

A Low-Temperature Amorphous Phase in a Fragile Glass-Forming Substance

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We have observed what appears to be a first-order phase change from deeply supercooled liquid triphenyl phosphite at 1 atm to a rigid, “apparently” amorphous phase which we denote as the “glacial phase”. This is a new, crisper, and rather different addition to the examples of polyamorphism that have recently been studied. In order to “deeply” supercool the liquid, it must be quick-quenched to a low temperature: if heated slowly, but immediately, it crystallizes; if allowed to stand for several hours at low temperature, it transforms to the glacial phase; and if subsequently heated it, too, crystallizes, but at a higher temperature than that for liquid crystallization. The glacial phase can be clearly distinguished from both the normal crystal and the ordinary glass. We propose a model for the formation of this “apparently” amorphous glacial phase.

Introduction

We have studied the fragile¹ glass-forming substance triphenyl phosphite (TPP) and have identified a formerly unknown rigid, “apparently” amorphous phase, denoted as the “glacial phase”, which is stable relative to the supercooled liquid and glass but metastable relative to the crystal. A brief report on this glacial phase has already been presented.² The glacial phase is distinct from and denser than both the supercooled liquid and the glass. We define a glass as a supercooled liquid whose structural relaxation times, as a consequence of having been further cooled below the glass temperature T_g , are longer than the available experimental times.³ We classify the glacial phase as “amorphous” because its low-resolution X-ray scattering very closely resembles that of the supercooled liquid and glass, but the glacial phase is readily distinguishable from the others. A first-order transition from supercooled liquid to glacial phase can be clearly detected visually, by means of viscosity measurements and by light scattering, all at temperatures well above T_g , where the glass cannot exist. The ³¹P spin–lattice relaxation times, which reflect near-neighbor interactions, are quite different for all three phases: glassy liquid, glacial, and crystal. The transition from glacial phase to crystal also appears to be first order, as established visually and calorimetrically. The phenomenon of polyamorphism, the existence of more than one condensed amorphous phase, has recently been a topic of research interest.⁴ We envisage the possibility of the glacial phase forming in many one-component glass-forming systems and interpret their existence and properties as closely connected to those of supercooled liquids; this suggests that a general theory of supercooled liquids and glasses should also incorporate the glacial phase. Our view of the glacial phase has led us to hypothesize that the glacial phase, and perhaps other “apparently” amorphous phases with order parameters difficult to describe and detect, may not be truly amorphous.^{5,6} Although the underlying theory, discussed in part below, has not been fully worked out, enough has been done to give reasonable plausibility to this picture.

Triphenyl phosphite (TPP) crystals melt at $T_m = 295$ K, but it is difficult to get the pure liquid to freeze at temperatures above an “upper effective freezing point” $T_{uf} \approx 245$ K. In the temperature range from T_{uf} down to a “lower effective freezing temperature” $T_{lf} \approx 227$ K, the supercooled liquid freezes to

crystal quite rapidly (*i.e.*, in a matter of minutes or less). But if one quick-quenches the liquid to temperatures below T_{lf} (*i.e.*, in a matter of minutes), the homogeneous crystallization process is slowed appreciably, and below about 220 K one sees no evidence of crystallization, even heterogeneous crystallization, on the cavity walls. In this way one can form and study supercooled liquids at temperatures from T_{lf} down to the glass temperature $T_g \approx 176$ K,⁷ a region in which crystallization and vitrification can be avoided. If the supercooled liquid is heated slowly (*i.e.*, at about 1 K/min), it crystallizes at temperatures above T_{lf} , but if allowed to stand for some time at a fixed temperature in the range of about 225–213 K, the supercooled liquid converts in a matter of hours to the rigid, dense glacial phase; the time needed for complete transformation to the glacial phase (which we denote as *glaciation*, in contrast to vitrification to the glass) increases with decreasing temperature, and below 213 K the time is presumably too long for appreciable transformation to be observed in our experiments. Once the glacial phase is formed, it appears to be stable indefinitely provided the temperature is not raised above an upper glacial temperature of about $T_{ug} \approx 237$ K. At temperatures above T_{ug} the glacial phase transforms rather quickly to the less dense crystalline phase, and at T_m the crystal melts. (Note that $T_{ug} > T_{lf}$, *i.e.*, that the glacial phase does not readily convert to crystal until heated to temperatures above that at which the supercooled liquid readily converts to crystal.) Some of the relevant characteristic temperatures are summarized in Figure 1. Supercooled liquids below T_{lf} can be quickly heated above the melting point without passing through the crystalline phase, but if the low-temperature glacial phase is heated rapidly, it converts to crystal before melting at T_m , at least it did so in all our experiments no matter how quickly we heated it.

