

Applicability of Extended Hydrodynamical Model to Dielectric Relaxation in Simple Polar Liquids

T. Grochulski and L. Pyszczótkowski

Institute of Physics PAN, 02-668 Warsaw, Poland

M. Kempka

Physics Department, University of Poznań, 61-614 Poznań, Poland

(Received 16 March 1992)

Dielectric relaxation profiles and self-diffusion coefficients were measured for 1,1,1-trichloroethane, *t*-butyl chloride, and 2,2-dinitropropane in liquid and plastic phases. For all three samples no significant change in the relaxational behavior is observed when going from liquid to plastic-crystal phases. The comparison of the results with the extended hydrodynamic model shows that the model overestimates the effect of translational-rotational coupling on dielectric properties of liquids.

PACS numbers: 77.40.+i, 66.10.-x

The dielectric relaxation in liquids of high density of dipole moment has been the subject of numerous theoretical and experimental studies [1-3]. One can expect that in strongly polar liquids the long-range anisotropic dipole-dipole interaction can lead via dielectric friction to non-Debye relaxation. This problem was described by Nee and Zwanzig [4] and Hubbard and Wolynes [5] on the basis of the continuum model.

Recently, Bagchi and Chandra [6] have presented a more general approach based on extended hydrodynamical theory and take into account the influence of translational motion on dielectric friction. The model explains a number of important features observed in molecular-dynamics simulations by Pollock and Alder [7] like slowing down of the total polarization relaxation relative to the single-particle orientational relaxation with an increase of the polarity of the liquid and the existence of dipolarons in the longitudinal component of the dielectric tensor.

The model also predicts that for polar molecules the non-Debye relaxation should be observed in the absence of translational motion. The inclusion of translations may result in recovery of a near Debye form of the relaxational profile, the final distortion of which depends on the ratio of translational and rotational diffusion constants. This interesting theoretical prediction was confronted only qualitatively with experiment because of the lack of sufficiently precise experimental data. The authors estimated the magnitude of the parameters of their model for liquid water, methanol, and acetonitrile and have shown that in these liquids the hydrodynamical model predicts a single relaxation time as observed experimentally.

We decided to check the applicability of the model to another group of simple liquids, namely, the liquids forming plastic crystals. In this kind of material the phase transition from liquid to solid occurs in two (or more) steps, with the first one being the freezing out of translational degrees of freedom. We therefore have an analog of the situation discussed theoretically by Bagchi and Chandra in which the translational motion is "switched

on" in the liquid phase or "switched off" in the plastic phase while the rotational motion is practically unchanged [8]. The near spherical shape of molecules forming plastic phases is also compatible with the simplifying assumption about spherical symmetry that has been used in the model in order to obtain some numerical results.

The existing experimental data which could be used for qualitative analysis of the problem are far from complete. Some dielectric data show the appearance of deformations in the relaxational semicircle when going from the liquid to the plastic phase [9], while other experiments show the same dielectric behavior in both phases [10]. The data concerning the self-diffusion are in most cases lacking.

In order to give a more precise answer to the question of applicability of the extended hydrodynamical model to real systems, three polar, near spherical molecules (1,1,1-trichloroethane, *t*-butyl chloride, and 2,2-dinitropropane) were chosen and their rotational and translational characteristics were examined by dielectric spectroscopy and self-diffusion measurements. All selected substances form plastic phases and hence on going from the liquid to the plastic-crystal phase it is possible to observe experimentally the effect of freezing out of translational degrees of freedom on the shape of the relaxational profile and carry out a qualitative comparison with the extended hydrodynamical theory.

The samples of trichloroethane and *t*-butyl chloride were commercial products (Fluka) of better than 99% purity and were used without further purification. The sample of dinitropropane was prepared by nitration of the sodium salt *d*-acinitropropane with sodium nitrate and its purity was better than 99.4% as shown by chromatographic analysis.

The translational properties of the samples were studied by means of self-diffusion measurements performed by the pulsed spin-echo method described by Stejskal and Tanner [11]. The homemade spectrometer built by one of the authors (Kempka) used in this study enabled the measurements of D_T down to $10^{-8} \text{ cm}^2 \text{ s}^{-1}$ with better

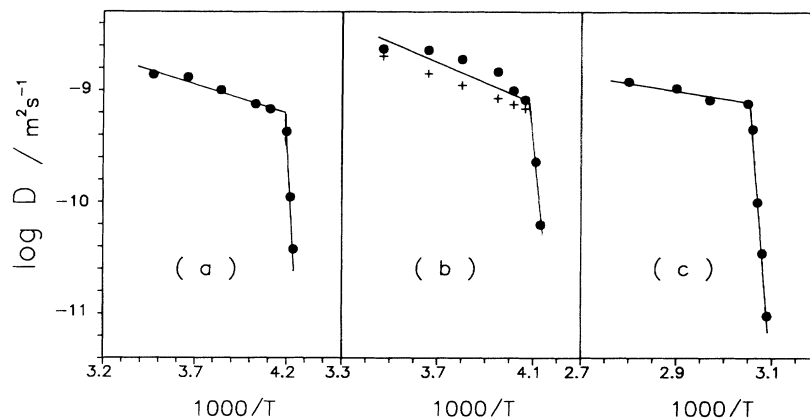


FIG. 1. The self-diffusion coefficient as a function of reciprocal temperature for (a) 1,1,1-trichloroethane, (b) *t*-butyl chloride, and (c) 2,2-dinitropropane. Filled circles, results of current experiment; crosses, data from Ref. [12].

