



Fast dynamics in glass-forming salol investigated by dielectric spectroscopy

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ABSTRACT

We analyze dielectric-loss spectra of glass forming salol extending up to 400 GHz allowing for the detection of the high-frequency minimum, where the fast critical dynamics predicted by the mode-coupling theory of the glass transition should prevail. Indeed, we find such a minimum which, moreover, well fulfills the critical scaling predicted by the theory. This includes the spectral shape of the minimum, the critical temperature dependence of the minimum frequency and amplitude, and the critical temperature dependence of the α -relaxation rate at high temperatures. The minimum exponents a and b leading to a system parameter $\lambda \approx 0.63$ and the critical temperature $T_c = 256$ K are all in reasonable agreement with previous investigations of salol using different methods. Salol was one of the first materials where mode-coupling theory was tested and initial dielectric measurements were taken as an argument against the universal applicability of this theory.

1. Introduction

Salol is a typical example of a dipolar molecular glass former which can be easily supercooled. Investigations of such materials are commonly employed to help elucidating the mysteries of the glass transition and the glassy state of matter [1–3]. Numerous competing theories have been proposed to understand these mysteries [3–6]. Among them, one of the most prominent approaches is the mode coupling theory (MCT) [7]. Its central concept is the non-linear coupling of density fluctuations in supercooled liquids, which leads to a critical slowing down and, finally, to a structural arrest in a non-ergodic state at a critical temperature, well above the thermodynamic glass-transition temperature where the system falls out of equilibrium. One of the key predictions of MCT is the universal occurrence of fast critical dynamics, also termed fast β process. It should arise in the time or frequency regime between the structural α -relaxation process and the microscopic dynamics, observed in the vibrational frequency range and dominated by phonon-like or local molecular excitations. In susceptibility spectra, as obtained by experimental methods that are sensitive to the dynamics of the glass-forming entities (molecules in the case of salol), this dynamics should lead to a typical shallow minimum. Moreover, the temperature dependence and shape of this susceptibility minimum are predicted to obey characteristic scaling laws and to exhibit critical behavior revealing a critical temperature T_c located above the glass temperature T_g . Within idealized MCT, T_c marks a dynamic phase transition, which can be regarded as a kind of ideal glass transition below which the molecules are totally arrested [7]. However, in fact this transition is smeared

out and less directly affecting the actual material properties due to additional hopping processes, treated in extended versions of the MCT [7,8]. Nevertheless, the critical behavior close to T_c still should be observable in the experimental data.

Early tests of these far-reaching predictions were performed by inelastic scattering experiments like neutron [9,10] or light scattering [10–14], enabling to access the relevant frequency range in the GHz–THz range. Indeed, the existence of this minimum with significant self-similar enhancement above background contributions as well as the scaling and critical behavior were verified by these experiments. The MCT predicts that, for all experimental methods that couple to the glass-transition dynamics, this shallow susceptibility minimum should be present, exhibiting the same critical exponents and temperature. However, in the beginning stages of experimental tests of MCT, dielectric measurements did not detect the predicted minimum in the dielectric loss. Especially, such measurements performed for salol, extending into the 10 GHz range, were used to argue that there may be even no minimum at all in spectra of the dielectric loss and that there is no indication of critical behavior in these measurements [15]. Thus, it seemed that the MCT predictions are not verified by dielectric spectroscopy which is the most applied experimental method to reveal information about glassy dynamics. However, due to the development of advanced coaxial reflection and transmission techniques and of sub-millimeter spectroscopy [16], it was later possible to measure the dielectric loss in an extended frequency range with high precision. Indeed, these experiments proved the validity of MCT by dielectric spectroscopy, at least for temperatures above T_c [1,17–21]. The first

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such measurements were performed for the molecular glass formers glycerol [17] and for the ionic glass former [Ca(NO₃)₂]_{0.4}[KNO₃]_{0.6} [18]. However, to our knowledge, until now no tests of MCT based on dielectric results were actually provided for salol. This is done in the present work, presenting dielectric data up to about 400 GHz, nicely revealing the predicted loss minimum and its scaling properties. Admittedly, the discussion about the dielectric high-frequency response of salol dates back more than 20 years [15,22]. Nevertheless, we think the present data are of interest to the community, especially because salol is an often investigated glass former and our results allow for a critical comparison with investigations by various other methods within this frequency/time range [13,23–27], also including relatively recent works [28,29]. We believe that the present results on salol are a significant further test of the predictive power even of the idealized MCT.

2. Experimental procedures

Salol (phenyl salicylate) with a purity of 99% was obtained from Aldrich Inc. Before the measurements, the crystalline material was heated above its melting point of about 41 °C and filtered, which resulted in a negligible probability for devitrification. Broadband dielectric measurements of supercooled salol were performed using a combination of experimental methods [1,16,30]. In the high-frequency range beyond GHz, relevant for the present work, coaxial transmission measurements using a HP 8510 network analyzer were carried out, covering frequencies of 100 MHz–25 GHz [16]. For this purpose, the sample material is filled into a specially designed coaxial line, sealed with Teflon discs. At frequencies 60 GHz < ν < 1.2 THz, a quasi-optical sub-millimeter spectrometer was employed [31], designed similar to a Mach - Zehnder interferometer. For temperature variation, closed-cycle refrigerators and N₂-gas cryostats were used.