Experimental Section

Here we describe a number of different experiments, each aimed at characterizing some feature of the glacial phase and transitions to and from this phase. We draw whatever conclusion we can from each experiment.

Opacity. When the temperature of the TPP sample is suddenly lowered and kept constant in the range between $T_{lf} \approx 227$ and 213 K over a period of hours, the sample first gets cloudy, then turns nearly opaque, and eventually clears up

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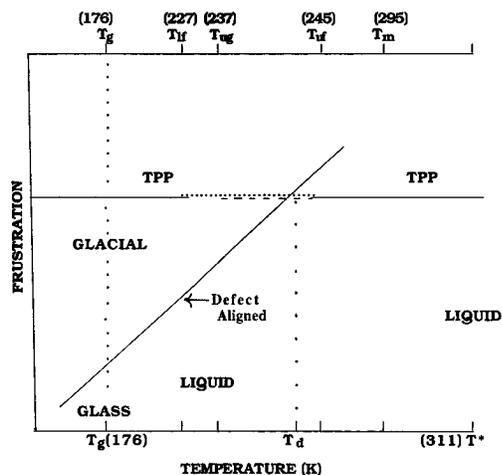


Figure 1. Schematic phase diagram for frustrated system: frustration versus temperature. Broken and horizontal lines indicate regions where crystallization dominates. Each liquid has its specific frustration. Numbers given are for TPP. T_g and T^* are obtained from eq 10 in ref 7.

TABLE 1

	T_g	T_{lf}	T_{ug}	T_{uf}	T_m	T^*	viscosity
TPP	176 ^a	225	237	245	295	311	of glacial phase (very high)
H ₂ O	139	152	160	236	273		of ASW (very high)

^a Temperature at which viscosity equals 10^{13} P, based on data and extrapolation with eq 10 of ref 7.

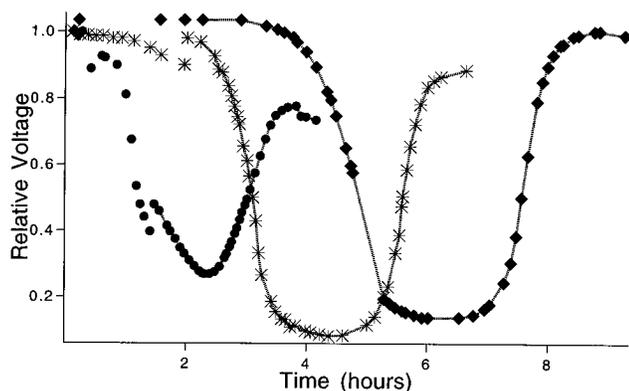


Figure 2. Photodiode voltage (due to transmitted light) versus time for TPP at 219 (●), 214 (*), and 213 K (◆). The lines are drawn merely to guide the eye.

again. This phenomenon was studied quantitatively by measuring the changing intensity of a transmitted laser beam as a function of time. See Figure 2. We have attributed the scattering at short times to glacial clusters in the liquid; below we study the dynamics of this growth. (See section on Fischer clusters.) Since the clusters grow in number and size, and ultimately coalesce, the scattering at long times is attributed to liquid puddles in a rigid glacial matrix. At some time, close to the complete “clear-up” time, the clear (but now rigid) system develops cracks, presumably due to strain. Also, some samples, particularly those at higher temperatures near $T_{lf} \approx 227$ K, showed “snowflake-like” structures (believed to be crystals formed heterogeneously) near the liquid–vapor interface and container walls. The simultaneous presence of both cracks and opaque snowflake crystals can sometimes interfere with the measurement by blocking the laser beam; in order to overcome this effect, the laser beam had to be readjusted. Note the occasional irregularity in Figure 2 due to such readjustments.

