



Isomorph theory prediction for the dielectric loss variation along an isochrone



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ABSTRACT

This paper derives a prediction for the variation of the amplitude of the dielectric loss from isomorph theory, and presents an experimental test of the prediction performed by measuring the dielectric relaxation behavior of the van der Waals liquid 5-phenyl-4-ether (5PPE). The liquid is studied at isochronal states in the temperature range 266–333 K and pressure range 0.1 – 300 MPa, for relaxation times around 10^{-3} s and 10^{-4} s. From the isomorph statement that there is structural and dynamic invariance of isomorph states in reduced units for Roskilde simple liquids we derive four equivalent isomorph-invariant terms, one of which is used in analyzing our data. It is the frequency-dependent term $\chi_e(f)\rho^{\gamma-1}$, with electric susceptibility χ_e , density ρ , and density-scaling factor γ . Due to the unique design of our experimental setup, we obtain dielectric loss data where the amplitude is reproducible ± 0.1 %. We moreover find that the empty capacitance of the capacitor cell is stable within ± 0.3 % in our measuring range and can be assumed to be constant. Using this we predict for two isomorph states there is $C_2(f) = C_1(f)(\rho_1/\rho_2)^{\gamma-1}$ to scale the imaginary capacitance, where C_1 is the capacitance measurement at ambient pressure and C_2 is the predicted capacitance at elevated pressure. We visually compare the predicted and measured plots and there is a good match between the two plots among the 42 pairs of isochronal states from the measurement.

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1. Introduction

The isomorph theory deals with a group of liquids called Roskilde simple liquids [1], which is developed through a series of papers [2–6]. It has been predicted from computer simulations that van der Waals liquids are generally considered simple [7].

For Roskilde simple liquid there are curves in the phase diagram along which structure and dynamics are invariant in reduced units [5]. If states 1 and 2 are two states on the same isomorph curve, they have proportional Boltzmann factor for physical relevant microstates, and the proportionality is constant and state dependent. Thus two isomorph states have one-to-one correspondence between their microscopic configurations [5]. From this point we can derive some isomorph-invariant predictions for different physical properties.

The isomorph theory can explain density scaling [7–9] and isochronal superposition [7,10,11], which have been experimental observations made from high-pressure dielectric measurements before the development of the theory. It has moreover been shown that isomorph theory can lead to non-powerlaw density scaling and this behavior is likewise confirmed experimentally [12] in line with earlier results suggesting non-powerlaw density scaling [13–15].

The isomorph theory has proven very strong in predicting the behavior of computer-simulated liquids. A lot of the predictions from isomorph theory which are tested by computer simulation are difficult to test experimentally. They refer to microscopic properties that are not experimentally accessible or they require very large density changes which are difficult (or impossible) to obtain in experiments [16].

Among the work done for density scaling there is one previous paper which tests a prediction of the isomorph theory without fitting or scaling parameters [17]. It shows for a silicon oil the density-scaling exponent γ_{scale} is the same as the fluctuation exponent γ_{isom} which can be determined from linear-response experiments at ambient pressure [17]. The work is experimentally heavy, data from 6 different techniques are used, and it is not easily extended to a large number of samples.

In this paper we develop a prediction from isomorph theory which is directly related to an experimentally accessible property; the amplitude of the dielectric loss. The prediction can be tested with just two types of relatively standard data: PVT-data in order to determine an equation of state and high-pressure dielectric data. Moreover it involves no fitting or scaling parameters. We show a test of the prediction on one van der Waals liquid, 5-phenyl-4-ether (5PPE), but this can be extended to other samples with a much smaller effort than any earlier predictions coming from the isomorph theory.

However, there is one experimental challenge; the amplitude of the dielectric signal has to be measured with high precision. The analysis of

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dielectric data is often focused on the shape and position of the loss peak, whereas the amplitude is rarely discussed [18–20]. It is difficult to measure the amplitude because it depends on the cell dimension, which often has a strong (and sometimes uncontrolled) dependence on temperature and pressure. To overcome this problem we have developed a new cell which is capable of giving reliable loss-amplitude data.