3. Results and discussion

3.1. Broadband spectra

For an overview, Fig. 1 shows broadband loss spectra of salol, covering about 14 frequency decades [30,32]. As in the present work we are concentrating on the high-frequency response, in the following we only will briefly discuss the observations at frequencies below GHz. Under cooling, the dominating α -relaxation peak strongly shifts to lower frequencies, which mirrors the glassy freezing of molecular motion when approaching the glass-transition temperature $T_g \approx 218$ K. Below about 233 K, a typical excess wing develops, well known to occur in various other glass formers. It shows up as a second power law at the high-frequency flank of the α -relaxation peaks and was ascribed to a

secondary relaxation process, whose loss peak is partly hidden under the dominating α peak [33–37]. The latter notion indeed is confirmed by the spectrum at 211 K, which was taken after an aging time of 6.5 days to ensure thermodynamic equilibrium. It exhibits a clear curvature, indicating a secondary relaxation process (see Ref. [35] for details).

The experimental data at low temperatures, $T \leq 238$ K, were fitted by the sum of a Havriliak-Negami (HN) function [38] for the α relaxation and a Cole-Cole (CC) [39] function for the β relaxation, both commonly used empirical functions for the description of dielectric relaxation data (solid lines in Fig. 1). At higher temperatures, a single HN function was used for the fits. It is given by the formula:

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{[1 + (i\omega\tau)^{1-\alpha}]^\beta} \quad (1)$$

where $\epsilon^* = \epsilon' - i\epsilon''$ is the complex permittivity, ϵ_s is the static dielectric constant, ϵ_∞ its high-frequency limit, and τ the relaxation time. α and β are the spectral width parameters determining the symmetric and asymmetric broadening of the loss peaks, respectively. For $\beta = 1$, the formula is identical with the CC equation. For $T \geq 263$ K, satisfactory fits could be achieved with the parameter α fixed to zero. Then Eq. (1) corresponds to the often employed Cole-Davidson (CD) formula [40].

3.2. Susceptibility minimum

Fig. 2 shows the evolution of the dielectric loss ϵ'' in the frequency regime between structural relaxation and the boson peak, expected to occur at about 1 THz [1], for temperatures between 263 and 361 K [41]. In this frequency regime, the dielectric loss of salol reveals a clear susceptibility minimum. According to MCT, it should approximately follow the sum of two power laws, namely:

$$\epsilon'' = \frac{\epsilon_{\min}}{a + b} \left[a \left(\frac{\nu}{\nu_{\min}} \right)^{-b} + b \left(\frac{\nu}{\nu_{\min}} \right)^a \right] \quad (2)$$

Here the exponent $-b$ accounts for the increase towards the structural relaxation at low frequencies, and exponent a for the increase at high frequencies. ϵ_{\min} and ν_{\min} are the minimal dielectric loss and the minimum frequency, respectively. Indeed, good fits over up to 2.5 frequency decades can be achieved in this way (solid lines in Fig. 2). We find exponent parameters $a = 0.352$ and $b = 0.75$. Following the MCT prediction, both are directly linked to each other via the relation:

$$\lambda = \frac{\Gamma^2(1 - a)}{\Gamma(1 - 2a)} = \frac{\Gamma^2(1 + b)}{\Gamma(1 + 2b)} \quad (3)$$

where λ is the system parameter and Γ denotes the Gamma function. In the present case, $\lambda \approx 0.63$. It should be noted that a and b are

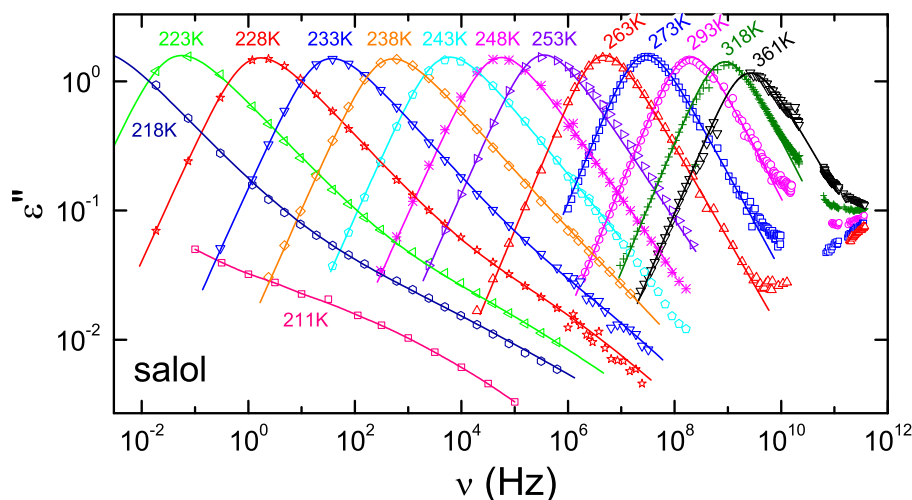


Fig. 1. Broadband dielectric loss spectra of glass forming salol at selected temperatures [30,32]. For $T \geq 243$ K the solid lines represent fits with a HN function, Eq. (1), ignoring the high-frequency minimum (for $T \geq 263$ K, α was zero, corresponding to a CD function). For smaller temperatures, the data were fitted by the sum of a HN function for the α relaxation and a CC function for the β process. The line through the 211 K data is a guide to the eye.

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