Time-Temperature Superposition in Viscous Liquids

Niels Boye Olsen, Tage Christensen, and Jeppe C. Dyre

Department of Mathematics and Physics (IMFUFA), Roskilde University, Postbox 260, DK-4000 Roskilde, Denmark
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Dielectric relaxation measurements on supercooled triphenyl phosphite show that time-temperature superposition (TTS) is obeyed for the primary relaxation process at low temperatures. Measurements on other molecular liquids close to the calorimetric glass transition indicate that TTS is linked to an $\omega^{-1/2}$ high-frequency decay of the loss, while the loss peak width is nonuniversal.

Liquids approaching the calorimetric glass transition have very high viscosities and very long relaxation times compared to, e.g., room-temperature water. The study of highly viscous liquids is fascinating because—independent of the chemical nature of the intermolecular bonds—these liquids share a number of common features [1–11]. The two most significant common features are non-Arrhenius temperature dependence of the average relaxation time and non-Debye linear response functions. This paper addresses an old empiricism relating to the latter, *time-temperature superposition* (TTS) [12].

Linear response experiments are usually reported in terms of the frequency dependence of the imaginary part of the response function in question $\chi(\omega)$, the "loss." If the shape of the loss peak in a log-log plot is temperature independent the liquid obeys TTS with respect to the response function. Mathematically, if T is temperature and $\tau(T)$ is the average relaxation time, TTS is obeyed whenever functions N and ϕ exist such that $\chi(\omega, T) = N(T)\phi[\omega\tau(T)]$.

When TTS applies response functions are easily determined over many decades of frequency. This is done by combining measurements at different temperatures. This procedure works even if only one or two decades of frequency are directly accessible (as in, e.g., mechanical relaxation probed by the torsion pendulum technique).

TTS has a long history [13]. For many years TTS was assumed uncritically and used extensively. As accuracy increased and frequency ranges widened, more and more systems were found not obeying TTS. It turned out that TTS violations were not just exceptions but, in fact, quite common. These violations were initially often explained as due to interference from an additional minor relaxation process, the so-called β relaxation often found at frequencies higher than those of the dominant α relaxation. More recently, it has been the general opinion that the α process usually itself violates TTS. Anyway, if TTS does not always work it cannot be assumed *a priori*. Thus the option of using TTS to arrive at wide-frequency "master" curves was no longer available.

In this situation the nonpolymeric scientific community became skeptical of TTS (for polymers TTS is still often assumed [14]). For several years now there has been little interest in TTS for nonpolymeric viscous liquids close to T_g. In the less viscous regime at higher temperatures where mode-coupling theory is believed to apply, this theory's TTS prediction has received some confirmation from both experiment [15] and computer simulations [16]. From the mode-coupling perspective, breakdowns of TTS in the very high viscosity regime correlate with the well-known breakdown of ideal mode-coupling theory here.

We are mainly interested in the behavior of highly viscous liquids (just above T_g). Our motivation for reinvestigating the validity of TTS in this regime is the following. Dielectric relaxation often exhibits a high-frequency tail a few decades above the α peak, known as the Nagel wing [17–19], a feature which is clearly involved in TTS violations. Although generally thought to be part of the α process, it has recently been suggested that the Nagel wing instead derives from a partly hidden β process [20–22]. This was subsequently confirmed by long-time annealing experiments on propylene carbonate and glycerol by Schneider, Brand, Lunkenheimer, and Loidl [23] (for glycerol β relaxation was previously reported at high pressures [24]). Accepting this interpretation of the Nagel wing, the following question arises: What happens at temperatures low enough that any influence of β relaxation is eliminated—is it possible that α relaxation does obey TTS after all?

