Scaling in the Relaxation of Supercooled Liquids

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We have measured the dielectric susceptibility of several glass-forming liquids over 13 decades of frequency. The primary relaxation for all the liquids, over the entire frequency and temperature range studied, can be collapsed onto a single scaling curve with only two parameters, peak position and width. This curve is different from any of the theoretical forms suggested in the literature. The relaxation evolves smoothly from Debye behavior at high temperature.

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Many liquids can be cooled slowly into an amorphous solid called a glass. The most apparent feature of the "glass transition," observed as a liquid is supercooled, is the rapid increase of the characteristic relaxation time. This has been observed by many different probes,[1] including specific heat,[2] dielectric susceptibility,[3,4] ultrasonic attenuation,[5] shear modulus,[6] viscosity,[7] and light[8] and neutron[9] scattering. Because the relaxation time τ becomes inaccessibly large so rapidly as the liquid is supercooled, it is impossible to determine if it actually diverges at a nonzero temperature. However, in the region where it can be measured, τ increases faster than activated, or Arrhenius, dependence. Different expressions have been used to fit this behavior including that of Vogel-Fulcher,[1] $\tau = \tau_0 \exp[A/(T-T_0)]$, scaling,[10] $\tau = \tau_0[(T-T_0)/T_0]^{-\gamma}$, and variations of these forms.[11] While able to fit the data over limited ranges of temperature, no single form has yet been found that fits the entire temperature range covered by experiment.

Moreover, the shape of the relaxation shows characteristic non-Debye behavior as the glass transition is approached. There have been several empirical forms proposed to describe the behavior, such as that given by the Cole-Cole,[12] $\phi(\nu) \propto 1/[1+(i2\pi\nu\tau)^{1-\alpha}]$, Davidson-Cole,[3] $\phi(\nu) \propto 1/[1+i2\pi\nu\tau]^{\delta}$, and stretched-exponential (Kohlrausch-Williams-Watts) forms,[13] $\phi(\nu) \propto \{$the Fourier transform of $(d/dt)[-\exp-(t/\tau)^{\beta}]\}$. Again, none of these forms can be regarded as more than an approximation to the data. In the absence of a common family of fitting functions for the relaxation properties of supercooled liquids, there is no compelling evidence to establish that universal behavior governs these phenomena. It remains ambiguous whether a true glass phase transition exists at all.

In the present paper, we present dielectric relaxation data taken on several different glass-forming liquids that span 13 decades in frequency: 10^{-3} Hz $< \nu < 2\times10^{+10}$ Hz. We have covered a large frequency range in order to determine how the glassy relaxation evolves from the liquid as the temperature T is lowered. Since τ (which is inversely proportional to the characteristic frequency ν_p) is a strong function of T, we need a wide frequency range to follow the relaxation over an appreciable span of temperature. We have taken data on a variety of glass-forming liquids in order to see if any universal behavior can be identified over this frequency range in all the samples. The samples studied were glycerol, propylene glycol, salol, dibutyl-phthalate, α-phenyl-o-cresol (with 13% o-terphenyl impurity to suppress crystallization), and o-terphenyl (with 9% and 33% o-phenylphenol). These molecules have very different structures with very different dipole moments and internal rigidity. They also span a considerable range of the strong-to-fragile classification of glass formers proposed by Angell.[14] A secondary relaxation peak[15] appears in the frequency range of our experiment and interferes with the measurement of the primary relaxation for four samples: dibutyl-phthalate, α-phenyl-o-cresol, and the two o-terphenyl samples. For these cases, we therefore only report our data on the lowest 9 decades (10 decades for α-phenyl-o-cresol) of frequency where there is no overlap of the two relaxation processes.

The data were taken by a variety of means. For $\nu < 10^4$ Hz, data were taken with a parallel-plate capacitor using a voltage source and current amplifier. Digital lock-in techniques[16] were used to improve the sensitivity. At intermediate frequencies, 10^4 Hz $< \nu < 10^7$ Hz, the data were taken with a four-probe impedance analyzer. Above 5×10^7 Hz the data were taken in both transmission and reflection with a 50-Ω coaxial transmission line and network analyzer.

Figure 1 shows the real and imaginary parts of the dielectric susceptibility, ε' and ε'', for salol over the available range of frequency. Each curve corresponds to a different temperature. In ε'' as the temperature is lowered, the peak frequency ν_p decreases, and the width

