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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.

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 $V\mathbf{P}$ is a vector sum

$$V\mathbf{P} = \sum_{i=1}^{N} \mathbf{p}_i \tag{1}$$

where $\mathbf{p}_i$ is the dipole moment of the ith 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

$$V\mathbf{P}(t) = \int_0^\infty V\epsilon_0\chi_e(t')\,\dot{\mathbf{E}}\,(t-t')\mathrm{d}t' \tag{2}$$

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

$$\begin{aligned} V\mathbf{P}(t) &= E_0\int_0^\infty V\epsilon_0\chi_e(t')\delta(t-t')\mathrm{d}t' \\ &= E_0V\epsilon_0\chi_e(t) \end{aligned} \tag{3}$$

where δ is the delta function.

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

$$\int_0^t \mu(t')\mathrm{d}t' = \frac{1}{2\mathrm{k_B}T}\left\langle(V\mathbf{P}(t)-V\mathbf{P}(0))^2\right\rangle \tag{4}$$

where $\mathrm{k_B}$ 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 $V\epsilon_0\chi_e(t) = \int_0^t \mu(t')\mathrm{d}t'$ [26]. Therefore,

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

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

$$\chi_e\left(\tilde{t}\right) = \frac{\rho}{T}\frac{1}{2\epsilon_0\mathrm{k_B}N}\left\langle\left(V\mathbf{P}\left(\tilde{t}\right)-V\mathbf{P}(0)\right)^2\right\rangle. \tag{6}$$

The central statement of this paper is that the term $\left\langle\left(V\mathbf{P}\left(\tilde{t}\right)-V\mathbf{P}(0)\right)^2\right\rangle$ 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 $1/(2\mathrm{k_B}\epsilon_0 N)$ is constant for a specific system, it follows from Eq. (6) that $\chi_e\left(\tilde{t}\right)T/\rho$ 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

$$\chi_e\left(\tilde{t}\right) = \frac{1}{\rho^{\gamma-1}}\frac{\Gamma}{2\epsilon_0\mathrm{k_B}N}\left\langle\left(V\mathbf{P}\left(\tilde{t}\right)-V\mathbf{P}(0)\right)^2\right\rangle. \tag{7}$$

It follows that $\chi_e\left(\tilde{t}\right)\rho^{\gamma-1}$ is predicted to be isomorph invariant. By applying Laplace transformation we also obtain the invariance of $\chi_e\left(\tilde{f}\right)T/\rho$ and $\chi_e\left(\tilde{f}\right)\rho^{\gamma-1}$ 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]

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

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],

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

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

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

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

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

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.