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Comment on "Light-scattering investigation of α and β relaxation near the liquid-glass transition of the molecular glass Salol"

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Cummins and collaborators [Phys. Rev. A **46**, 3343 (1992)] have interpreted their recent dynamic light-scattering data on supercooled liquid Salol in terms of mode-coupling theory. They asserted that critical slowing down occurs at a temperature T_c which is much above T_0 where extrapolated relaxation times in the liquid diverge and above T_g where the liquid falls out of equilibrium and forms a glass. We argue that this interpretation is incompatible with dielectric susceptibility data on the same material.

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In a recent series of papers, Cummins and collaborators have investigated relaxations that occur in supercooled liquids using dynamic light scattering. They have interpreted their spectra for both the molecular glass Salol [1,2] and the ionic glass $Ca_{0.4}K_{0.6}(NO_3)_{1.4}$ [3,2] in terms of mode-coupling theory. After extensive analysis they have concluded that, in agreement with the predictions of that theory [4], there is a temperature, T_c, at which critical slowing down occurs. It is surprising and significant that this temperature occurs much above T_0, where the extrapolated relaxation times in the liquid diverge, and above T_g, the temperature where the liquid falls out of equilibrium on experimental time scales and therefore forms a glass.

We have measured the dielectric susceptibility of Salol [5] over a wide range of frequency: 10^{-3} Hz $< \nu < 2\times10^{10}$ Hz. There is no feature in these data at 256 K, the temperature identified as T_c in the light-scattering measurements. Figure 1(a) shows the evolution of the imaginary part of the dielectric response $\varepsilon''(\nu,T)$ for several temperatures as a function of frequency. The curves shift smoothly to lower frequency as the temperature is lowered. No break appears near 256 K in either the peak position, shown in Fig. 1(b), or in the *shape* of the entire relaxation curve. This can be seen in the inset which shows that the Salol data for all the measured temperatures (both above and below 256 K) can be fit onto a single master curve with scaling variables which vary smoothly and monotonically with temperature. The data for ν_p *do not* revert to Arrhenius behavior as T is lowered but can be fit with a Vogel-Fulcher form at low T with a divergence temperature close to the Kauzmann temperature. This argues against the possibility that a simple, uncorrelated, hopping mechanism becomes responsible for the relaxation at low enough T and is inconsistent with the variation proposed for δt_0 used for the fit described in Ref. [2]. In Fig. 1(c) we plot $\varepsilon''(\nu,T)$ versus temperature for different frequencies. Again, each curve is smooth throughout this temperature range with no sign of critical slowing down. It is important to realize that the highest frequencies shown here actually overlap the lowest frequencies used in the light-scattering experiments. Hence it cannot be argued that the critical slowing down is absent from the dielectric data due to a frequency cutoff that lies between the regions covered by the two techniques.

In Ref. [1], the authors show (Fig. 13) the behavior of the width of the α peak versus temperature. Within their error they indicate that for their light-scattering data the width is temperature independent above T_c which is consistent with the mode-coupling predictions. They also claimed that this result was consistent with our data from dielectric response which has much smaller error bars. However, these data, which are shown in Fig. 1(d), actually show that the width continues to decrease up to the highest temperature we measured, which is over 80 K above T_c. This is not what is expected from mode-coupling theory.

One explanation, that we consider unlikely, for this discrepancy between our dielectric data and the interpretation of the light-scattering results, is that the dielectric susceptibility and dynamic light scattering do not couple to any of the same relaxations. $\varepsilon(\nu)$ does show the α relaxations very clearly and in addition, the high-frequency part of this response shows a second power-law behavior. This high-frequency relaxation has been interpreted [6] as the onset of β relaxation (known as the von Schweidler relaxation). This corresponds to the low-frequency regime of the light-scattering data which was fit by a power law ω^{-b}. Consistent with this interpretation, mode-coupling theory has attempted to fit the dielectric data [7]. (We note here that if this is not the onset of the β relaxation but instead is an intrinsic part of the α peak, then the light-scattering analysis needs to include this second power-law regime in the α peak before obtaining the parameters for β relaxation.) Thus the dielectric response does couple to both the α and the low-frequency part of the β relaxation. It finds no evidence for T_c in either case. In this interpretation of the dielectric data it is also clear that the von Schweidler relaxation persists

