

Communication: Two measures of isochronal superposition

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A liquid obeys isochronal superposition if its dynamics is invariant along the isochrones in the thermodynamic phase diagram (the curves of constant relaxation time). This paper introduces two quantitative measures of isochronal superposition. The measures are used to test the following six liquids for isochronal superposition: 1,2,6 hexanetriol, glycerol, polyphenyl ether, diethyl phthalate, tetramethyl tetraphenyl trisiloxane, and dibutyl phthalate. The latter four van der Waals liquids obey isochronal superposition to a higher degree than the two hydrogen-bonded liquids. This is a prediction of the isomorph theory, and it confirms findings by other groups. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4821163>]

The relaxation time of a supercooled liquid depends strongly on temperature and pressure. Different thermodynamic state points with same relaxation time are said to be on the same isochrone. A liquid obeys “isochronal superposition” if its dynamics is invariant along the isochrones. More precisely, a liquid obeys isochronal superposition (IS) if the complex, frequency-dependent response function $R(\omega, Q)$ in question at state point Q can be written

$$R(\omega, Q) = R_0(Q)\tilde{R}(\omega, \tau(Q)) + K_0(Q). \quad (1)$$

Here $R_0(Q)$ and $K_0(Q)$ are state-point dependent real constants. The function $\tilde{R}(\omega, \tau(Q))$ describes the shape of the relaxation spectrum; this function depends on the state point Q only via its relaxation time $\tau(Q)$. For the imaginary part of the response function, IS implies $R''(\omega, Q) = R_0(Q)\tilde{R}''(\omega, \tau(Q))$. This paper suggests two quantitative measures of how well IS is obeyed and applies them to test six glass-forming liquids for IS.

Tölle first demonstrated IS for a single liquid, orthoterphenyl, in data for the intermediate scattering function determined by neutron scattering.¹ Soon after, systematic investigations of IS were initiated by Roland *et al.*² and Ngai *et al.*³ using dielectric spectroscopy. These seminal papers established IS for the van der Waals liquids studied, but reported that hydrogen-bonded liquids often violate IS. This was a striking discovery presenting a serious challenge to theory: Why would some liquids, for which the relaxation time spectrum generally varies throughout the thermodynamic phase diagram, have invariant spectra along its isochrones? And why do other liquids disobey IS?

By visually comparing the imaginary part of response functions along a liquid’s isochrones the analysis of IS has traditionally followed the age-old method for investigating time-temperature superposition (TTS). The present paper takes the analysis one step further by suggesting two measures of the *degree of IS* — such measures are relevant because one does not expect any liquid to obey IS with mathematical rigor. First, however, a few experimental details are given (further details are given in the supplementary material⁴).

We studied four van der Waals liquids: polyphenyl ether (5PPE), diethyl phthalate (DEP), dibutyl phthalate (DBP), and tetramethyl tetraphenyl trisiloxane (DC704), as well as two hydrogen-bonded liquids: 1,2,6 hexanetriol (1,2,6-HT) and glycerol (details are given in Table I). New measurements have been obtained for four of the liquids, while the data on DC704 are from Ref. 10 and the data on DBP are from Ref. 11. The four liquids studied in this work were all studied before, also by use of dielectric spectroscopy under high pressure.^{9,12–16}

Glycerol was dried in an exicator for 20 h and 1,2,6-HT was dried for 2 h; the other liquids were used as acquired from Sigma Aldrich. The experiments were performed on the high-pressure equipment described in Refs. 9 and 17. The electrical measurement equipment is described in Ref. 18. Pressures go up to 600 MPa, temperatures range from 233 to 333 K. The sample cell consists of two round stainless steel plates with a diameter of 19.5 mm separated by a 0.05 mm thick Kapton spacer, which has inner diameter 17.5 mm and outer diameter 19.5 mm. To document reproducibility all measurements were repeated. The relaxation time was identified from the dielectric loss-peak frequency.

Hydrogen-bonded liquids have generally much larger dipole moment than van der Waals liquids, which leads to much better dielectric relaxation signals for the former liquids. Figure 1 shows typical dielectric relaxation data for the six liquids studied.

To develop quantitative measures of IS, consider first perfect IS. A loss peak is characterized by, in principle, infinitely many shape parameters X, Y, Z, \dots . In practice, a few parameters are enough to characterize the shape, for instance fitting-model based parameters such as the stretching exponent β , the Havriliak-Negami parameters, the Cole-Davidson β_{CD} , etc., or model-independent parameters such as the half width at half depth or the loss peak area in a log-log plot. Perfect IS is characterized by constant shape parameters along an isochrone: $0 = dX|_{\tau} = dY|_{\tau} = dZ|_{\tau} = \dots$, in which $|_{\tau}$ signals that the variation is considered at constant relaxation time.

