Evidence for a Divergent Susceptibility at the Glass Transition

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We present evidence for the divergence of the static dielectric susceptibility in liquids as they are supercooled towards T_0, the temperature where the dynamics in the liquid come to a halt. This divergence occurs when the width of the imaginary part of the dielectric response approaches a finite limit derivable from a scaling form for the susceptibility. Fits to the temperature dependence of the width indicate that this divergence may occur at T_0.

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It has long been known that cooling a liquid below its melting point increases its viscosity and all the associated relaxation times for molecular motion. What has not been clear is whether this slowing down is associated with an underlying phase transition to a glass at a finite temperature or whether it is simply due to kinetic effects which would not lead to any divergent relaxation times except at $T = 0$. Certainly one reason for the glass transition remaining a puzzle is that, although the relaxation times often seem to diverge at a finite temperature, there has never been any convincing evidence for a divergent static susceptibility or for a growing correlation length which diverges at the same temperature at which the relaxation times extrapolate to an infinite value. Evidence for a divergent susceptibility would greatly constrain any theoretical attempt [1] to understand this phenomenon.

In this Letter we present evidence for a divergent susceptibility based on an empirically determined scaling form for the frequency and temperature dependent dielectric susceptibility data of supercooled liquids. All arguments dealing with the glass transition rely on the extrapolation of quantities measured in an experimentally accessible regime to a temperature close to the transition. In this discussion we will likewise make three separate assumptions whose validity will be analyzed in this Letter: (i) the scaling curve is valid down to the temperature where the dynamics has been completely arrested (at T_0), (ii) it gives the asymptotic high frequency behavior, and (iii) the width of the relaxation extrapolates to a critical value at T_0. Although these are sizable extrapolations, we suggest that the analysis presented here may be the best available procedure to determine the behavior near the transition region.

The dielectric response, $\varepsilon(\nu) = \varepsilon'(\nu) + i\varepsilon''(\nu)$, has been measured over a wide range of frequency ν and temperature T for a variety of simple liquids [2]. The data for ε'' have been scaled onto a single master curve using only three parameters: ν_p (a frequency characteristic of the peak in ε''), W (the full width at half maximum of the peak in ε''), and $\Delta\varepsilon \equiv \varepsilon'(\nu = 0) - \varepsilon'(\nu = \infty)$ (the strength of the response). Figure 1 shows the real and imaginary parts of $\varepsilon(\nu)$ for the supercooled liquid glycerol [3] at one temperature. The scaling procedure employed to collapse the data uses an unusual choice of scaling axes: $Y \equiv w^{-1} \log(\varepsilon'' \nu_p / \Delta\varepsilon \nu)$ for the ordinate and $X \equiv w^{-1}(1 + w^{-1}) \log(\nu/\nu_p)$ for the abscissa. Here w is the normalized width: $w \equiv W/W_D$ where $W_D = 1.14$ decades is the full width at half maximum for a single relaxation time Debye peak. The master curve using these axes is shown in Fig. 2. The inset to that figure shows the local slope of the master curve dY/dX versus X. The derivative of $\varepsilon''(\nu)$, which we will need below, can be obtained from this slope:

$$\frac{d\log\varepsilon''(\nu)}{d\log\nu} = 1 + \left(1 + \frac{1}{w}\right)\frac{dY}{dX}. \tag{1}$$

This scaling procedure has been used successfully not only for simple supercooled liquids [2–4] but also for some glass-forming polymers [5]. (Although there has been some controversy [6] as to whether the data for these polymers fall on the master curve below the frequency ν_p, there is no dispute as to whether they fall on the master curve above ν_p. Since the argument we give below only concerns the high frequency portion of the

