

Comment on “Depolarized light scattering study of molten zinc chloride”

K. L. Ngai and C. M. Roland

Naval Research Laboratory, Washington, D.C. 20375-5320

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Lebon *et al.* [Phys. Rev. E **51**, 4537 (1995)] have shown that the depolarized light scattering susceptibility spectrum of ZnCl_2 at each temperature is well represented by the sum of contributions from the α process, the boson peak, and the microscopic peak. In this Comment, we point out that the fast α process of the coupling model of relaxation makes a very weak contribution to the susceptibility in nonfragile glass formers, such as ZnCl_2 . Consequently, the coupling model prediction for the fast dynamics in ZnCl_2 is essentially the same as the approach of Lebon *et al.* [S1063-651X(96)10512-2]

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In a recent paper [1], Lebon, Dreyfus, Li, Aouadi, Cummins, and Pick (LDLACP) reported depolarized light scattering data for molten zinc chloride, ZnCl_2 , one of the simplest “nonfragile” (in the Angell sense [2,3]) inorganic glass formers. The short time susceptibility spectrum $\chi''(\omega)$ exhibited three features: (i) a low-frequency structural or α -relaxation peak; (ii) a broad, high-frequency vibrational peak, comprised of a boson peak and a higher-frequency component, called the microscopic peak; and (iii) a minimum in $\chi''(\omega)$, at frequencies intermediate between (i) and (ii). In their paper, the authors analyzed the data in two ways. The first was guided by the predictions of mode coupling theory (MCT) [4], and included examination of the frequency dependence of the susceptibility minimum for $T > T_c$, where T_c is the critical temperature. Due to the existence of a strong boson peak [5] in ZnCl_2 's depolarized spectra, LDLACP could not properly test MCT; consequently, the theory's predictions concerning the shape of the susceptibility minimum and the existence of a fast β -relaxation process were neither substantiated nor refuted [1].

The second approach adopted by LDLACP was to assume that at each temperature the susceptibility spectrum was the sum of the α -relaxation process and a vibrational contribution. The latter was approximated by the sum of two Lorentzians, representing the boson peak around 500 GHz and the microscopic peak above 2000 GHz. The frequency and width of the latter were assumed to be temperature independent, while its intensity, as well as all three parameters for the boson peak, were allowed to vary with temperature. The α -relaxation dispersion was modeled using the Cole-Davidson function. The obtained fits to the ZnCl_2 spectra at different temperatures were quite satisfactory; notwithstanding, the analysis was considered to be only a phenomenological representation of the data, with no specific connection to any theory or model [1].

The purpose of this Comment is to point out that LDLACP's representation of the data is in accord with the coupling model [6–12] for ZnCl_2 and other “intermediate” and “strong” glass formers such as glycerol [13,14] and B_2O_3 [15]. Previously, neutron-scattering measurements obtained [16–19] on fragile polymeric glass formers have been

shown to conform to the coupling model, specifically its prediction of a prominent fast (~ 100 GHz) α relaxation. This fast α relaxation is reminiscent of the fast β process of MCT, but has distinctly different characteristics. While prominent in the spectrum of fragile glass formers, the fast α relaxation of the coupling model is quite weak for nonfragile liquids. As described in this Comment, the coupling model predictions are simultaneously consistent with LDLACP's data for the nonfragile ZnCl_2 and for the neutron-scattering data of fragile polymers [16–19].

In neutron-scattering studies of several polymers including poly(vinylchloride), polyisoprene, and polybutadiene, Colmenero and co-workers [16–18] and Zorn *et al.* [19] were able to remove the vibrational contribution from the experimental intermediate scattering function, thereby isolating the normalized relaxational contribution at each temperature. The boson peak contribution is weak in these fragile polymers. For the α relaxation, the density-density correlations function was found to exhibit a crossover in the vicinity of $t_c = 2$ ps from

$$C_{\text{rel}}(t) = \exp(-t/\tau_0), \quad t > t_c \quad (1)$$

to the Kohlrausch's stretched exponential form,

$$C_{\text{rel}}(t) = \exp[-(t/\tau^*)^\beta], \quad t > t_c. \quad (2)$$

Similar results were obtained from analysis of molecular-dynamics simulation data of *o*-terphenyl [11], a fragile small molecule liquid. Continuity requirement of $C_{\text{rel}}(t)$ at t_c leads to the relation

$$\tau^* = (t_c^{\beta-1} \tau_0)^{1/\beta}. \quad (3)$$

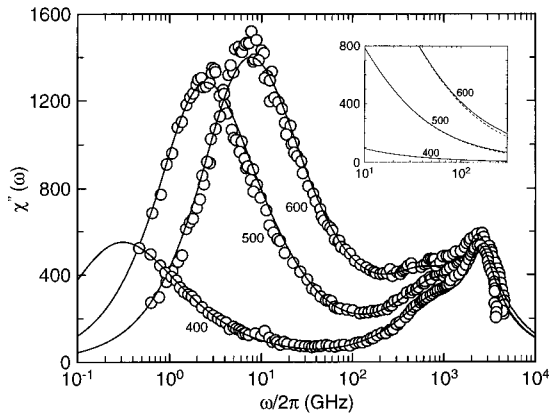


FIG. 1. Light scattering susceptibility spectra (open circles) at the indicated temperatures (in degrees Celsius) along with the sum (solid curves) of the α relaxation calculated according to the coupling model plus two Lorentzians, representing the boson peak and the microscopic peak. The parameters of the Lorentzians and the Kohlrausch exponent β were based on the fits reported by Lebon *et al.* [1]. The inset shows the negligible difference between the coupling model prediction of χ'' (solid lines) and the Kohlrausch stretched exponential function (dashed lines).