The time (τ_{op}) required to reach the point of maximum opacity, *i.e.*, about half the time for full conversion to the glacial

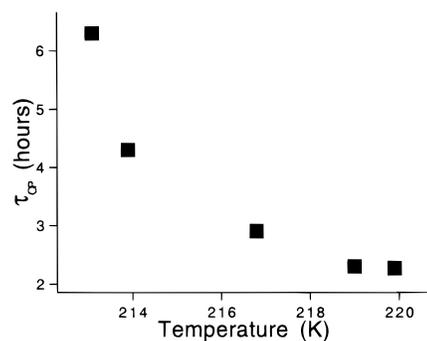


Figure 3. Variation of glacial phase growth time (τ_{op}).

phase, increases with decreasing temperature. See Figures 2 and 3. The time τ_{op} is characteristic of the rate of glacial phase formation.

Viscosity. The viscosity of supercooled TPP before the appearance of the cloudiness associated with the liquid-to-glacial first-order phase transition has recently been measured.⁷ Here we have tracked the increase in viscosity (η) associated with the growing presence of the glacial phase. See Figure 4. It can be seen that there is a threshold period (τ_η) before any detectable increase can be observed; thereafter, the viscosity increases at a rate which is faster than exponential. These results indicate that the glacial phase is much more viscous than the supercooled liquid; the rapid onset of the high viscosity, higher than we can measure, seems to indicate the existence of a percolation limit. We note an unexpected decrease in τ_η as the temperature is lowered, unexpected because according to the opacity measurements discussed above the rate at which the glacial phase develops decreases with decreasing temperature. Below, in the section entitled Liquid–Glacial Viscosity Percolation Limit we speculate on an explanation of this phenomenon.

In carrying out these experiments, we encountered a number of difficulties. Our apparatus could not be used below 219 K (due to the increasingly high viscosity), and so the trend in τ_η was observed only over a 4 deg range. Our temperature control was good to about ± 0.5 K, not good enough for accurate viscosity measurements in the supercooled regime but quite adequate for determining the threshold times τ_η . We used a falling-ball technique for measuring viscosity; actually, we used successive falling balls to measure viscosity as a function of time, *i.e.*, of glacial phase buildup. In most experiments, as the balls fell through the sample, heterogeneous crystallization took place on the balls; this alters the size, shape, and density of the falling object but is unlikely to account for the very large sudden decrease in the falling rate observed at time τ_η . In summary, these viscosity experiments cannot be considered quantitative, but nevertheless, we believe they demonstrate the trends in τ_η .

The viscosity in our experiments is proportional to $\Delta\rho/v$, where v is the velocity of a falling steel ball and $\Delta\rho$ is the difference in the densities of the ball and the TPP. Corrections were made for the density change in the TPP, and checks were made to ensure Newtonian flow. We designed a closed system, filled with dry N₂, which contained three precooled steel balls which could be dropped into the TPP at different times. However, the trends discussed above held regardless of whether the experiment was conducted with the TPP exposed to the air or with the TPP under dry N₂. The adequate constancy of the temperature was confirmed by the fact that the initial plateau regions in Figure 4 are quite flat; furthermore, since the viscosity was related to the velocities of a succession of falling balls at various heights in the sample, the flatness of the initial plateau region confirms that the temperature gradients were negligible.