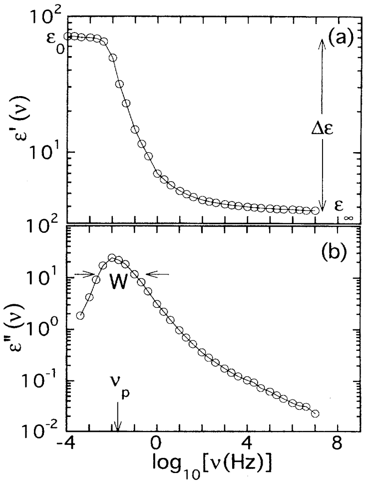

FIG. 1. (a) The real and (b) imaginary parts of the dielectric susceptibility of supercooled glycerol at 192 K versus $\log_{10}\nu$. The asymptotic low and high frequency values ε_0 and ε_∞ are indicated along with their difference $\Delta\varepsilon$. The full width at half maximum W and a frequency characteristic of the peak ν_p are also identified. The data are from Ref. [3].

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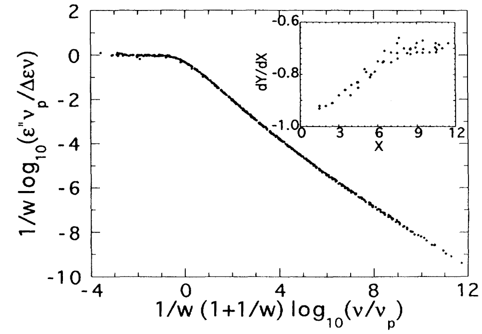

FIG. 2. Compiled data of $\varepsilon''(\nu)$ for glycerol is plotted at a number of temperatures using the scaling axes $Y \equiv w^{-1}\log_{10}(\varepsilon''\nu_p/\Delta\varepsilon\nu)$ and $X \equiv w^{-1}(1+w^{-1})\log_{10}(\nu/\nu_p)$. The inset shows dY/dX for $X > 0$. The slope tends to an asymptotic high frequency value: $-\gamma = -0.72 \pm 0.02$.

curve, the controversy concerning the low frequency end is immaterial for the present discussion.) Even more remarkable, some recent dielectric data on a crystalline system with orientational disorder, cyclo-octanol, have also been reduced by the same scaling variables to a single master curve that is almost identical to the one on which all the simple liquids and polymers lie [7]. That a crystalline system scales in the same way as the liquids indicates that this scaling form may have a much broader realm of applicability than had previously been realized.

We now argue that the asymptotic high frequency shape of the master curve dictates an upper bound, w^*, on the width of the relaxation [8]. As we will show below, this argument relies on the fact that $\varepsilon''(\nu)$ must decrease monotonically at frequencies above ν_p:

$$\frac{d\log\varepsilon''(\nu)}{d\log\nu} \leq 0 \quad \text{for } \nu > \nu_p\,, \tag{2a}$$

which in terms of the scaling variable gives

$$\frac{dY}{dX} \leq \frac{-w}{1+w} \quad \text{for } X > 0\,. \tag{2b}$$

As seen in the inset to Fig. 2, this slope changes from -1 close to the peak to an apparently asymptotic value of $-\gamma$ at the largest value of X to which the data extends:

$$\left.\frac{dY}{dX}\right|_{X\to\infty} \equiv -\gamma = -0.72 \pm 0.02\,. \tag{3}$$

Taken together, Eqs. (2b) and (3) give $w < w^* = \gamma/(1-\gamma)$. This leads to a limiting width for the dielectric susceptibility of $w^* = 2.6 \pm 0.3$. The fact that dY/dX appears to have an asymptotic limit $-\gamma$ indicates that $\varepsilon''(\nu)$ varies as a power law at high frequency:

$$\varepsilon''(\nu) \propto \nu^{-\sigma} = \nu^{1-\gamma(1+1/w)}. \tag{4}$$

The power law behavior in the high frequency region is visible in the unscaled data (as in the inset to Fig. 3) for which there is a sufficient range of frequency above ν_p. The prefactor of this high frequency power law can also be derived from the master curve and goes to a finite limit as w approaches w^*.

