*[26]

To examine the role of collective phenomena for time-dependent processes, we compare in Fig. 3 the integral dielectric relaxation time $\bar{\tau}_M$ with the reorientational correlation time $\bar{\tau}_{OH}$ and the estimated single-particle relaxation time $\bar{\tau}_\mu \cong 3\bar{\tau}_{OH}$. This procedure presumes that the motion of the OH axis mimics the motion of the dipole moment vector. According to MD simulations of ethanol,[19] the integral relaxation times of the dipolar and O–H axes differ over a wide range of temperatures by about only 10%. There are no
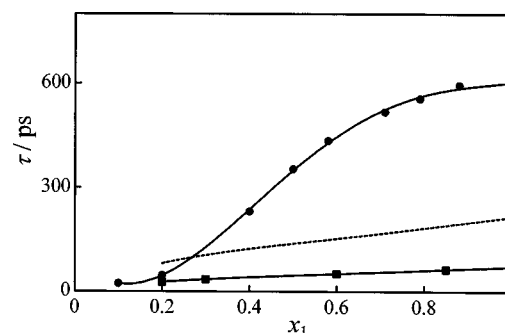

FIG. 3. Integral dielectric relaxation times $\bar{\tau}_M$ (circles) compared with the reorientation time $\bar{\tau}_{OH}$ (squares) for mixtures of n-pentanol with CCl_4 at 298.15 K. The dashed line shows the dipolar relaxation time $\bar{\tau}_\mu$ as estimated by $\bar{\tau}_\mu \cong 3\bar{\tau}_{OH}$.
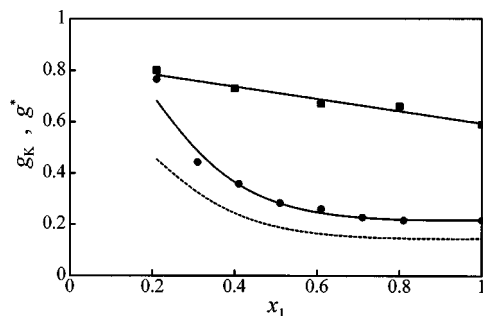
FIG. 4. Kirkwood factors g_K in mixtures of DMEP with CCl_4 (squares) compared with the quantity $g^* = \bar{\tau}_M / \bar{\tau}_\mu$ (circles) as estimated by $\bar{\tau}_\mu$ based on $\bar{\tau}_\mu = 3 \bar{\tau}_{OH}$. The dashed line shows a lower bound by assuming that $\bar{\tau}_\mu$ is by 50% longer than given by this estimate. x_1 is the mole fraction of DMEP. The temperature is 298.15 K.

FIG. 5. Integral dielectric relaxation times $\bar{\tau}_M$ (circles) compared with the reorientation time $\bar{\tau}_{OH}$ (squares) for mixtures of *n*-pentanol with CCl_4 at 298.15 K. The dashed lines show a lower bound for the dipolar relaxation times $\bar{\tau}_\mu$, as estimated by $\bar{\tau}_\mu = 3 \bar{\tau}_{OH}$, and an upper bound, if $\bar{\tau}_\mu$ is 50% longer than this estimate.

similar data for solutions in CCl_4, but at infinite dilution, $\bar{\tau}_M \to \bar{\tau}_\mu$ must hold rigorously. Thus, the observed limiting behavior $\bar{\tau}_M / 3 \bar{\tau}_{OH} \to 1$ confirms that $\bar{\tau}_{OH}$ is a reasonable measure for $\bar{\tau}_\mu$ in dilute solutions as well.

The similarity of the curves for g_K and $g^* = \bar{\tau}_M / \bar{\tau}_\mu$ in Fig. 2 is striking. The results qualitatively correspond to those reported by us previously for *n*-butanol.[16] It is immediately seen that the cross correlations slow down dielectric relaxation in the concentration range, where $g_K > 1$, and enhance relaxation in the range, where $g_K < 1$. More quantitatively, Fig. 2 suggests that the Kirkwood factor g_K is a decisive quantity in determining the interrelation between the dielectric relaxation time and the orientational relaxation time of the molecular dipoles.