Figure 1 shows the dielectric loss of triphenyl phosphite. Our dielectric setup, which is briefly described in Ref. [26], covers frequencies from 1 mHz to 1 MHz; the absolute temperature uncertainty is below 0.1 K. Figure 1a gives raw data, while Fig. 1b shows the same data scaled to check TTS. Clearly, TTS is obeyed to a good approximation. The β loss peak of triphenyl phosphite lies at higher frequencies than for most other viscous liquids and consequently α and β relaxations are well separated. Two things are to be noted from Fig. 1. First, TTS applies for the α relaxation whenever temperature is low enough that β relaxation does not interfere; in other words, as temperature is lowered TTS applies in a wider and wider frequency range around the α loss peak frequency. Second, the high-frequency slope of the α peak is close to $-1/2$. How general are these findings? This question is looked into in Fig. 2.
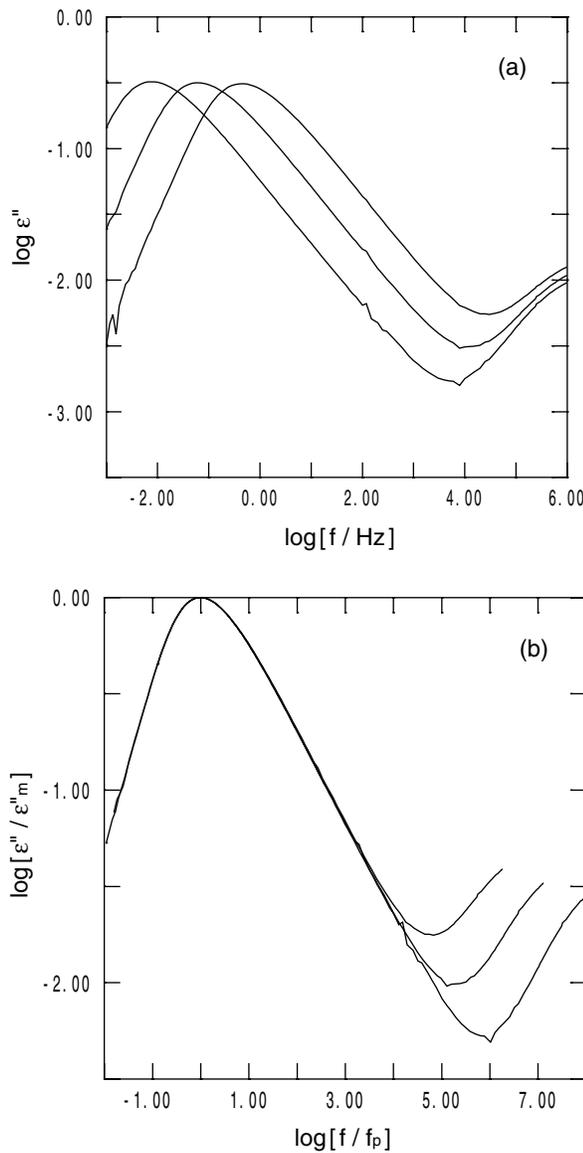
FIG. 1. Time-temperature superposition for dielectric relaxation of triphenyl phosphite (99%). To avoid the "glacial" phase [25] the liquid was cooled fast to 208.0 K. (a) Log-log plot (base 10) of the dielectric loss as a function of frequency f at 204.0, 206.0, and 208.0 K. As temperature is lowered the loss curve is displaced towards lower frequencies. (b) Same data scaled by the maximum loss ϵ''_m on the y axis and by the loss peak frequency f_p on the x axis. TTS is obeyed at low (scaled) frequencies but violated at high (scaled) frequencies where β relaxation sets in.