The method in this paper is straightforward. From theory: use the fluctuation–dissipation theorem and isomorph theory to predict the dielectric-relaxation invariant expression for isomorph states. By experiment: find isochronal states of 5PPE and check if the dielectric relaxation obeys the prediction. We here make use of the fact that an isochrone is an isomorph – if the liquid in question is Roskilde simple. The paper is structured as follows. In Section 2 we derive the invariant terms from isomorph theory and develop the method of applying the invariance to the measured dielectric signal; in Section 3 we describe the experimental setup and show the result from 5PPE measurement in Section 4.

2. Prediction

In this section we start from the analysis of dipole-moment response to an external electric field and its fluctuation. From the structural and dynamic invariance of polarization of isomorph states in reduced units we develop four equivalent isomorph-invariant terms, one of which is used subsequently to analyze the dielectric signal in our measurement.

2.1. Isomorph prediction

Suppose an isotropic material consists of N rigid dipolar molecules in volume V with polarization \mathbf{P} per unit volume. Then the total dipole moment \mathbf{VP} is a vector sum

$$\mathbf{VP} = \sum_{i=1}^N \mathbf{p}_i \quad (1)$$

where \mathbf{p}_i is the dipole moment of the i th molecule. In the case where there is no external electric field the total sum is zero on average. When an external electric field \mathbf{E} is applied, there is a change in the total average dipole moment given [21–23] by

$$\mathbf{VP}(t) = \int_0^\infty V\epsilon_0\chi_e(t') \dot{\mathbf{E}}(t-t') dt' \quad (2)$$

where ϵ_0 is the permittivity of free space, χ_e is the electric susceptibility of the material, and $\dot{\mathbf{E}}$ is the time derivative of the field. For a step change of the external field at $t = 0$ from 0 to E_0 we find

$$\mathbf{VP}(t) = E_0 \int_0^\infty V\epsilon_0\chi_e(t') \delta(t-t') dt' = E_0 V\epsilon_0\chi_e(t) \quad (3)$$

where δ is the delta function.

According to the fluctuation–dissipation (FD) theorem one has [24–26]

$$\int_0^t \mu(t') dt' = \frac{1}{2k_B T} \langle (\mathbf{VP}(t) - \mathbf{VP}(0))^2 \rangle \quad (4)$$

where k_B is the Boltzmann constant, T is the temperature of the material and μ is the so-called memory function, related to the response function of Eq. (3) by $V\epsilon_0\chi_e(t) = \int_0^t \mu(t') dt'$ [26]. Therefore,

$$V\epsilon_0\chi_e(t) = \frac{1}{2k_B T} \langle (\mathbf{VP}(t) - \mathbf{VP}(0))^2 \rangle. \quad (5)$$

Defining $\rho \equiv N/V$ [5], and using reduced unit for the time t , here $\tilde{t} = t/t_0 = t\rho^{1/3} \sqrt{k_B T/m}$ [5], where m is the average molecular mass of the material, the above equation becomes

$$\chi_e(\tilde{t}) = \frac{\rho}{T 2\epsilon_0 k_B N} \langle (\mathbf{VP}(\tilde{t}) - \mathbf{VP}(0))^2 \rangle. \quad (6)$$

The central statement of this paper is that the term $\langle (\mathbf{VP}(\tilde{t}) - \mathbf{VP}(0))^2 \rangle$ is preserved along an isomorph curve. The argument is simple: along an isomorph the structure and dynamics are the same (as function of reduced time \tilde{t}) – only the intermolecular distances are scaled but that does not affect the molecular orientation (note that the molecule size is not scaled). From this isomorph invariance, it is possible to derive other isomorph invariant terms which are more directly related to what we measure in experiments.