We now show that if the master curve remains valid throughout the supercooled liquid region then the static susceptibility $\Delta\varepsilon$ diverges as w approaches $w^* \approx 2.6$. The Kramers-Kronig relations [9] relate the zero frequency limit of the real part of the response to an integral over all frequencies of the imaginary part:

$$\Delta\varepsilon = \frac{2}{\pi}\int_0^\infty \varepsilon''(\nu)\,\frac{d\nu}{\nu}\,. \tag{5}$$

In the high frequency regime, $\varepsilon''(\nu) \propto \nu^{-\sigma}$ until ν reaches a typical phonon frequency (i.e., the Debye frequency). The lower limit of this regime is ν_T where the power law $\nu^{-\sigma}$ crosses over to the lower frequency behavior $[\varepsilon''(\nu) \propto \nu^{-1/w}]$. ν_T is essentially proportional to ν_p, varying only slightly with w. The integral converges as long as $\sigma > 0$. However, as ν_T approaches zero (along with ν_p), $\Delta\varepsilon$ will diverge if σ also approaches zero. This divergence comes from the low frequency response of the system even though the $\nu^{-\sigma}$ behavior appears on the high frequency side of ν_p. We are interested in isolating $\delta\Delta\varepsilon$, the contribution to $\Delta\varepsilon$ from the power law $\nu^{-\sigma}$ (see the inset to Fig. 3):

$$\delta\Delta\varepsilon \propto \int_{\nu_T}^\infty \left(\frac{\nu}{\nu_T}\right)^{-\sigma} - \left(\frac{\nu}{\nu_T}\right)^{-1/w}\frac{d\nu}{\nu}\,. \tag{6}$$

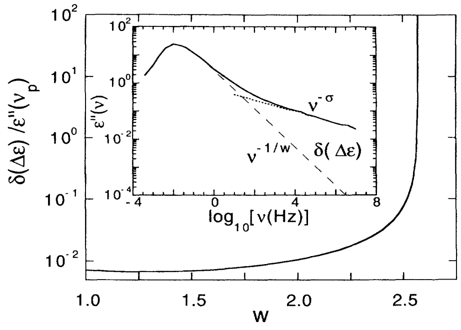

FIG. 3. The dependence on w, predicted from Eq. (6), of $\delta\Delta\varepsilon$, the high frequency contribution to $\Delta\varepsilon$, normalized to the height of the peak, $\varepsilon''(\nu_p)$. A true divergence will only occur if ν_T approached zero and w approaches w^*. The inset shows the data from Fig. 1(b) for $\varepsilon''(\nu)$ versus ν identifying two regimes: $\nu^{-1/w}$ (dashed line) just above the peak and $\nu^{-\sigma}$ (dotted line) at high frequency. ν_T is the crossover frequency between these regimes.

Figure 3 shows the variation of $\delta\Delta\varepsilon$ as a function of w (using $\gamma = 0.72$). To demonstrate the increase in this contribution relative to the peak height, we have normalized $\delta\Delta\varepsilon$ to $\varepsilon''(\nu_p)$. As expected from the above argument, as ν_T goes to zero $\delta\Delta\varepsilon$ diverges at $w^* = \gamma/(1-\gamma) \approx 2.6$.

We now discuss the temperature dependences of the three parameters used in producing the master curve. The frequency ν_p has a very strong temperature dependence, commonly fit with a Vogel-Fulcher form: $\ln(\nu_p) = \ln(\nu_0) - A/(T - T_0)$. In the few cases where a comparison has been made, the value of T_0 used in these fits is close to the Kauzmann temperature [10] where the entropy of the liquid extrapolates to a value lower than that of the equilibrium crystal [11]. Although the time scales appear to diverge at a finite temperature T_0, neither of the other two parameters have previously been shown to display any unusual temperature dependence in the accessible temperature or frequency range. In Fig. 4(a), we show the data for the measured values of the static susceptibility $\Delta\varepsilon$ as a function of $1/T$. In the range measured, $\Delta\varepsilon$ appears to vary approximately as a Curie law ($\Delta\varepsilon \propto 1/T$) and does not appear to diverge near T_0 if this Curie behavior is indeed the correct extrapolation to lower temperature [12]. However, such an extrapolation does not take account of the growth in $\delta\Delta\varepsilon$ that leads to a divergence when the width in $\varepsilon''(\nu)$ approaches w^*. In order for $\delta\Delta\varepsilon$ to contribute appreciably to $\Delta\varepsilon$, w must closely approach w^* (see Fig. 3). Figure 4(b) shows that $\delta\Delta\varepsilon$, which is still a very small part of the entire response over the experimentally accessible range, is beginning to grow significantly. To see if w approaches more closely to w^*, data must be collected at even lower temperatures than has been done already. The possibility of getting such data is constrained by the necessity of going to lower and lower measuring frequencies. The lowest temperature data presented here was taken at 10^{-4} Hz. It is not clear how much lower in frequency one can go.