In order to determine how much a given shape parameter X varies along an isochrone, we assume that a metric ds

TABLE I. The liquids studied. “H” is hydrogen bonded and “vdW” is van der Waals bonded. Where no reference is given, $\Delta\varepsilon$ is from our measurements. Details on the density data are given in the supplementary material.⁴

Liquid	Abbr.	Bonding	T_g (K)	$\Delta\varepsilon$	T (K)	p (MPa)	Density	Ref.
1,2,6 hexanetriol	1,2,6-HT	H	203 ⁵	~ 40	236–251	100–400	This work	This work
Glycerol		H	193 ⁶	~ 60	237–250	100–300	Ref. 7	This work
Polyphenyl ether	5PPE	vdW	245 ⁸	$\sim 2^8$	255–332	0.1–400	Ref. 9	This work
Diethyl phthalate	DEP	vdW	187 ⁶	~ 8	235–271	100–400	This work	This work
Tetramethyl tetraphenyl trisiloxane	DC704	vdW	211 ⁸	$\sim 0.2^8$	253–283	39–304	Ref. 9	Ref. 10
Dibutyl phthalate	DBP	vdW	177 ¹¹	~ 8	206–254	0–389	Ref. 7	Ref. 11

has been defined in the thermodynamic phase diagram. Since $d \ln X = dX/X$ gives the relative change of X , the rate of relative change of X along an isochrone is given by the operator L defined by

$$L(X) \equiv \left| \frac{d \ln X}{ds} \right|_{\tau}. \quad (2)$$

How to define a reasonable metric ds ? A state point is characterized by its temperature T and pressure p , so one option is $ds^2 = dT^2 + dp^2$. This metric depends on the unit system used, however, which is not acceptable. This problem may be solved by using logarithmic distances, i.e., defining $ds^2 = (d \ln T)^2 + (d \ln p)^2$. Actually, using pressure is not optimal because there are numerous decades of pressures below ambient pressure where little change of the physics take place; furthermore, a logarithmic pressure metric does not allow for negative pressures. For these reasons we instead quantify state points by their temperature and density ρ , and use the following metric:

$$ds^2 \equiv (d \ln T)^2 + (d \ln \rho)^2. \quad (3)$$

Equations (2) and (3) define a quantitative measure of IS. In practice, suppose an experiment results in data for the shape parameter X along an isochrone. This gives a series of numbers X_1, X_2, \dots , corresponding to the state points $(T_1, \rho_1), (T_2, \rho_2), \dots$. Since $\ln X_{i+1} - \ln X_i = \ln(X_{i+1}/X_i)$, etc., the discrete version of the right-hand side of Eq. (2) is $|\ln(X_{i+1}/X_i)/\sqrt{\ln^2(T_{i+1}/T_i) + \ln^2(\rho_{i+1}/\rho_i)}|$.

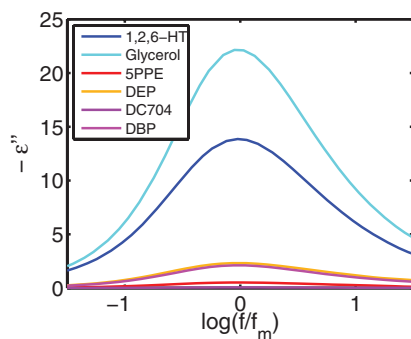


FIG. 1. One dielectric relaxation spectrum for each of the six liquids plotted on a linear scale. The hydrogen-bonded liquids (blue) have much larger signals than the van der Waals liquids (reddish). The spectrum of DC704 is too small to be visible.

An alternative measure of IS corresponding to the purely temperature-based metric $ds^2 = (d \ln T)^2$ is defined by

$$L_T(X) \equiv \left| \frac{d \ln X}{d \ln T} \right|_{\tau}. \quad (4)$$

This measure is considered because density data are not always available. If the density-scaling exponent $\gamma \equiv (d \ln T/d \ln \rho)|_{\tau}$ is known for the range of state points in question, Eq. (3) implies $ds^2 = (d \ln T)^2(1 + 1/\gamma^2)$. This leads to the following relation between the two IS measures:

$$L(X) = \frac{L_T(X)}{\sqrt{1 + 1/\gamma^2}}. \quad (5)$$

This relation is useful in the (common) situation where gamma is reported in the literature but the original density data are difficult to retrieve.