It has been known for a long time that the principal dielectric relaxation times $\tau^{(1)}$ of pure alcohols such as *n*-pentanol are unusually long.[1,18] The conventional rationale is that dielectric relaxation reflects the motion of large, slowly reorienting dipolar aggregates rather than single dipoles. This is, of course, well in accordance with the interpretation in terms of dynamical correlations discussed here. On the other hand, the behavior at low alcohol concentrations is more difficult to explain. As noted, Kirkwood factors $g_K < 1$, observed in this regime, signal the formation of dimers and small aggregates with preferred antiparallel dipole orientations as a first step towards the formation of larger aggregates in concentrated solutions. We find here that the resulting cross correlations enhance relaxation. In the usual pictures of the effect of aggregate formation upon reorientational motions, this finding is certainly counterintuitive, but such a behavior is clearly predicted by the Kivelson–Madden relation.

DMEP. In looking for further examples for such a relaxation enhancement by antiparallel dipole correlations, we have focused on branched alcohols, where the OH group is little exposed, and only small aggregates are formed. Many branched alcohols such as DMEP are known to possess low dielectric constants, caused by Kirkwood factors smaller than unity.[1] Infrared spectra and cluster calculations for pure DMEP show that there is a substantial fraction of monomers, and aggregation leads to dimers only.[17,24] Our measurements yield an unusually low dielectric constant of pure DMEP,
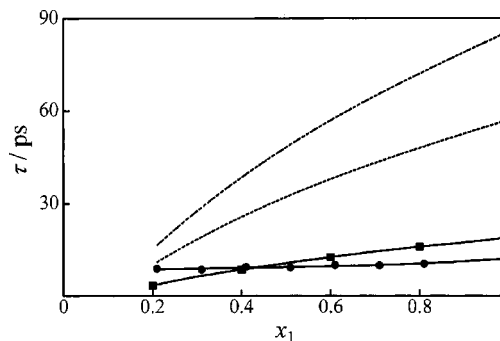
$\epsilon_S = 3.09$, corresponding to $g_K = 0.59$. Figure 4 shows that in mixtures with CCl_4, g_K increases monotonically, and smoothly extrapolates to $g_K = 1$ at infinite dilution. The large differences in the Kirkwood factors of DMEP and *n*-pentanol can be traced back to a different behavior of the amplitudes $S^{(1)}$ of the low-frequency process (Table I).

In the case of DMEP, the examination of the Kivelson–Madden turns out to be more complex than in the case of *n*-pentanol. Unpublished MD simulations by Paschek[27] indicate a substantial motional freedom of OH group in monomers and dimers of DMEP, which leads to pronounced anisotropic reorientation. In terms of the integral reorientation times $\bar{\tau}_2^s$, the simulations predict that the CO axis fluctuates by a factor of 4 more slowly than the OH axis. Thus, in contrast to the situation encountered with *n*-pentanol, the reorientational anisotropy of DMEP has to be considered.

The quality of the approximation of $\bar{\tau}_\mu$ by $\bar{\tau}_{OH}$ depends crucially on the direction of the dipole vector in the DMEP molecule. To locate this direction relative to the OH axis, we have performed GAUSSIAN calculations. Infrared data and GAUSSIAN calculations indicate that three rotational isomers of DMEP should be considered.[17] In the most relevant conformer, the dipole vector is practically collinear with the OH axis, so that $3 \bar{\tau}_{NMR}$ indeed mimics $\bar{\tau}_\mu$. In a less populated conformer, the dipole vector cuts the plane spanned by the OH and CO axes, but the direction is still closer to the OH axis. This would increase $\bar{\tau}_\mu$ relative to $\bar{\tau}_{OH}$ by up to a factor of 2. In a third conformer of minor relevance, the dipole vector is perpendicular to this plane, and its correlation time is difficult to assess. In total, $\bar{\tau}_{OH}$ seems to be a fairly reasonable measure for $\bar{\tau}_\mu$, if allowance is made that $\bar{\tau}_\mu = 3 \bar{\tau}_{OH}$ represents a lower bound, and, as judged by the populations of the rotational isomers, $\bar{\tau}_\mu$ may be up to 50% larger than this estimate.