In Fig. 5(a) we show the data for w for several glass-forming liquids. The width is clearly temperature dependent and increases as T is lowered. However, from these data it is impossible to ascertain unambiguously whether w continues to increase until it reaches $w^* = \gamma/(1-\gamma)$. The best that we can hope to do is see if a reasonable extrapolation of the data would be consistent with this possibility. The solid lines through the data are fits by a simple form [13] which is constrained to give $w = 1$ at high temperatures and $w = w^* = 2.6$ at T_0:

$$\frac{1}{w^* - w} = \frac{1}{w^* - 1} + \frac{C}{T - T_0}, \tag{7}$$

in analogy with the Vogel-Fulcher form. In this fitting procedure, T_0 is the temperature at which the relaxation times have diverged [i.e., where $\nu_p(T)$ has extrapolated to zero in a Vogel-Fulcher fit]. The form produces a reasonable fit *with only one free parameter, C.* This fitting form implies that the static susceptibility diverges at the same temperature where the relaxation times become infinite and indicates the existence of a true phase transition with a diverging correlation length at the transition temperature. Figure 5(b) shows the data plot in an alternative way so that an extrapolation of the data to the origin implies $w = w^*$ at $T = T_0$ independent of any fitting function. A strong trend is certainly observed.

In conclusion, we have presented evidence based on dielectric data indicating the existence of a divergent static susceptibility associated with the glass transition. The question of whether we should believe in a diverging static susceptibility reduces to three assumptions: (i) the continued validity of (the high frequency part of) the master curve down to low temperatures, (ii) asymptotic power law behavior out to frequencies large compared to ν_p, and (iii) the extrapolation of w to $\gamma/(1-\gamma)$ at T_0, the temperature where the dynamics has been completely arrested. In regard to the first two assumptions, we can only argue that this scaling procedure has worked extremely well over an enormous frequency and temperature range, and it is plausible that it is the asymptotically correct behavior. Failure of the scaling form at frequencies comparable to a Debye frequency of the liquid will not affect the divergence since, as T is lowered, ν_T moves (along with ν_p) to lower frequency so that the growth in $\Delta\varepsilon$ is associated with lower and lower frequencies in $\varepsilon''(\nu)$. As far as the third point is concerned, the quality of the one-adjustable-parameter fits to w shown in Fig. 5(a) and the approach of w to w^* at T_0 in Fig. 5(b) are encouraging.

That a divergent susceptibility should appear in a linear response function such as the dielectric susceptibility is surprising. In spin glass systems, which have quenched rather than annealed disorder, the nonlinear susceptibility diverges whereas the linear one does not [14]. However, it is noteworthy that, at the transition temperature, a limiting width for the magnetic susceptibility close to 2.8 (which is within error of our value of 2.6) is also obtained in certain spin glass models [15]. It is remarkable that the same numerical value appears for the limiting width in these two very different glassy systems. Measurements of the spin glass susceptibility in the high frequency