Since $1/(2k_B\epsilon_0 N)$ is constant for a specific system, it follows from Eq. (6) that $\chi_e(\tilde{t})T/\rho$ is also invariant.

The isomorph theory also states that defining $\Gamma \equiv \rho^\gamma/T$, Γ is a constant along any isomorph curve where γ is the density-scaling factor [5,7]. Thus, from Eq. (6) we get

$$\chi_e(\tilde{t}) = \frac{1}{\rho^{\gamma-1} 2\epsilon_0 k_B N} \langle (\mathbf{VP}(\tilde{t}) - \mathbf{VP}(0))^2 \rangle. \quad (7)$$

It follows that $\chi_e(\tilde{t})\rho^{\gamma-1}$ is predicted to be isomorph invariant. By applying Laplace transformation we also obtain the invariance of $\chi_e(\tilde{f})T/\rho$ and $\chi_e(\tilde{f})\rho^{\gamma-1}$ in the frequency domain. It is the latter of these expressions which we use to test the prediction in Section 3.

There is another prediction derived from the original invariance which connects to classical dielectric theory. In the Kirkwood–Fröhlich formula [22,24,27]

$$\epsilon_s - \epsilon_\infty = \frac{\mu^2}{3\epsilon_0 k_B} Fg \frac{\rho}{T} \quad (8)$$

where “ F ” is the local field correction factor and “ g ” is the correlation factor, and μ is the permanent dipole moment of each molecule, the dielectric loss strength $\epsilon_s - \epsilon_\infty$. The dielectric loss strength can also be obtained by integrating the imaginary part [22,24,28],

$$\epsilon_s - \epsilon_\infty = \frac{2}{\pi} \int_0^\infty \epsilon_r''(\tilde{f}) d \ln \tilde{f}. \quad (9)$$

Combining Eqs. (8) and (9), and using $\epsilon_r''(\tilde{f}) = \chi_e''(\tilde{f})$, we find

$$\frac{\pi\mu^2}{6\epsilon_0 k_B} Fg = \int_0^\infty \frac{T}{\rho} \chi_e''(\tilde{f}) d \ln \tilde{f}. \quad (10)$$

It follows that the product of the correction and correlation factor, Fg , is isomorph invariant. Thus the prediction actually tells us that the “ Fg ” factor should be constant for states along an isomorph curve.

In summary the four isomorph-invariant terms are

$$\left\{ \begin{array}{l} \langle (\mathbf{VP}(\tilde{t}) - \mathbf{VP}(0))^2 \rangle; \\ \chi_e(\tilde{t})T/\rho \quad (\text{or } \chi_e(\tilde{f})T/\rho); \\ \chi_e(\tilde{t})\rho^{\gamma-1} \quad (\text{or } \chi_e(\tilde{f})\rho^{\gamma-1}); \\ \text{and } Fg \text{ in the Kirkwood–Fröhlich formula.} \end{array} \right.$$

The first term is used to derive the following three equivalent isomorph-invariant ones; the second and third can be further used in loss-peak-amplitude scaling; the last one is added to make a connection to the classical dielectric theory.