Equations (1)–(3) constitute the predictions of the coupling model, whose utility has been demonstrated in various applications [7,8]. The coupling parameter n of the coupling model is to be identified with $1 - \beta$.

The prominence of the fast α process, described by Eq. (1), depends on the parameters τ^* and β of the slow α process given by Eq. (2). We define prominence by the amount of decay, $1 - \exp[-t_c/\tau_o(T)]$, transpiring up to the crossover time t_c . This dependence of the fast alpha prominence on the characteristics of the slow process can be traced to the continuity condition [Eq. (3)] at $t=t_c$. Since t_c is temperature insensitive [6–12], the prominence of the fast process diminishes with larger τ^* and/or β . This property of the fast α relaxation has been demonstrated in Figs. 1(a)–1(c) of Ref. [12].

Phenomenologically, it has been established that glass formers having larger β are less fragile [3,20]. Consequently, the coupling model predicts a marked decrease in the prominence of the fast α relaxation when going from fragile to strong glass formers. Experimentally, most polymers have been found, both from short- [16–19] and long-time measurements [3,8,20], to have significantly smaller β 's than even the fragile small molecules, glass-forming liquids, and certainly smaller than ZnCl_2 , which is only an intermediate liquid ($\beta \sim 0.8$ [1–3]). The expectation is that in comparison to polymers, the fast α process in ZnCl_2 should be barely visible in the depolarized light scattering and neutron-scattering spectra. Unfortunately, this near disappearance of the fast α process, while actually a confirmation of the coupling model, may be misconstrued as indicating a departure of experimental data from the model [13,14].

In light of these considerations, we reexamine the ZnCl_2 data of LDLACP, utilizing the fitting parameters determined therein (see Tables I and III of Ref. [1]) from the second

method outlined above. The fast α relaxation time $\tau_o(T)$ of Eq. (1) is calculated from LDLACP's fit parameters, $\tau^*(T)$ and $\beta(T)$, using

$$\tau_o(T) = t_c^{1-\beta(T)} [\tau^*(T)]^{\beta(T)}, \quad (4)$$

which is another way of writing Eq. (3). We take $t_c = 1$ ps, consistent with the value found from high-frequency conductivity relaxation data of another ionic melt, $0.6 \text{ Ca}(\text{NO}_3)_2 - 0.4 \text{ KNO}_3$ [21] and within a factor of 2 of the (longer) value found for several polymers [16–19] and *o*-terphenyl [11]. In Fig. 1 we show the susceptibility, which is the sum of the relaxation part, described by the Fourier transform of Eqs. (1) and (2), and the vibrational components (the boson and microscopic peaks), as deduced by LDLACP. For all temperatures up to the highest 650°C , the fast α process in ZnCl_2 is fairly inconspicuous. This is illustrated in the inset to Fig. 1, which shows that the exponential decay, $\exp[-t_c/\tau_o(T)]$, differs only slightly from the Kohlrausch function for $t < t_c$. The point is that while the fast α process of ZnCl_2 does exist, it is weak, making only a negligible contribution to the experimental spectrum. A similar conclusion was reached by an analysis [14] of neutron-scattering data on glycerol [13] and molecular-dynamics simulation data of methanol [22]. At intermediate frequencies, a susceptibility minimum is observed with increasing frequency as a result of the decline of $\chi''(\omega)$ on the high-frequency side of the relaxational peak, along with the subsequent rise on the low-frequency side of the broad vibrational component.

Depolarized light scattering spectra of B_2O_3 obtained by Brodin *et al.* [15] are similar to the present ZnCl_2 results. The Kohlrausch exponent β for the slow α process in B_2O_3 is at least as large as that of ZnCl_2 [i.e., $\beta(\text{B}_2\text{O}_3) > 0.80$]. With this information it can be shown that the fast α process makes negligible contribution to the susceptibility spectra of B_2O_3 at all temperatures of experimental investigation ($300 < T < 1273$ K). This finding is consistent with experimental data indicating that the fast dynamics consist mainly of vibrational contributions at temperatures above or below T_c of MCT [15].

In conclusion, we reiterate that the phenomenological fit of LDLACP to susceptibility spectra of ZnCl_2 differs minimally from our fit using the coupling model. The slight deviation occurring at high frequency is masked by the boson peak and the vibrational contribution at these temperatures. Furthermore, the uncertainty in the exact form needed to describe the boson peak makes it impossible to distinguish between the respective fits. Therefore, the success of their phenomenological approach is in fact a demonstration that the coupling model's description of the fast dynamics of ZnCl_2 is consistent with the data. The spirit of this Comment is that there is a theoretical scheme, the coupling model [6,7,10], which provides a basis for the phenomenological approach of LDLACP. It is noteworthy that the coupling model predictions are consistent, on the one hand, with data on fragile glass-forming polymers [16–19], which exhibit prominent fast relaxations, and, on the other hand, with data of intermediate and strong glass formers, including ZnCl_2 , B_2O_3 , and glycerol, which show hardly any trace of the fast α process.

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