As one shape parameter we used the half width at half depth, $W_{1/2}$, defined as the number of decades of frequency from the frequency of maximum dielectric loss to the higher frequency (denoted $f_{1/2}$) where the loss value is halved: $W_{1/2} \equiv \log(f_{1/2}/f_m)$.⁶ Here and henceforth “log” is the logarithm with base 10.

The $W_{1/2}$ -values are plotted in Fig. 2(a) as functions of temperature for each isochrone studied. This figure suggests that IS is not obeyed for the two hydrogen-bonded liquids (blue), but for the four van der Waals liquids. There is more scatter in the values for the van der Waals liquids than for the hydrogen-bonded liquids, which is due to the smaller dielectric signals (see Fig. 1).

From Fig. 2(a) it is seen that the $W_{1/2}$ is almost constant at all state points for DEP and DC704, suggesting that IS in these cases is a consequence of TTS (or more specifically, time-temperature-pressure superposition). However, the isochrones in Fig. 2(a) are separated from one another in the case of 5PPE and DBP, just as they are in the case of 1,2,6-HT and glycerol. This shows that IS can apply even when the spectra broaden upon supercooling, which is also supported by earlier works where IS has been found for systems without TTS.^{10,19}

For a quantitative IS analysis, we apply the L and L_T operators to the shape parameter $W_{1/2}$ (Figs. 2(b) and 2(c)). From these figures it is clear that the measures for the hydrogen-bonded liquids are higher than for the van der Waals liquids. It is not straightforward to estimate the systematic uncertainties involved in the measurements, but an attempt to do so is presented in the supplementary material.⁴ We see from Fig. 2

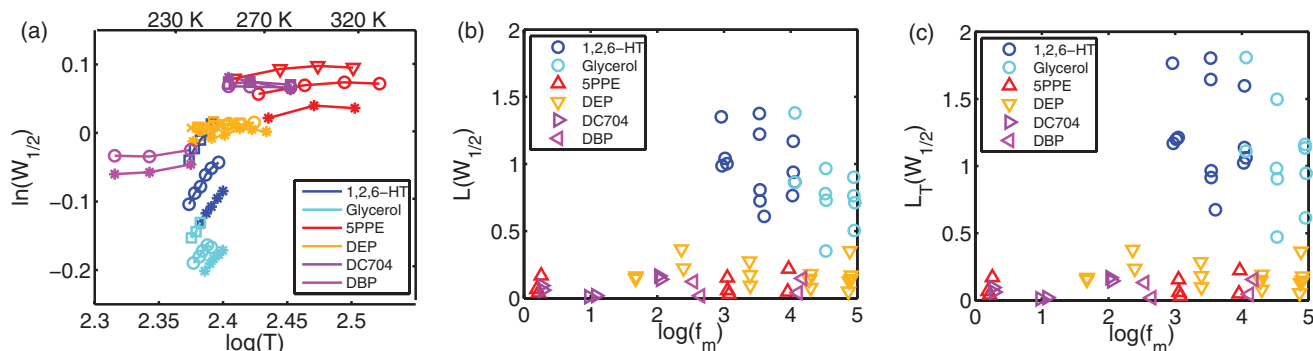


FIG. 2. Analysis of isochronal superposition (IS) based on the half width at half depth of the dielectric loss peak, $W_{1/2}$. (a) Data for $W_{1/2}$ along isochrones marked by connecting lines as functions of temperature. (b) The measure $L(W_{1/2})$ giving the rate of relative change of $W_{1/2}$ along an isochrone. (c) The measure $L_T(W_{1/2})$. Both measures are considerably higher for the hydrogen-bonded liquids than for the van der Waals liquids; thus the latter obey IS to a higher degree than the hydrogen-bonded liquids.

that the two measures $L(W_{1/2})$ and $L_T(W_{1/2})$ lead to similar overall pictures and the same conclusion.