Figure 2a shows how α peak widths vary with temperature for triphenyl phosphite and several other molecular liquids. As a measure of the peak width we use the quantity w introduced by Dixon *et al.* [17], defined as the width at half maximum in the log-log plot relative to the same quantity for a Debye process. In Fig. 2a w is plotted as a function of loss peak frequency—the latter quantity providing a convenient measure of temperature [17]. When TTS is obeyed w is temperature independent, which is
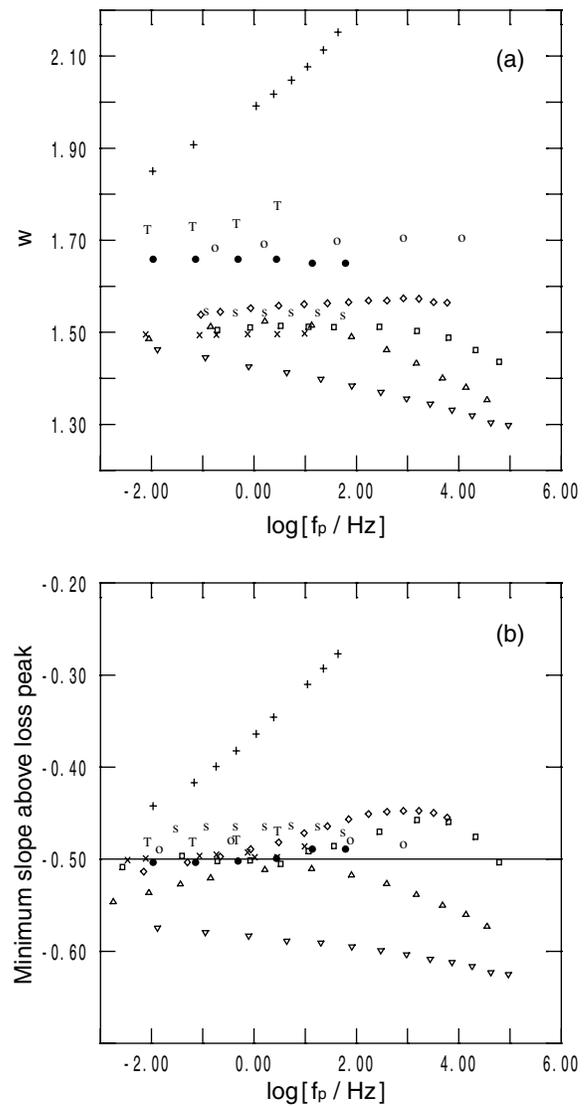
FIG. 2. Loss peak width and exponent of approximate high-frequency power law for α relaxations as functions of log (base 10) of the loss peak frequency f_p, a measure of temperature (with low temperatures to the left and high to the right). (a) Loss peak width w defined by $w = W/W_D$, where W is the width at half maximum in the log-log plot and W_D is the same quantity for a Debye relaxation process [17]. When TTS is obeyed w is temperature independent. This happens for some, but not all, liquids at low temperatures. Data are shown for the following liquids: triphenyl phosphite (99%) (T), salol (purified) (S), pyridine-toluene solution [26] ($+$), tripropylene glycol (97%) ($\diamondsuit$), dipropylene glycol (techn.) ($\triangle$), dibutyl phthalate (unspecified purity) ($\square$), diethyl phthalate (99%) ($\times$), glycerol (99%) ($\triangledown$), MS704 silicone (diffusion pump) oil (O), five year old bottle of triphenyl phosphite [27] ($\bullet$). (b) Minimum slope above the loss peak of the dielectric loss (in log-log plot) for the same liquids. A comparison with (a) indicates that the minimum slope is close to $-1/2$ whenever TTS is obeyed.

the case for many liquids to a good approximation at low temperatures.

How about the α loss peaks for the liquids that obey TTS—do they have anything in common?   The width

is clearly nonuniversal. Now, if the α process follows a high-frequency power law the exponent may be estimated by evaluating the minimum slope above the loss peak (in the log-log plot). Figure 2b shows this minimum slope for the same liquids, again as a function of loss peak frequency. Comparing to Fig. 2a we find that the minimum slope is close to $-1/2$ whenever w is virtually temperature independent. This is the case for seven of the ten liquids represented.

The liquids in Fig. 2 come in three classes: (a) Liquids that obey TTS at low temperatures and have minimum slope close to $-1/2$, (b) liquids which seem to converge to this behavior if observations over years were possible, and finally (c) one liquid (dipropylene glycol) that does not seem to converge to TTS. All other liquids we have studied fall in one of these three classes. For instance, dimetyl phthalate obeys TTS and has minimum slope close to $-1/2$. We have no exception to the rule that *whenever TTS applies to a good approximation the α high-frequency slope is close to $-1/2$*. There are strong indications that this rule applies also for the frequency-dependent shear modulus which we can measure between 1 mHz and 50 kHz [28]; the shear data, however, are more noisy than the dielectric data. Examples of liquids obeying TTS for the shear modulus are dibuthyl phthalate [29], MS704 silicone oil, and o-terphenyl. In all cases the high frequency slope of the α peak is close to $-1/2$. Interestingly, triphenyl phosphite does not obey TTS as well for the shear modulus as for dielectric relaxation.