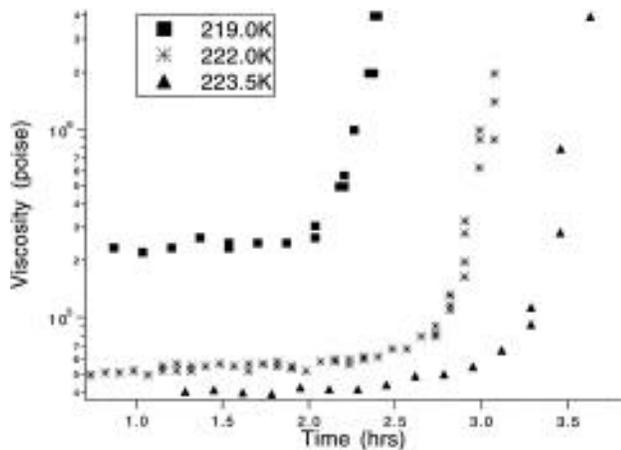


Figure 4. Viscosity as a function of time for TPP at various temperatures that have been reached by quenching from 313 K.

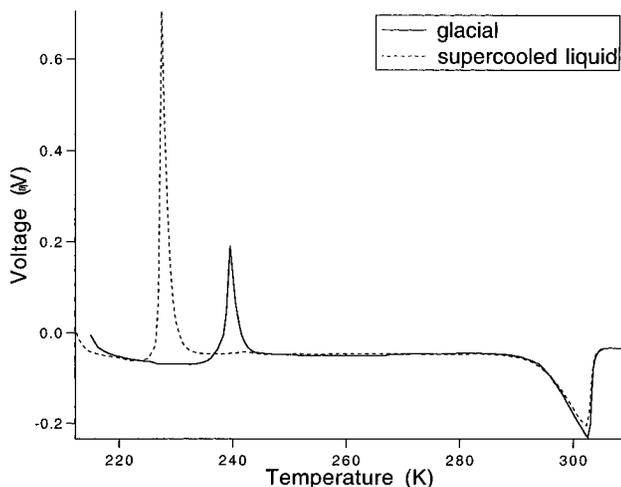


Figure 5. Differential scanning calorimetric curves for glacial and supercooled liquid TPP.

Calorimetry. In order to study the first-order transitions from the supercooled and from the glacial phases to the crystal, we carried out differential scanning calorimetric measurements. See Figure 5. The heating rate was about 1 K/min. First-order transitions were observed as both the supercooled liquid and the glacial phase converted to crystal, the former at $T_{lf} \approx 227$ K and the latter at $T_{ug} \approx 237$ K. The enthalpy of transition was negative in both cases, a characteristic of the transition from a metastable to a stable phase. The melting of the crystal, with positive enthalpy of transition, is also observed in Figure 5; however, the glass transition at $T_g \approx 176$ K was not observed because our calorimeter could not readily be taken down to such low temperatures.

X-ray. X-ray diffraction studies were carried out with a Picker diffractometer, modified by Crystal Logic, operating with 0.7107 Å molybdenum radiation. The sample was cooled by the flow of cold N_2 gas, which enabled us to prepare the samples within the apparatus, thereby avoiding significant heating of the small sample-containing capillary and consequent unwanted crystallization upon transfer of glacial phase samples to the diffractometer. However, the temperature control was imperfect and created difficulties and uncertainties in our studies; pure glacial phase samples were difficult to obtain.

We have taken X-ray scans of liquid (glass), glacial, and crystal (polycrystalline or powder) phases. See Figures 6–8. The spectrum of the empty capillary (shown in Figure 6) has been subtracted from the raw spectra as a first-order approximation to complete deconvolution of the data, and it is these

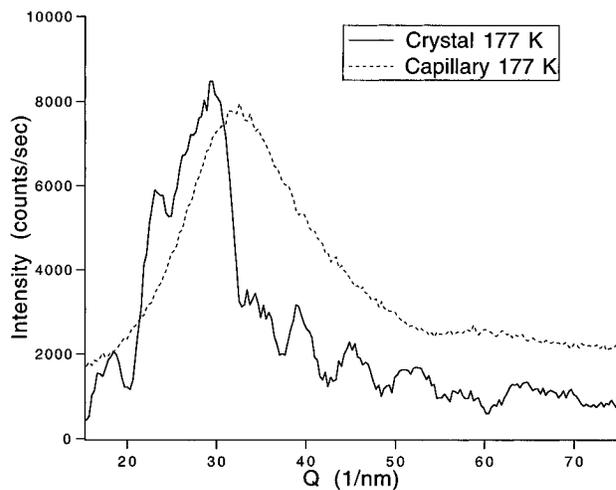


Figure 6. X-ray scan of crystalline TPP. The scan of the empty capillary (also shown) has been subtracted from the actual crystal scan.