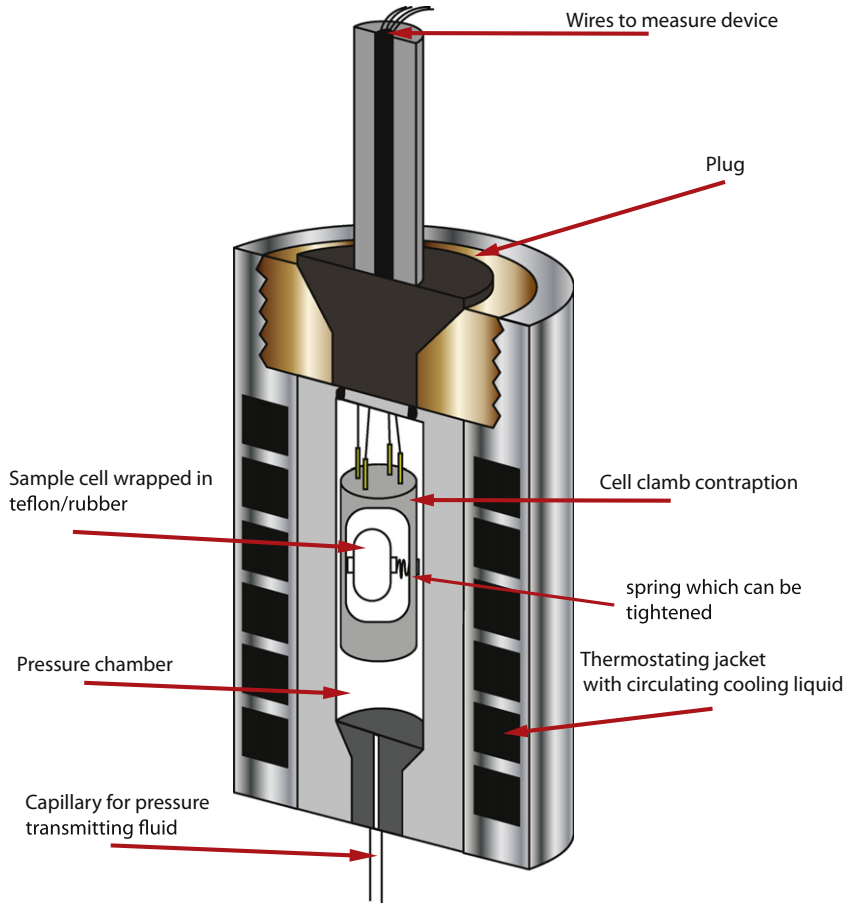


Fig. 1. Sketch of the pressure chamber. The chamber has an inner diameter of 30 mm, inner height of 70 mm, and outer radius of 150 mm, and the dielectric cell is 20 mm in diameter.

The result is the dielectric special case of the well established isomorph prediction that the relaxation function and relaxation time (in reduced units) are invariant along an isomorph [5]. This leads to the prediction of isochronal superposition, as we discuss in details in Ref. [29]. The new development is that we now predict exactly how the amplitude varies along the isomorph. In the next section we derive the method to apply the invariance of $\chi_e(\tilde{f})\rho^{\gamma-1}$ to the data from our measurement.

2.2. From prediction to data

Here we show how the invariance of $\chi_e(\tilde{f})\rho^{\gamma-1}$ can be tested by experiment. A similar use of $\chi_e(\tilde{f})T/\rho$ is presented in the Appendix A. For two isochronal states (P_1, T_1) and (P_2, T_2) , with density ρ_1, ρ_2 , electric susceptibility $\chi_e^{(1)}, \chi_e^{(2)}$, and relative permittivity $\epsilon_r^{(1)}(\tilde{f}), \epsilon_r^{(2)}(\tilde{f})$, there is the following relationship $\chi_e^{(1)}(\tilde{f})\rho_1^{\gamma-1} = \chi_e^{(2)}(\tilde{f})\rho_2^{\gamma-1}$.

The measured quantity is the capacitance $C(\tilde{f})$ of a full cell and the relative permittivity is found by dividing with the empty capacitance $\epsilon_r(\tilde{f}) = C(\tilde{f})/C_{\text{empty}}$. The real part of the relative permittivity is affected (and sometimes dominated) by the atomic polarization while isomorph theory only predicts the configurational polarization. By inspecting the imaginary part of ϵ_r we avoid the effect from the atomic polarization and we have $\text{Im}(\epsilon_r(\tilde{f})) = \text{Im}(\chi_e(\tilde{f}))$.