Invariance of one shape parameter such as $W_{1/2}$ is not enough to prove IS. As a second, model-independent shape parameter we used the area of dielectric loss over maximum loss in a log-log plot, denoted by A . We integrated from -0.4 decades below the loss peak frequency to 1.0 decade above it. This was done by adding data for the logarithm of the dielectric loss taken at -0.4 , -0.2 , 0.2 , 0.4 , 0.6 , 0.8 , and 1.0 decades relative to the loss peak frequency. This area measure focuses on the high-frequency side of the peak. This is motivated in part by the occasional presence of dc conductivity on the low-frequency side of the peak, in part by the fact that for molecular-liquids this side of the peak is generally characterized by a slope close to unity, i.e., it varies little from liquid to liquid.²⁰ In Fig. 3, the measures $L(A)$ and $L_T(A)$ are shown. Clearly, the measures are higher for the hydrogen-bonded liquids than for the van der Waals liquids. Thus also with respect to the area shape parameter, the van der Waals liquids obey IS to a higher degree than the hydrogen-bonded liquids.

As a third parameter, we used the model-dependent shape parameter β_{DC} from the Cole-Davidson fitting function.²¹ Details on the fits are given in the supplementary material.⁴ Results from using the L operators on β_{CD} are shown in Fig. 4. It is seen that also with respect to the model-dependent shape parameter β_{CD} the van der Waals liquids obey IS to a higher degree than the hydrogen-bonded liquids.

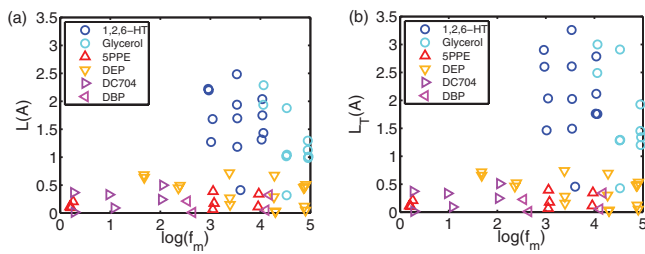


FIG. 3. The measures of isochronal superposition based on the area A of the dielectric loss peak plotted in a normalized log-log plot, obtained by integrating from -0.4 to $+1.0$ decades around the loss-peak frequency. (a) The measure $L(A)$. (b) The measure $L_T(A)$.

The conclusion that van der Waals liquids obey IS better than hydrogen-bonded liquids is not new. This was reported as a clear tendency in the pioneering papers on IS from 2003 and 2005 by Roland *et al.*² and Ngai *et al.*³ In 2009, this finding was given a theoretical basis via the isomorph theory,^{22,23} which applies for liquids that have strong correlations between their virial and potential-energy equilibrium fluctuations at constant volume.^{24–26} Due to the directional nature of hydrogen bonds, liquids dominated by these do not show strong virial potential-energy correlations.²⁴ The isomorph theory predicts that density scaling, as well as IS, applies for van der Waals liquids, but not for hydrogen-bonded liquids, a result that is consistent with previous experiments.^{27–30} Only few experimental studies have yet been made with the explicit purpose of testing the isomorph theory, see, e.g., Ref. 31, which supports the theory.

In this paper, we have focused on systems with no visible beta relaxation or excess wing. Capaccioli *et al.*¹⁹ demonstrated IS in systems with beta relaxation, suggesting that the beta and alpha relaxations are connected. This result can be rationalized in terms of the isomorph theory, which predicts IS to hold for all intermolecular modes. It would be interesting to use the quantitative measures suggested in this paper for systems with a beta relaxation.

To summarize, we have proposed two measures of isochronal superposition that quantify the relative change of a given relaxation-spectrum shape parameter along an isochrone. The measures were tested for six liquids with re-

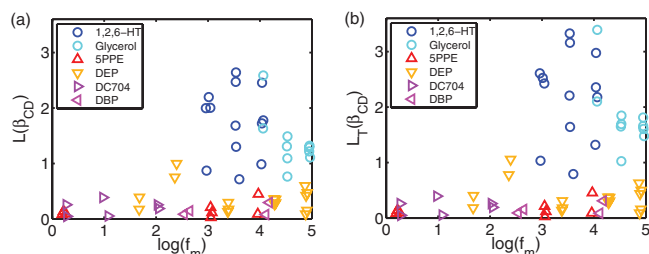


FIG. 4. The measures of isochronal superposition based on the shape parameter of the Cole-Davidson function β_{CD} . (a) The measure $L(\beta_{CD})$. (b) The measure $L_T(\beta_{CD})$.

gard to two model-independent shape parameters characterizing dielectric loss peaks, the half width at half depth and the loss-peak area in a normalized log-log plot, and one model-dependent shape parameter, the Cole-Davidson β_{CD} . The two measures lead to similar overall pictures; in particular both support the conclusion that van der Waals liquids obey IS to a higher degree than hydrogen-bonded liquids.

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