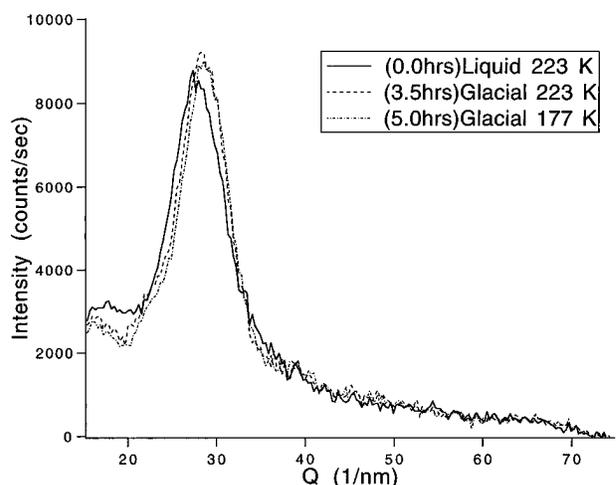


Figure 7. X-ray scans of liquid and glacial phase TPP. The scan of the empty capillary has been subtracted from the actual scans. The sample was kept at 223 K for 5 h and then quenched to 177 K. The initial times for the 30 min scans are indicated in the figure.

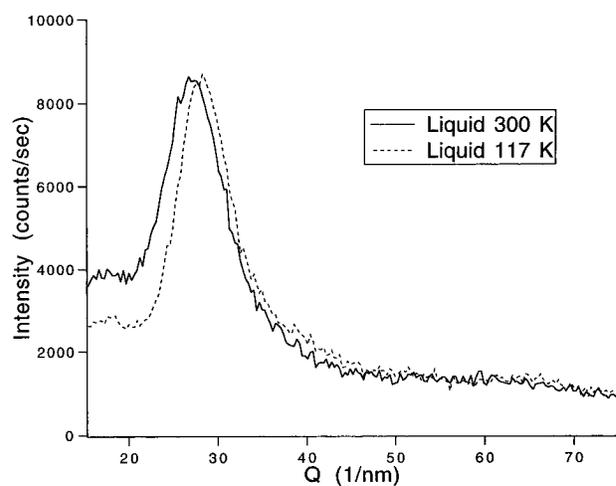


Figure 8. X-ray scans of liquid TPP. The scan of the empty capillary has been subtracted from the actual scans.

partially deconvoluted data that are shown in the figures. The scan of the polycrystalline phase exhibits broadened Bragg peaks and is clearly distinct from that of the two others, but as shown in Figures 7 and 8, the liquid (glass) and glacial phases are very similar, which is why we denote the glacial phase as “amorphous”.

Although our X-ray studies are preliminary in nature and designed only to demonstrate the "amorphous" character of the glacial phase, one can interpret the data in somewhat more depth. While the high- Q regions of Figures 7 and 8 are the same for glacial and liquid phases at all temperatures, slight differences are observed at lower values of Q . Indeed, if one believes that the salient properties of supercooled liquids and, in particular, of the glacial phase are associated with length scales characteristic of domains or fluctuations large compared to molecular dimensions, then it is in the low- Q regime that differences should be found. Therefore, low-angle scattering experiments should be useful.

The scans shown in each of the Figures 7 and 8 represent experiments carried out with a single capillary, but different capillaries were used for the experiments in each of the figures. The capillary scan shown in Figure 6 was subtracted from the raw data to produce all the other spectra in Figures 6–8; while there are slight differences in the spectra of different capillaries, particularly at high Q 's, the qualitative nature of the comparisons is not affected.