Figure 5 compares the integral dielectric relaxation time $\bar{\tau}_M$ with the integral reorientation time deduced from magnetic relaxation, and the estimated dipolar relaxation time $\bar{\tau}_\mu$. The dashed lines shown embrace the possible range of values for $\bar{\tau}_\mu$, with $\bar{\tau}_\mu = 3 \bar{\tau}_{OH}$ as a lower bound. The prime result is that, independent of the detailed choice, $\bar{\tau}_\mu$ is definitely longer than $\bar{\tau}_M$. Thus, the cross terms indeed enhance dielectric relaxation. In more detail, we compare in Fig. 4 the

factor $g^* = \bar{\tau}_M / \bar{\tau}_\mu$ with the Kirkwood factor g_K. It is seen that g^* reflects the monotonic increase of g_K, and, at least qualitatively, corresponds to the predictions of Kivelson–Madden theory. More quantitatively, it would seem that the role of the collective effects for dynamics is even more accentuated than in the static case.

V. CONCLUSIONS

The time correlation function observed in dielectric relaxation does not simply reflect the reorientation of the molecular dipoles, but involves cross terms that reflect the coupling of dipole moments of different particles. We have demonstrated that these cross terms slow down relaxation in the case of parallel dipole orientations and enhance relaxation in the case of antiparallel dipole reorientations. The observations are, at least at the qualitative level, in agreement with Kivelson–Madden theory[2,4] and with results of several MD simulations for pure liquids.[6–9] Thus, the experimental results confirm that the static Kirkwood factor is the decisive quantity in relating the collective dynamics to the single-particle dynamics. With regard to n-pentanol ($g_K > 1$), the observations correspond to the conventional interpretation that aggregate formation slows down dielectric relaxation. The more intriguing result obtained for dilute solutions of n-pentanol and for DMEP ($g_K < 1$) implies that antiparallel dipole correlations enhance dielectric relaxation. This confirms Kivelson–Madden theory, but has escaped broad attention.

One may, however, note that such a relaxation enhancement has been observed in MD simulations of acetonitrile by Guàrdia *et al.*,[9] although it has not been commented upon in detail. The experimental Kirkwood factor of acetonitrile is $g_K = 0.75$ at 298 K. The authors have performed simulations for three acetonitrile models involving different interaction potentials. Since, both in experiment and simulation, dielectric relaxation of acetonitrile is essentially describable by a single Debye process, the integral dielectric relaxation time reflects the Debye relaxation time. In all cases, the simulations have confirmed the Kivelson–Madden relation with the bare Kirkwood factor as the coupling factor. Two model potentials could reproduce a Kirkwood factor $g_K < 1$, and in both cases, $\bar{\tau}_M / \bar{\tau}_\mu < 1$ was observed beyond the limits of uncertainty. A third model yielded $g_K \cong 1$ and $\bar{\tau}_M / \bar{\tau}_\mu > 1$. The observations agree excellently with the conclusions drawn here.

While we have shown the decisive role of cross correlations for comparatively simple systems, the account for such collective modes may also form an essential part in the understanding of dielectric processes in more complex biomolecular systems. As an example, we mention dielectric relaxation of protein solutions, in which cross correlations between distinct species can even give rise to distinct modes in the dielectric spectra, in the literature known as δ-relaxation.[11]

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