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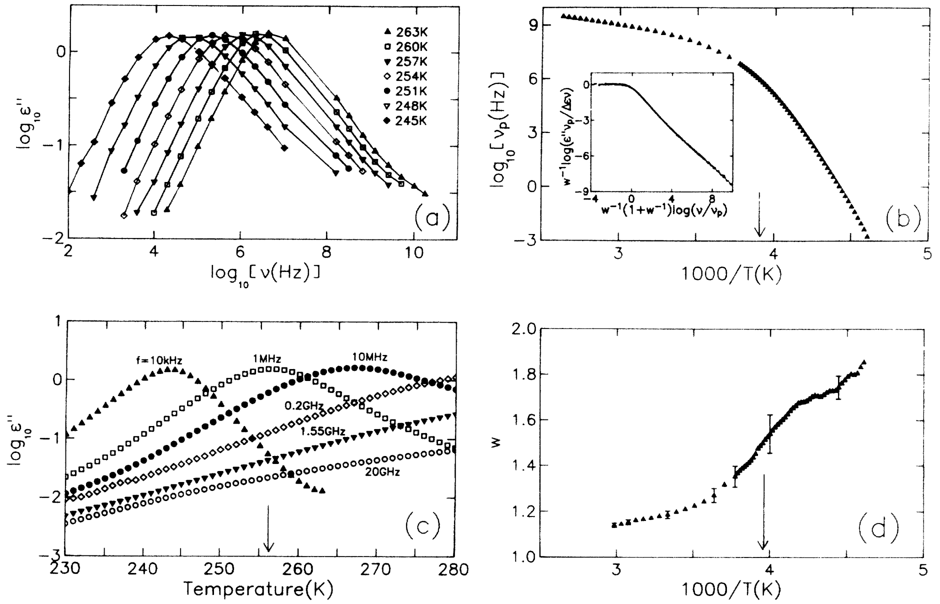

FIG. 1. (a) The frequency dependence of $\varepsilon''(\nu,T)$ of Salol for different temperatures. (b) $\log_{10}\nu_p$ vs inverse temperature. Inset: A master curve for the Salol data at all temperatures showing that data from above as well as below 256 K fit onto the same curve. $\Delta\varepsilon \equiv \varepsilon_0 - \varepsilon_\infty$ and w is the full width at half maximum of $\varepsilon''(\nu)$ normalized to a Debye width. (c) The temperature dependence of $\varepsilon''(\nu,T)$ of Salol for various frequencies. Note that no feature or change of shape appears in any of the data at, or near, the purported critical-slowing-down temperature, $T_c = 256$ K (marked by arrows), identified in the light-scattering data. (d) The normalized width of the α peak determined by dielectric susceptibility. The width w is the full width at half maximum divided by the value for a Debye model (1.14 decades). Note that the width continues to decrease up to the highest temperature measured which is over 80 K above $T_c = 256$ K (marked by an arrow).

through the temperature T_c.

For a number of reasons, some of which have already been addressed in a paper by Zeng, Kivelson, and Tarjus [8], we are unconvinced by the interpretation of the light-scattering data in terms of a temperature T_c where critical slowing down occurs.

(1) The light-scattering data [1] show a dominant peak at high frequencies near 1 THz which was interpreted as the "microscopic excitation band." (It exists over a broad frequency range in which there are several pronounced Raman modes in the pure crystal.) The minimum occurs between this microscopic peak and the α peak occurring at lower frequencies. Since we know that the α peak moves to lower frequency as the temperature is lowered and that the measured microscopic peak does not shift, the minimum between them must shift to lower frequency. This conclusion does not rely on any appeal to mode-coupling theory and it too will give rise an $\omega_{\min}$ which decreases with decreasing temperature but will *not* show any characteristic temperature T_c at which the behavior changes. To show convincingly that T_c marks a true change of behavior that is apparent in the temperature dependence of $\omega_{\min}$, the behavior of $\omega_{\min}$ below T_c must be experimentally determined. Unfortunately, such data were not presented in either the analysis using the ideal mode-coupling theory [1] or the one using the extended theory [2].

(2) Figure 10(b) of Ref. [1] shows the crucial point of how the "knee" can be rescaled onto a universal curve. However, none of the curves lies convincingly upon any other and they do not fall on the thick curve which represents the theoretical prediction over any significant range of frequency. It is the shift parameters obtained in this figure which are used in their Fig. 18(b) to show the temperature dependence of τ_β^+. Since it is not clear that the curves can be scaled at all, it becomes unclear whether the temperature dependence ascribed to τ_β^+ can really be taken to advocate the existence of a critical temperature.

In contrast with the light-scattering data, no minimum is seen in $\varepsilon''(\nu,T)$. We presume that this is due to the fact that the dielectric response does not couple to the microscopic (phonon) modes. However, as we have already argued, $\varepsilon''(\nu,T)$ does couple both to the α and to the lower-frequency (i.e., the von Schweidler) part of the β relaxation. From that analysis we have seen that the dielectric response shows no sign of a critical temperature in either quantity. Whether or not it couples to the highest-frequency relaxations is not essential for our argument. It is not clear in the light-scattering data where the microscopic peak ends and a new relaxation phenomenon begins. The phonon density of states, as well as the Raman spectra, in a glass can often be significantly broader than in a crystal [9]. It remains to be determined what part of the light-scattering data is simply this peak and what part can be specified as a distinct relaxation phenomenon.

From these considerations we conclude that there is no convincing evidence that the temperature T_c near 256 K exists in this liquid where critical slowing down occurs.

No evidence is seen for its existence in the dielectric response which has been used extensively in the past as corroboration of different aspects of mode-coupling theory. The light-scattering data do not in our mind give compelling evidence for the existence of such a temperature.

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