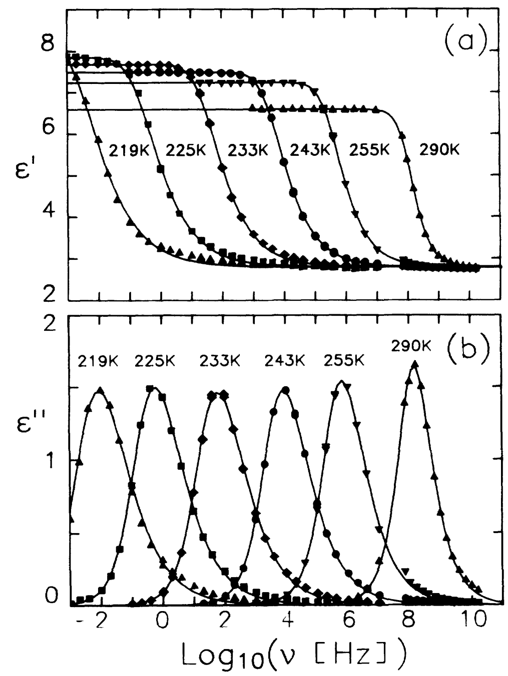

FIG. 1. The real and imaginary parts, ε' and ε'', of the dielectric susceptibility of salol vs frequency at the labeled temperatures. The solid lines are stretched-exponential fits to the data and are inadequate in the high-frequency tails.

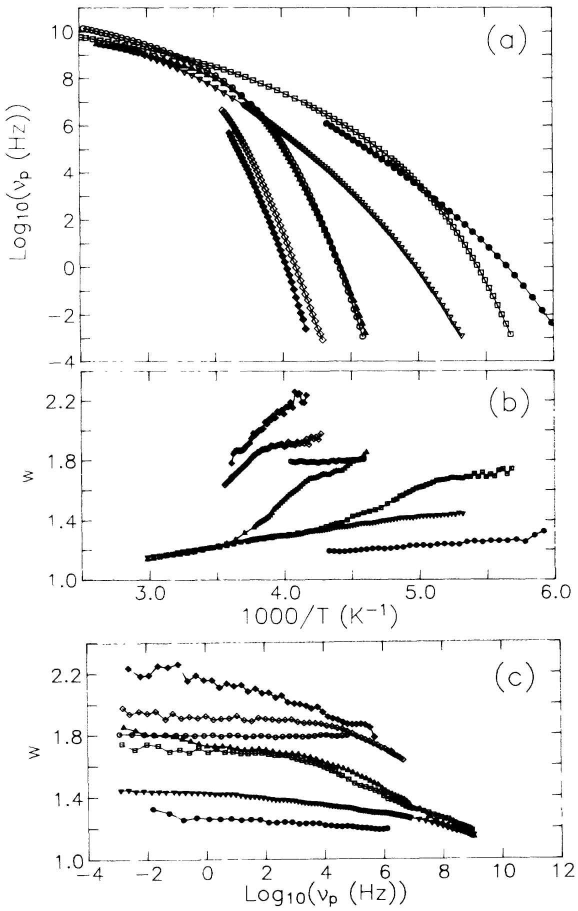

FIG. 2. (a) $\log_{10}\nu_p$ vs $1/T$ for the different liquids studied: glycerol (▽), propylene glycol (●), salol (▲), dibutyl-phthalate (□), α-phenyl-o-cresol [with 13% o-terphenyl impurity (○)], and o-terphenyl [with 9% (◆) and 33% (◇) o-phenylphenol]. (b) The normalized width of ε'', $w = W/W_D$, vs $1/T$ for all the liquids studied. (c) The width w vs $\log_{10}\nu_p$ for all the samples. Note that w approaches 1 as ν_p approaches a typical phonon frequency $\nu_p \approx 10^{12}$ Hz.

W broadens. This behavior is characteristic of all the samples. A fit with a stretched-exponential form does not work well; although it does an adequate job near ν_p, the peak of ε'', it does a poor job in the high-frequency tail. In Fig. 2(a) we show $\log_{10}(\nu_p)$ vs $1/T$ for all the liquids. The frequency range covered by our experiment for each sample can be found by looking at the frequency axis. We note that these curves do not approach an Arrhenius form at low temperature as has been suggested[7] from the viscosity data. At the lowest temperatures studied all of the dielectric curves still show considerable curvature. In the absence of additional viscosity data, we should beware of asserting that the two probes, dielectric and viscosity, measure different time scales: The significant scatter in the low-temperature viscosity data may hide the curvature on an Arrhenius plot.

It is natural to normalize the full width at half maximum W of our susceptibility curves to a Debye width ($W_D \cong 1.14$ decades) which corresponds to the case of a single relaxation time: $w \equiv W/W_D$. In Figs. 2(b) and 2(c), we show w vs $1/T$ and vs $\log_{10}\nu_p$, respectively. We have covered a wide range of widths: $1.17 < w < 2.22$ (even in a single sample, salol, w is found to vary from 1.17 to 1.92). Note that as ν_p approaches a characteristic phonon frequency $\approx 10^{12}$ Hz, w approaches 1.0; that is, Debye relaxation with a single relaxation time.