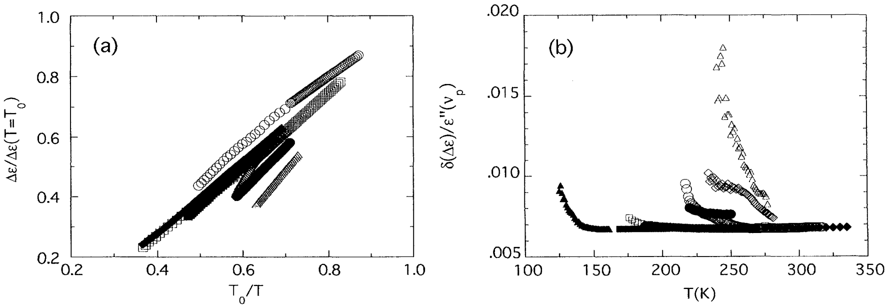

FIG. 4. (a) $\Delta\varepsilon(T)/\Delta\varepsilon(T = T_0)$ versus T_0/T for several glass-forming liquids. T_0 is the temperature derived from a Vogel-Fulcher fit to the peak frequencies. $\Delta\varepsilon(T = T_0)$ is obtained by linear extrapolation. (b) $\delta\Delta\varepsilon/\varepsilon''(\nu_p)$ versus T for the same liquids. The samples along with their values of T_0 were salol, 185 K (○); dibutylphthalate, 146 K (□); glycerol, 130 K (◆); propylene glycol, 109 K (■); α-phenyl-o-cresol [with 13% o-terphenyl], 155 K (●); o-terphenyl with 9%, 175 K (△) and 33%, 164 K (◇) mixtures of o-phenylphenol (all data taken from Ref. [2]).

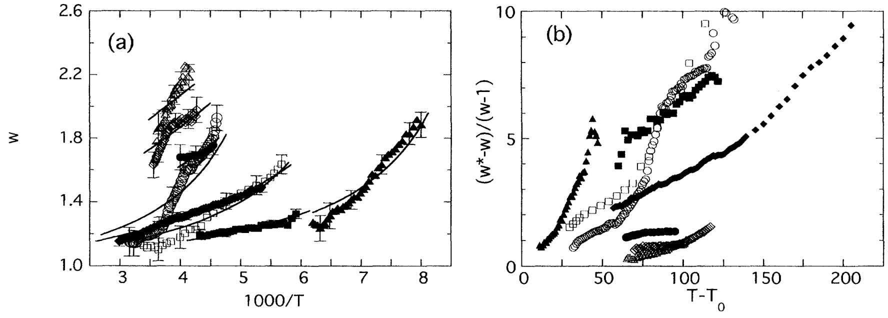

FIG. 5. (a) The temperature dependence of the normalized width w for the same set of liquids shown in Fig. 4 with the addition of benzyl chloride ($T_0 = 114$ K) (▲) (Ref. [4]). The solid lines are single-parameter fits by Eq. (7). (b) The same data plot in such a way that if $w^* = 2.6$ at $T = T_0$ then each data set should extrapolate to the origin.

regime may prove valuable in seeing if there are further similarities. It is also significant that the temperature at which w reaches w^* is within experimental uncertainty of both the temperature where the time scales appear to diverge as well as the Kauzmann temperature. All these facts are circumstantial evidence for the existence of an underlying phase transition at that temperature.

Because of the inevitable necessity of having to extrapolate the data over large temperature ranges, any conclusions about a divergent $\Delta\varepsilon$ must be regarded as speculative. However, the dielectric data on which the arguments are based are some of the most accurate available and cover an extremely large range of frequency. They have approached as closely as possible the temperature where one suspects that the transition may exist. Although tentative, these conclusions are probably the best available clue to the nature of the dynamics as it slows to a halt and are evidence that there is a diverging static susceptibility and correlation length in supercooled liquids approaching the glass transition.

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[12] As we approach the divergence in $\Delta\varepsilon$, it may no longer be appropriate to use $\Delta\varepsilon$ itself in forming the scaling variable Y. The area under the first power law ($\nu^{-1/w}$) will still remain finite so that $\Delta\varepsilon - \delta\Delta\varepsilon$ might be used in place of $\Delta\varepsilon$. Over the range of temperature that we have data, it is not possible to see any difference between these two choices of scaling parameters.

[13] Other one-parameter fitting forms such as $1 + 1.6\exp[-C(T - T_0)]$ and $1 + 1.6(T/T_0)^{-\nu}$ are of comparable quality to the fits shown in Fig. 5(a).

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