Thus the prediction becomes $\text{Im}(C_1(\tilde{f})/C_{\text{empty}}^{(1)})\rho_1^{\gamma-1} = \text{Im}(C_2(\tilde{f})/C_{\text{empty}}^{(2)})\rho_2^{\gamma-1}$. Because the ambient pressure is more stable than

elevated pressure, we use the plot of $-C_1^r(\tilde{f})$ from the ambient-pressure measurement to predict the curve $-C_2^r(\tilde{f})$ at elevated pressure,

$$-C_2^r(\tilde{f}) = -C_1^r(\tilde{f}) \left(\frac{\rho_1}{\rho_2}\right)^{\gamma-1} \frac{C_{\text{empty}}^{(2)}}{C_{\text{empty}}^{(1)}} \quad (\text{prediction}). \quad (11)$$

Eq. (11) is later used to treat data from our measurement, and a similar equation can be derived from the invariance of $\chi_e(\tilde{f})T/\rho$ (see Appendix A). It predicts the $-C_2^r(\tilde{f})$ plot at high-pressure state isochronal to the ambient state, if the density data, the density-scaling factor of the liquid, and the change of the empty capacitance are known.

For isomorph theory the consideration of reduced unit is inevitable in theoretical analysis and computer simulations when large changes of density are possible. However, in physical experiments, because of the relatively small changes of density, the influence of reduced unit can be neglected (To see the influence of reduced unit on actual data, see Fig. 3 in Appendix A.). Therefore, in practice Eq. (11) contains isochronal superposition in the classical sense first presented in Refs. [10,11], and it moreover predicts the scaling between isochronal states beyond normalization for isochronal superposition.

3. Experimental setup

The experimental setup consists of a homemade sample cell, a pressure chamber connected to a pressure pump (MV1) from Unipress Equipment in Warsaw Poland [30], a thermal bath Julabo F81-ME [31] and an electrical controlling system that is home made. The pressure

setup is described in details in Refs. [30,32,33]. Fig. 1 is a drawing of the vertical cross section of the pressure chamber.

The thermal liquid, a mixture of 40% water and 60% ethylene glycol, surrounded the pressure chamber, and the thermal couple was about 0.5 cm away from the cell.

From $10^{-2} - 10^2$ Hz we measured the capacitance with a custom-built voltage generator in combination with an HP 3458A multimeter and an HP 4284A LCR meter in the $10^2 - 10^6$ Hz range. See details on the measuring equipment in Ref. [34].

The capacitor consisted of two stainless-steel disks each 20 mm in diameter. To have a large and stable capacitance four square-sapphire spacers with dimension $0.5 \text{ mm} \times 0.5 \text{ mm} \times 0.05 \text{ mm}$ were glued to one of the disks. After the liquid was inserted between the disks (excess liquid was put around the cell gap) a Teflon ring and three layers of Teflon tape and latex were wrapped around the cell to separate the sample liquid from the pressure liquid. Since the sample liquid might expand and push the two disks further apart upon heating [21], a spring force was applied to hold them tight. This was a crucial part in keeping the measured capacitance reproducible. It was then put into a pressure chamber filled with pressure liquid (silicon oil) where we were able to

control the pressure within ± 3 MPa accuracy. Assuming the glue added no thickness to the spacers, this gave an empty capacitance of 55.6 pF. However, our measurements yielded 51 pF, suggesting that the size of the glue was not negligible.

An earlier experiment [33] identified states along two isochronal curves, 7 states in total at 0.1 MPa, 100 MPa, 200 MPa and 300 MPa, with loss-peak frequencies around 10^3 and 10^4 Hz respectively. In our measurements we also measured nearby isobaric states to obtain more isochronal states. Using the formula for the characteristic discharge flow time for pressure-driven channel flow [21,35] and isothermal bulk modulus and viscosity data for 5PPE [36,37], we estimated the corresponding flow times to be most 60 s and 6 s. This meant that even though the spacing was narrow the liquid flowed freely and could come into hydrostatic equilibrium on a timescale of a few minutes. To make sure the cell was in thermal equilibrium, we waited at least 1 h before each measurement. We made two measurements at each measuring point 15 min apart in order to see if there was any change. The reproducibility of data was also checked by repeating the measuring protocol, i.e., we increased the pressure to 300 MPa in steps and dropped it symmetrically and then increased again, see details in Ref. [38], where the repeated measurements in the latter two processes showed $\pm 0.1\%$ variation, and these data are used in further analysis.