Since no form has been found to fit these data, we will attempt to create a single scaling curve on which all the data can be placed. The natural first guess as to how to create such a figure is to plot $w\varepsilon''/\Delta\varepsilon$ vs $w^{-1}\log_{10}(\nu/\nu_p)$. Here ν_p is taken from Fig. 2(a) and is a function of temperature and $\Delta\varepsilon \equiv \varepsilon_0 - \varepsilon_\infty$ is the measured static susceptibility. The division of ν by ν_p aligns the peaks for every temperature at one point and dividing the logarithm by w adjusts all the curves to have the same half-width. Likewise, multiplication by $w/\Delta\varepsilon$ on the vertical axis should account[17] for the temperature dependence of the height of $\varepsilon''(\nu_p)$. This scaling of the data is adequate only if the range of w is small (e.g., propylene glycol and glycerol); it does a poor job, especially below ν_p, for samples where w changes by a significant amount (e.g., salol).

Our next attempt to find a scaling form was more successful. In Fig. 3(a) we show the data for salol over 13 decades of frequency collapsed onto a single curve. The

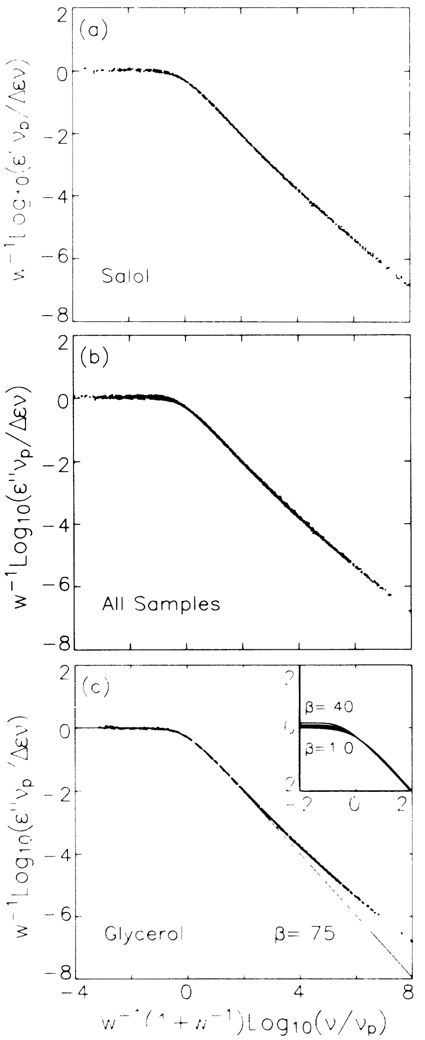

FIG. 3. (a) The scaling plot for the 13 decades of data for salol. $(1/w)\log_{10}(\varepsilon''\nu_p/\nu\Delta\varepsilon)$ is plotted against $(1/w)(1/w+1)\log_{10}(\nu/\nu_p)$. (b) The scaling plot for all the primary relaxation data for all the samples studied. (c) The scaling plot for the 13 decades of data for glycerol. The solid line is a stretched-exponential fit with $\beta=0.75$. The inset shows that as β is varied from 0.4 to 1.0 the stretched-exponential scaling is not exact below ν_p. Above ν_p the scaling is independent of β.

abscissa is $(1/w)(1/w+1)\log_{10}(\nu/\nu_p)$. The ordinate is $(1/w)\log_{10}(\varepsilon''\nu_p/\nu\Delta\varepsilon)$. The division by w was motivated by an analogy with multifractal scaling used in theories of chaos.[18] The division ν/ν_p tilts the entire function so that it is monotonic in the abscissa variable. This scaling leads to an excellent collapse for all 13 decades of data.

We have plotted the primary relaxation data for each of our samples in this way. For each sample the data collapse was comparable to what we have shown in Fig. 3(a). Moreover, the different samples showed the same scaling form for the data. In Fig. 3(b) we plot the data for all samples on a single curve. It is virtually impossible to distinguish one set of data from another because all the sets fall so closely on top of one another.

We may now ask whether this scaling plot is the same as we would have gotten from one of the forms used in the literature. Figure 3(c) shows what a stretched-exponential form (solid line) gives if plotted in this way for various values of β. The data used in this figure are for glycerol over 13 decades of frequency. This form does a poor job in fitting the high-frequency tail and is only adequate out to approximately 1.3 decades from the peak. The inset shows how a stretched-exponential form varies on this scaling plot at low frequencies.

In conclusion, we have shown that the dielectric susceptibility data, over a wide range of temperature and frequency, can be scaled in such a way as to lie on a single curve. It is significant that this scaling works over a wide temperature range even far from T_0, the temperature where the relaxation time seems to diverge. Moreover, this curve seems to be universal from one sample to another even though the samples themselves are quite different on a microscopic level. Only two parameters, the width and peak position, are necessary to describe the relaxation at each temperature. We also find that at high temperature the relaxation function approaches a Debye form when the peak frequency approaches a typical phonon frequency. Although we do not have a theory for the glass transition, these data underscore the hope that we have long held that there is indeed universal behavior in the relaxation of supercooled liquids.

What is the meaning of the type of scaling plot shown in Fig. 3? If there were no additional factor of $1+1/w$ in the abscissa, this form would be reminiscent of multifractal scaling. However, the necessity of this factor suggests that a more elaborate explanation may be necessary.

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