To conclude, we find that (i) TTS is sometimes — but not always — obeyed for the α relaxation at low temperatures; (ii) whenever TTS applies the α loss decays roughly as $\omega^{-1/2}$ at high frequencies; (iii) the α loss peak width is nonuniversal, even when TTS applies. To some extent these points reflect the opinion prevailing in this research field 30 years ago, now generally regarded as obsolete. Thus at that time there was considerable focus on TTS, as well as on the $\omega^{-1/2}$ high-frequency α behavior. Several theories were proposed to explain the latter [30]; some of these theories also predicted TTS.

Extrapolating the above in the spirit of Johari and Goldstein, who conjectured that β relaxation is "a characteristic property of the liquid in or near the glassy state" [31], the following conjectures immediately come to mind: (i) There is always a β relaxation [20–23,31], though it is sometimes hidden under the α process and only visible as a Nagel wing; (ii) whenever additional relaxations do not interfere, the α relaxation obeys TTS with a loss decaying as $\omega^{-1/2}$ at high frequencies. These conjectures, however, are unscientific in the following sense: Any deviation from TTS may always be "explained" as a result of interference from one or more ultra-low-frequency "β processes," in effect making the conjecture impossible to falsify. From a more pragmatic point of view, if TTS does apply for, e.g., glycerol at low temperatures, it appears from Fig. 2a that the loss peak frequency at these low temperatures is much

smaller than the smallest we measure at. Measurements in ultralow frequencies are difficult because they require extremely high sensitivity and months or years of uninterrupted measurements. For this reason alone it would be next to impossible to show that glycerol eventually obeys TTS.

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[1] W. Kauzmann, Chem. Rev. **43**, 219 (1948).

[2] R. O. Davies and G. O. Jones, Adv. Phys. **2**, 370 (1953).

[3] M. Goldstein, in *Modern Aspects of the Vitreous State,* edited by J. D. Mackenzie (Butterworths Scientific, London, 1964), p. 90.

[4] G. Harrison, *The Dynamic Properties of Supercooled Liquids* (Academic, New York, 1976).

[5] E.-J. Donth, *Glasübergang* (Akademie-Verlag, Berlin, 1981).

[6] S. Brawer, *Relaxation in Viscous Liquids and Glasses* (American Ceramic Society, Columbus, OH, 1985).

[7] C. A. Angell, J. Non-Cryst. Solids **131–133**, 13 (1991).

[8] S. V. Nemilov, *Thermodynamic and Kinetic Aspects of the Vitreous State* (CRC, Boca Raton, FL, 1995).

[9] P. G. Debenedetti, *Metastable Liquids: Concepts and Principles* (Princeton University, Princeton, 1996).

[10] J. C. Dyre, J. Non-Cryst. Solids **235–237**, 142 (1998).

[11] C. A. Angell, K. L. Ngai, G. B. McKenna, P. F. McMillan, and S. W. Martin, J. Appl. Phys. **88**, 3113 (2000).

[12] Other names for TTS are time-temperature superposition principle, time-temperature scaling, time-temperature reducibility, method of reduced variables, or (for mechanical properties) thermorheological simplicity.

[13] Time-temperature superposition is such an enormous subject that it is impossible to get a full view of it. We here present the history of TTS as we recall it from many years of reading the literature on nonpolymeric viscous liquids.

[14] I. Morfin, P. Lindner, and P. Boue, Macromolecules **32**, 7208 (1999); R. Z. Li, Mater. Sci. Eng. A **278**, 36 (2000); M. McBreaty and S. Perusich, Polym. Eng. Sci. **40**, 201 (2000); Y. Miyano, M. Nakada, H. Kudoh, and R. Muki, J. Compos. Mater. **34**, 538 (2000).

[15] W. Götze, J. Phys. Condens. Matter **11**, A1 (1999).

[16] S. Kammerer, W. Kob, and R. Schilling, Phys. Rev. E **58**, 2131 (1998); **58**, 2141 (1998).

[17] P. K. Dixon, L. Wu, S. R. Nagel, B. D. Williams, and J. P. Carini, Phys. Rev. Lett. **65**, 1108 (1990).