It is not trivial to determine the capacitance variation of the empty capacitor upon isochronal-state change, and details are discussed in Ref. [38]. Since the specification of the glue upon pressure jump is not known and it may undergo plastic deformation above 100 MPa, we first ignore the glue and only consider the deformation of the stainless-steel disks and the sapphires upon temperature and pressure change, and the estimated change of the empty capacitance is at most 0.1% within the measuring range. We further made a computer-fitting program to estimate the expansion coefficient and the height of the glue, and the estimated change of the empty capacitance including the glue is about 0.1 – 0.3% [38]. Therefore, in the further data analysis one approximation is made: for any two isochronal states we assume that $C_{\text{empty}}^{(1)} = C_{\text{empty}}^{(2)}$, since the predicted amplitude changes we are looking for are of the order 10 – 20%, while the estimated change of the empty capacitance is about 0.1 – 0.3% and can be neglected.

4. Results

Fig. 2 is a visual presentation of the prediction (Eq. (11)). The density of 5PPE is found by extrapolation of the Tait equation whose parameters have been fixed by another experiment [32]. The density-scaling factor $\gamma = 5.5$ is determined by a previous experiment [17,32]. In total we have measured 155 state points, and found 42 pairs of isochronal states. The figure shows 10 pairs of isochronal states that have loss-peak frequencies spread evenly. Because we assume that $C_{\text{empty}}^{(1)} = C_{\text{empty}}^{(2)}$ and the prediction is formulated in terms of capacitance, Fig. 2 plots $-C''(f)$ instead of the dielectric constant ϵ_r . Within our measuring range the dielectric loss strength $\epsilon_s - \epsilon_\infty$ obtained is within 1.2 – 1.6. In Fig. 2 we see overall good match between the predicted plots of $-C''(f)$ (red curves) and the actual measurements (black circles) at all three elevated pressures. This is impressive because there are no fitting parameters or arbitrary scaling parameters involved. The data here is limited to one sample and also covers a limited range of pressure and temperature. Nevertheless it provides direct experimental support to the isomorph theory.

5. Summary

Based on the isomorph invariance of the structure and dynamics of Roskilde simple liquid, four equivalent isomorph invariant terms in dielectric relaxation are obtained. We have moreover developed the details needed to use one of these terms to analyze data.

The homemade capacitor cell has produced reliable data. By filling the cell with liquid 5PPE we have measured at isochronal states, and