NMR. NMR spectroscopy is sensitive to differences in the near molecular environment. Consequently, it can be used to distinguish the differences in the local environments of liquid (or glass), crystal, and glacial phase samples. Due to the extremely broad lines in solid state spectra, no appreciable differences in the chemical shifts of the different phases of TPP were observed at low temperatures. Magic-angle-spinning solid state NMR could not be used because weight imbalance prevented successful spinning of the sample.

However, samples in the different solid phases could be distinguished by measuring their spin–lattice relaxation times, T_1 . The T_1 's for all three samples (liquid/glass, glacial, and crystal) were measured at 200 K and 165 K where motional effects were negligible. The glacial samples crystallized during the time of transfer from the preparation Dewar to the NMR probe; therefore, the glacial samples had to be made within the probe. A room-temperature sample was inserted into the probe at 215 K and left there for 6 h, after which time the probe temperature was quickly dropped to 200 K for subsequent scanning.

The spin–lattice relaxation times (T_1) were found to be (in seconds)

	at 200 K	at 165 K
liquid/glass	18	44 ± 2
glacial	28	81 ± 2
crystal	84	116 ± 7

It is not the absolute, but the relative, T_1 values that concern us here; they confirm that on a molecular level the three phases (liquid/glass, glacial, and crystal) are indeed different, each with its own distinct spin–lattice relaxation rate.

These T_1 measurements were carried out using the inversion recovery method with XWin-NMR software on the Bruker ARX400 spectrometer, with the 5 mm quadruple nuclear probe (QNP) and with the Eurotherm B-VT (variable temperature) unit. The single ^{31}P peak of TPP was monitored in the T_1 measurements with a 180° transmitter high-power pulse of 9.0 μs duration and a 90° pulse of 4.5 μs duration.

Density. We have not measured the density of any of the phases, but we have obtained relevant indirect data concerning the densities. For example, upon direct crystallization of the liquid, the sample of TPP clearly takes up less volume in the container. The same is true when the supercooled liquid transforms to glacial phase; one actually notices that the sample pulls away from the container walls. These results indicate that

both the glacial phase and the crystal are denser than the liquid (and presumably than the glass).

Upon heating, the glacial phase turns to crystal. If the heating is carried out slowly, one often loses the sample due to breakage of the glass container. We interpret this as an indication of expansion from one rigid phase to another less dense rigid phase; *i.e.*, we conclude that the glacial phase is denser than the crystal. (The X-ray data did not yield useful information on this point.) We postulate that if heated rapidly, conversion from glacial phase to crystal occurs simultaneously throughout the sample so that the strains are distributed and minimized and are not restricted to parts near the container walls.

Crystallization. The processes being studied are slow, and several of them may have comparable relaxation times. This means that the system exhibits hysteresis, and the competing first-order transition processes (glaciation and crystallization) are not easily separable. Also, impurities play a role, a role that is not yet fully understood. We go into these matters here.

We have noted that crystallization from the liquid is slow for temperatures above $T_{\text{uf}} \approx 245$ K and below $T_{\text{lf}} \approx 225$ K; at temperatures in the range from about 225 K to about 219 K one often observes some crystallization competing with the glaciation process. (Presumably, as the temperature is lowered, the nucleation barrier decreases and the rate of critical nucleation increases, but the rate of crystal growth slows down because of the great increase in viscosity; at temperatures above 245 K it is the high barrier that prevents crystallization, and below 225 K it is the high viscosity.) For the most part, this crystallization, which decreases as the temperature is lowered, seems to be heterogeneous in that opaque, white crystalline matter (the amount being somewhat unpredictable) seems to form at surfaces.

The supercooled liquid looks like any normal transparent liquid. The crystal is a polycrystalline, opaque solid. The glacial phase looks like a transparent glass, but it has some cracks that are presumably the consequence of strain. The crystalline regions trapped in the glacial phase are treelike or starlike opaque regions that look quite different than the cracks. When cooled to 77 K, both the glass and the glacial phase fracture significantly; we have not studied this phenomenon, but we understand that it has been observed in other systems as well.