[18] A. Hofmann, F. Kremer, E. W. Fischer, and A. Schönhals, in *Disorder Effects on Relaxational Processes,* edited by R. Richert and A. Blumen (Springer, Berlin, 1994), p. 309.

[19] R. L. Leheny and S. R. Nagel, Europhys. Lett. **39**, 447 (1997).

[20] N. B. Olsen, in *Proceedings of the Third International Discussion Meeting on Relaxations in Complex Systems, Vigo, Spain, 1997* [J. Non-Cryst. Solids **235–237**, 399 (1998)].

[21] K. L. Ngai, Phys. Rev. E **57**, 7346 (1998); C. Leon, K. L. Ngai, and C. M. Roland, J. Chem. Phys. **110**, 11 585 (1999).

[22] H. Wagner and R. Richert, J. Chem. Phys. **110**, 11 660 (1999).

[23] U. Schneider, R. Brand, P. Lunkenheimer, and A. Loidl, Phys. Rev. Lett. **84**, 5560 (2000).

[24] G. P. Johari and E. Whalley, Faraday Symp. Chem. Soc. **6**, 23 (1972).

[25] I. Cohen, A. Ha, X. Zhao, M. Lee, T. Fischer, M. J. Strouse, and D. Kivelson, J. Phys. Chem. **100**, 8518 (1996); J. Wiedersich, A. Kudlik, J. Gottwald, G. Benini, I. Rogatz, and E. Rössler, J. Phys. Chem. B **101**, 5800 (1997); G. P. Johari and C. Ferrari, J. Phys. Chem. B **101**, 10 191 (1997); A. Hedoux, Y. Guinet, and M. Descamps, Phys. Rev. B **58**, 31 (1998); S. Dvinskikh, G. Benini, J. Senker, M. Vogel, J. Wiedersich, A. Kudlik, and E. Rössler, J. Phys. Chem. B **103**, 1727 (1999); M. Mizukami, K. Kobashi, M. Hanaya, and M. Oguni, J. Phys. Chem. B **103**, 4078 (1999); A. Hedoux, O. Hernandez, J. Lefebvre, Y. Guinet, and M. Descamps, Phys. Rev. B **60**, 9390 (1999).

[26] N. B. Olsen, T. Christensen, and J. C. Dyre, Phys. Rev. E **62**, 4435 (2000).

[27] Curiously, our very best example of TTS derives from a five year old bottle of triphenyl phosphite (97%) (data shown in Fig. 1 of N. B. Olsen, T. Christensen, and J. C. Dyre, e-print cond-mat/0006165). For this liquid, which has an α loss twice as large as that of newly purchased (99%) triphenyl phosphite, deviations from TTS are consistent with those expected from the 1 mK temperature inaccuracy of our cryostate (since the writing of Ref. [26] the temperature stability has been improved from 5 to 1 mK). Since five year old measurements on the 97% bottle were virtually identical to our present 99% measurements, it appears that the "old" liquid has undergone some chemical decomposition. The minimum slope above the loss peak of the old liquid is -0.503; the corresponding number for the "new" liquid is -0.482.

[28] T. Christensen and N. B. Olsen, Rev. Sci. Instrum. **66**, 5019 (1995).

[29] C. F. Behrens, T. G. Christiansen, T. Christensen, J. C. Dyre, and N. B. Olsen, Phys. Rev. Lett. **76**, 1553 (1996).

[30] S. H. Glarum, J. Chem. Phys. **33**, 639 (1960); M. A. Isakovich and I. A. Chaban, Zh. Eksp. Teor. Fiz. **50**, 1343 (1966) [Sov. Phys. JETP **23**, 893 (1966)]; A. J. Barlow, A. Erginsav, and J. Lamb, Proc. R. Soc. London A **298**, 481 (1967); C. J. Montrose and T. A. Litovitz, J. Acoust. Soc. Am. **47**, 1250 (1970); C. K. Majumdar, Solid State Commun. **9**, 1087 (1971); G. Wyllie, J. Chim. Phys. **76**, 1017 (1979).

[31] G. P. Johari and M. Goldstein, J. Phys. Chem. **74**, 2034 (1970); J. Chem. Phys. **53**, 2372 (1970).