than 10% precision. The operating frequency was 16.5 MHz and the maximum value of the pulsed field gradient was 120 G/cm with the background value equal to 1.0 G/cm. The self-diffusion coefficients were determined by linear regression.

Figure 1 shows the self-diffusion coefficient obtained in the current experiment plotted on a logarithmic scale against the reciprocal temperature. For *t*-butyl chloride some literature results in the liquid phase are also indicated [12]. All three plots show a sharp decrease of the self-diffusion coefficient at the liquid-plastic-crystal tran-

sition points. Because of the very short relaxation time T in the plastic phase it was not possible to determine the exact values of D_T in this temperature range. On the basis of current results we can estimate, however, that the diffusion constant drops by considerably more than an order of magnitude relative to its liquid-state value.

The rotational properties of the samples were studied by means of dielectric spectroscopy. The results of measurements of complex permittivity for low and moderate frequencies were taken from [13–16] while the measurements for frequencies higher than 40 GHz were carried out using the free-space mm-wave spectrometer described in [17].

The static dielectric constant was measured for all samples in order to ensure that the samples used in low- and high-frequency experiments were the same. The agreement between values published in [13–16] and the present results was of the order of experimental accuracy, i.e., at the level of below 1%. The combined complex permittivity data are presented in Fig. 2 in the form of the so-called Cole-Cole plots for each substance for liquid and plastic-crystal phases. It can be seen from the plots that the shapes of the relaxational profiles are very similar in both phases and numerical fits confirm Debye-like behavior. In the fifth column of Table I we give the values of the rotational diffusion constant calculated from the relaxation times obtained from the fit to the experimental data.

It can be concluded that the relaxation process in the plastic phase remains unchanged in spite of freezing out of the translational motion of molecules. We would now like to confront this experimental finding with the predictions from the generalized hydrodynamical model.

The importance of translational motion in polarization relaxation of a dipolar liquid is described in the hydrodynamical model [6] by means of the parameter $\rho' = D_T/2D_{R0}\sigma^2$, where D_T is the self-diffusion constant, D_{R0} is the rotational diffusion constant connected with the Stokes friction, and σ is the molecular diameter. The

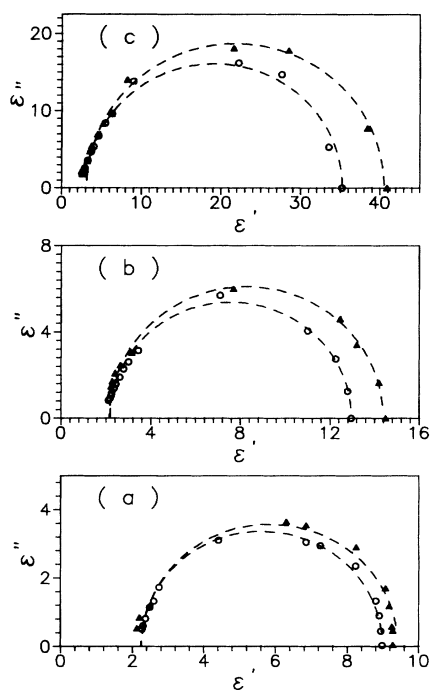


FIG. 2. Cole-Cole plots for (a) 1,1,1-trichloroethane, (b) *t*-butyl chloride, and (c) 2,2-dinitropropane in liquid phase (circles) and plastic-crystal phase (triangles).

TABLE I. Values of molecular diameter σ , self-diffusion coefficient D_T , rotational diffusion coefficient D_{R0} , and parameter of translational-rotational coupling p' for 1,1,1-trichloroethane (TCE), *t*-butyl chloride (TBC), and 2,2-dinitropropane (DNP) in liquid (l) and plastic-crystal (p) phases.

Substance	T (K)	σ (Å)	D_T (m ² s ⁻¹)	D_{R0} (s ⁻¹)	p'
TCE	248 (l)	5.52	7.0×10^{-10}	0.049	0.0230
	235 (p)		3.7×10^{-11} ^a	0.037	0.0016 ^a
TBC	253 (l)	5.66	1.2×10^{-9}	0.070	0.0270
	243 (p)		6.0×10^{-11} ^a	0.063	0.0015 ^a
DNP	330 (l)	5.72	7.6×10^{-10}	0.037	0.0310
	320 (p)		9.5×10^{-12} ^a	0.031	0.0042 ^a

^aEstimated upper limit.

lower the value of the parameter p' , the greater the deformation expected in the shape of the Cole-Cole semicircle. Numerical calculations carried out in [6] show that the limiting value of p' for which slight deformations are predicted is equal to 0.05.