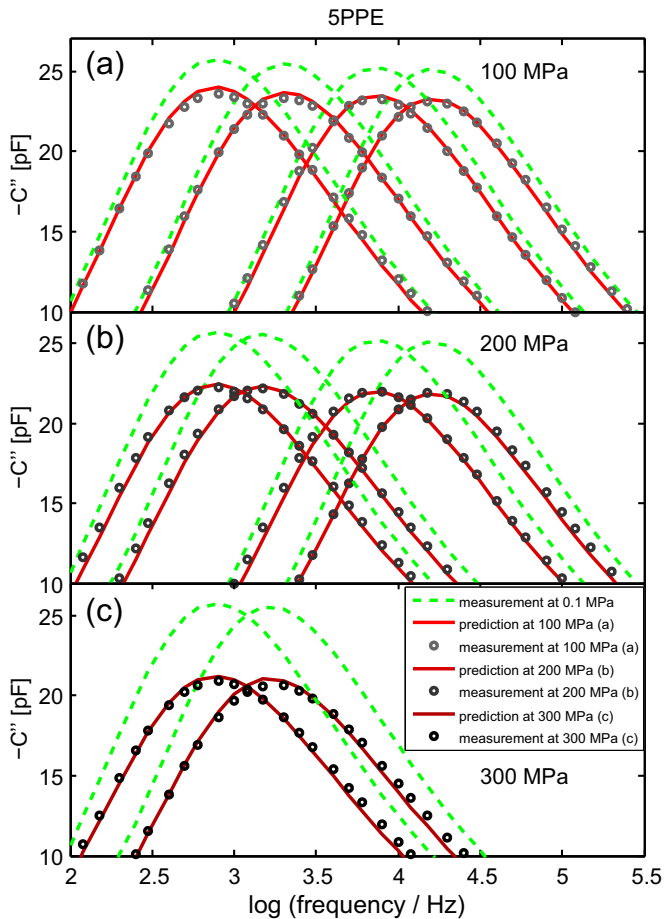


Fig. 2. Measurements of $-C''(f)$ at ambient pressure used to predict $-C''(f)$ of the corresponding isochronal states at 100 MPa, 200 MPa, and 300 MPa. The prediction is calculated from the isomorph invariance of $\chi_c(f)\rho^\gamma$ for $\gamma = 5.5$ [17], and compared to the actual measurements at elevated pressures. The green dashed lines are measurements at ambient pressure, the red curves are the predicted high-pressure $-C''(f)$ plots. There are no fitting parameters or arbitrary scaling involved in this prediction. The black circles are the high-pressure measurements that should coincide with the red curves. The 10 pairs of isochronal states in this figure are selected from 42 pairs in total such that they can be distinguished as different isochronal states visually. The empty cell capacitance is 51 pF at ambient pressure. Notice that the plots shown here are on a linear scale. The log–log plot scaled with the peak position is shown in Fig. 3 in the Appendix A along with a short discussion on isochronal superposition.

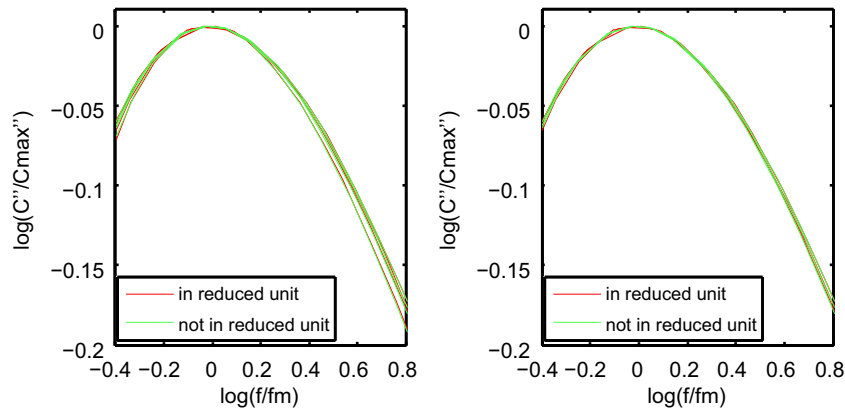


Fig. 3. A conventional isochronal-superposition examination of our 5PPE data at loss-peak frequency around 10^3 Hz, plotting the normalized imaginary capacitance by its amplitude C''_{\max} against normalized frequency by the loss-peak frequency f_m . The red curves are made for isochronal states in reduced units and the green ones not in reduced units. The plots on the left are plotted for states at 0.1 MPa, 100 MPa, 200 MPa and 300 MPa, while the plots on the right are at 100 MPa, 200 MPa and 300 MPa, to show that isochronal superposition is better obeyed for states at elevated pressures.

the measurement at ambient pressure is used to predict that of elevated pressure. Comparing the negative-imaginary-capacitance spectroscopy from the prediction and measurement at elevated pressures, we have seen an agreement between the two plots, providing support to the isomorph theory.