On the basis of present experimental results parameter p' can be calculated for all three substances in the liquid phase and an estimation of the upper limit of p' can be made for the plastic phase. Table I lists the values of all relevant parameters. Molecular diameters in the table were calculated by means of the increment method described by Kitaigorodsky [18] and the values of rotational diffusion constants were calculated from the simplified formula $D_R = 1/2\tau_D$.

From Table I we can see that in the liquid-phase parameter p' is of the order of 10^{-2} , i.e., it leads, according to the model, only to slight deformations in the relaxational profile. This is consistent with Debye-like behavior observed in this temperature range. In the plastic phase p' drops by at least 1 order in magnitude for all samples, indicating strongly non-Debye behavior, which is contrary to experimental findings. It should be stressed here that the value of the self-diffusion constant used for calculating p' is probably much lower than that estimated here. The experiments on a substance very similar to *t*-butyl chloride, although nonpolar, namely, neopropane, carried out by Tanner [19] demonstrate a drop in D_T of over four decades at the liquid-plastic-crystal transition point. If this were to be the case for the polar substances studied in this work, the parameter p' accounting for the coupling of rotations and translations in the plastic phase would be of the order of 10^{-5} , i.e., over three decades lower than the upper limit of p' , which in the extended hydrodynamical model leads to deformations in the relaxational profile. It is also worth noting that the studied liquids differ strongly in the magnitude of dipolar interaction. The ratio of energy of dipole-dipole interaction to thermal energy varies from a small fraction of unity in the case of 1,1,1-trichloroethane to values higher than 1

in the case of 2,2-dinitropropane. We might anticipate therefore that our conclusions about the lack of significant influence of rotational-translational coupling via dielectric friction on the shape of the relaxational profile are characteristic for the whole class of small, rigid and polar molecules.

The comparison of experimental data characterizing the rotational and translational motion in three simple, nearly symmetrical and polar liquids shows that the predictions of the extended hydrodynamical model presented recently by Bagchi and Chandra overestimate the effect of rotational-translational coupling on dielectric relaxation in liquid phase. In the light of this conclusion it seems that coupling via dielectric friction between translations and rotations may be of much less importance for the dielectric spectrum of real liquids than the other processes connected with the translational motion as, for instance, induction effects arising during collisions of polar molecules.

We are grateful to Dr. Enrico Tombari from IFAM Pisa for assistance and help in measurements of complex permittivity of trichloroethylene.

- [1] M. W. Evans, G. J. Evans, W. T. Coffey, and C. Grigolini, *Molecular Dynamics* (Wiley, New York, 1982).
- [2] P. Madden and D. Kivelson, *Adv. Chem. Phys.* **56**, 467 (1984).
- [3] C. J. F. Botcher and P. Bordewijk, *Theory of Dielectric Polarisation* (Elsevier, Amsterdam, 1978).
- [4] T. W. Nee and R. W. Zwanzig, *J. Chem. Phys.* **52**, 6353 (1970).
- [5] J. Hubbard and P. G. Wolynes, *J. Chem. Phys.* **69**, 998 (1978).
- [6] B. Bagchi and A. Chandra, *Phys. Rev. Lett.* **64**, 455 (1990).
- [7] E. L. Pollock and B. J. Alder, *Phys. Rev. Lett.* **46**, 950 (1981).
- [8] J. W. Sherwood, *The Plastically Crystalline State* (Wiley, Chichester, 1972).
- [9] A. Mansingh and D. B. McLay, *Can. J. Phys.* **45**, 3815 (1967).
- [10] B. Lassièr and C. Brot, *J. Chim. Phys.* **65**, 1723 (1968).
- [11] O. E. Stejskal and J. E. Tanner, *J. Chem. Phys.* **42**, 288 (1965).
- [12] D. E. O'Reilly *et al.*, *J. Chem. Phys.* **59**, 3576 (1973).
- [13] M. Godlewska *et al.*, *Phys. Status Solidi (a)* **73**, 6 (1982).
- [14] S. Urban, J. Lenik, and S. Wrobel, *Acta Phys. Pol. A* **41**, 91 (1972).
- [15] S. Urban *et al.*, *Phys. Status Solidi (a)* **10**, 271 (1972).
- [16] T. Grochulski and E. Tombari (unpublished).
- [17] T. Grochulski *et al.*, *J. Phys. E* **15**, 304 (1982); Z. Kisiel, K. Leibler, and A. Gerschel, *J. Phys. E* **17**, 240 (1984).
- [18] A. I. Kitaigorodsky, *Molecular Crystals and Molecules* (Academic, New York, 1973), p. 21.
- [19] J. E. Tanner, *J. Chem. Phys.* **56**, 3850 (1972).