The ambition is that the prediction presented in this paper can be used to test the isomorph theory on several liquids by us and even more importantly by other groups doing high-pressure dielectrics.

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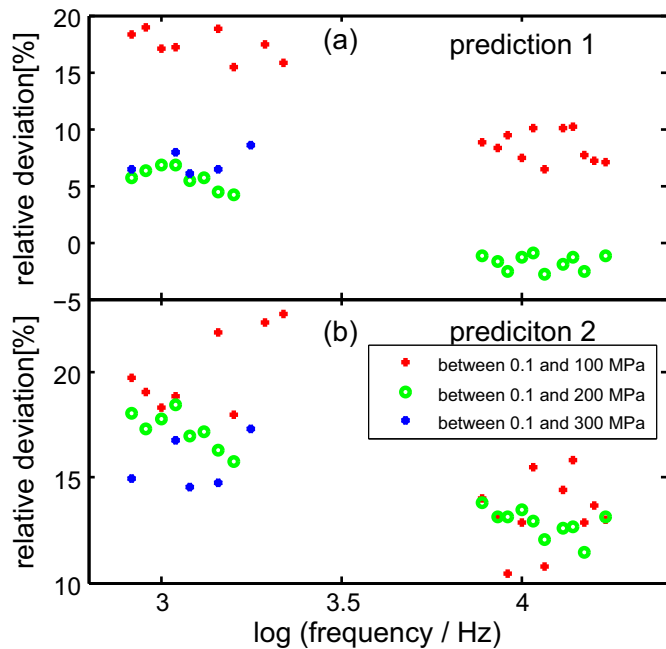


Fig. 4. Calculated “relative deviation” for both predictions. The “relative deviation” is defined as the ratio of differences in $-C''(f)$ amplitudes between the difference of the predicted curve and the actual measurement and the difference of the ambient pressure and high-pressure measurements. (a) is made for isomorph invariance of $\chi_e(f)\rho^{\gamma-1}$ – prediction 1 (Eq. (11)) and (b) for isomorph invariance of $\chi_e(f)T/\rho$ – prediction 2 (Eq. (12)). For prediction 1 the relative deviation is within (–3, 19) %, and for prediction 2 it is within (10, 24) %.

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Appendix A

Similar to Eq. (11), we derive the following equation based on the invariant term $\chi_e(f)T/\rho$,

$$-C''_2(f) = -C''_1(f) \frac{T_1 \rho_2 C''_{\text{empty}}(2)}{T_2 \rho_1 C''_{\text{empty}}(1)}. \quad (12)$$

The two equations are considered equivalent from isomorph theory. Now that a visual check (Fig. 2) supports the isomorph theory, we further show a way to quantify the degree of agreement between the prediction and measurement at elevated pressures. We have developed a measure called the “relative deviation”.

It has been shown that 5PPE obeys isochronal superposition to a high degree [29,33]. We have also done similar isochronal-superposition examination to our 5PPE data. The plot from Fig. 3 tells that 5PPE obeys isochronal superposition well, especially for states at elevated pressures. In addition there is no distinction in analyzing isochronal superposition of isochronal states in reduced unit or not. Thus it suffices to exploit the loss-peak amplitude of a $-C''(f)$ plot.

Our measure takes into account of the loss-peak amplitude A_0 of $-C''_1(f)$, the amplitude A_p of the predicted $-C''_2(f)$ plot, and the measured amplitude A_m of the measured $-C''_2(f)$ plot, and calculate the ratio $\delta = (A_p - A_m)/(A_0 - A_m)$. The smaller δ is the better the isomorph prediction works. From the 42 pairs of isochronal states we find that the values of relative deviation are within –3 – 19 % when applying the $-\epsilon_r''(f)\rho^{\gamma-1}$ prediction and within 10 – 24 % for the second prediction. Fig. 4 plots the relative deviation against loss-peak frequencies in a logarithmic scale for both predictions.

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