When the glacial phase is heated above $T_{\text{ug}} \approx 237$ K, its conversion to crystal is detected by the rapid growth of opaque crystals. At first the system develops an orange cast, and then at about 280 K it becomes white and more opaque; we interpret this to mean that the glacial phase first converts largely to microcrystals with characteristic diameters of several hundred nanometers and then at higher temperature converts entirely to large clumps of crystal (which melt at 295 K). However, these observations require more study.

In the temperature range where the crystallization rate is sufficiently slow that the supercooled liquid and glacial phases can be studied, measurements are constrained by the opposing requirements that they be sufficiently rapid so that the liquid–glacial–crystal concentrations remain constant during the experiment and yet sufficiently slow that mechanical (as in the viscosity measurements) and thermal equilibria can be established.

The TPP liquid when quenched and kept at temperatures in the narrow range 225–227 K behaved rather anomalously and irreproducibly. With time, the clear liquid became turbid, as expected, but then, instead of the expected completion of the transformation from liquid to glacial phase, apparent phase separation and coexistence were observed, *i.e.*, small opaque

ball-like regions floating in clear liquid. We are currently studying this phenomenon, but here we merely note that the indicated temperature range is that at which the transformations from liquid to crystal and from liquid to glacial phase are reasonably rapid and quite comparable.

Light Scattering. Fischer Clusters. Our work on the glacial phase grew out of our interest in the clusters reported by Fischer and co-workers in deeply supercooled liquids,^{8–10} particularly in the fragile¹ glass-forming liquid *o*-terphenyl.⁸ They studied both the structural and dynamical properties of these clusters. It is possible that these clusters (and clusters observed by the Fischer group in a number of other systems^{9,10}) are similar to those we observed in TPP;¹¹ whether the Fischer clusters would ultimately mature into a full-fledged phase change or whether (and why) such growth would be aborted has yet to be established. On this last point, we note that, as indicated above, such limited growth is found for TPP in the 225–227 K range.

Our dynamic polarized light-scattering experiments on TPP samples cooled below 223 K and maintained at a constant temperature well above T_g give evidence of the development of correlated structures or “clusters” over a period of about an hour.¹¹ The evidence is the appreciable increase of the Landau–Placzek ratio (the ratio of the integrated intensity of the central Rayleigh feature to the integrated intensity of the two Brillouin lines) and of the integrated Rayleigh intensity, and more specifically the onset of an angle (q) dependence of these *thermodynamic (structural)* quantities. This suggests the presence of clusters comparable in size to the wavelength of the light, *i.e.*, several hundred nanometers. In earlier work on *o*-terphenyl, Fischer and co-workers⁸ not only carried out similar experiments but also identified a low-frequency spectral component which appears to be associated with the motion of these very large clusters. The analysis, outlined below for TPP, as well as those of Fischer and co-workers on other systems, indicates that both the number and size of the clusters increase with time. We now believe that for TPP these clusters are “pieces” of glacial phase present in the early stages of the transition from supercooled liquid to glacial phase. It is the increasing size and number of these clusters that ultimately account for the increasing opacity of the system. We hypothesize that the clusters observed by Fischer and co-workers for *o*-terphenyl⁸ and other liquids^{9,10} are also associated with a glacial phase, but this has yet to be proved.

The magnitude q of the scattering vector q is related to the scattering angle θ by the relation

$$q = (4\pi n/\lambda) \sin(\theta/2) \quad (1)$$

where n is the refractive index and λ the wavelength *in vacuo* of the laser radiation (530 nm in our case). To study the light-scattering spectrum as a function of q , one can collect the scattered light at various fixed angles, as done by Fischer and co-workers.^{8–10} However, for strong scattering such as that observed in the presence of appreciable concentrations of clusters, the forward scattering can be imaged on a screen and the angular dependence of the incident scattered radiation used to determine the q dependence of the integrated intensity of the scattered light; we used this “forward imaging” technique in our study of clusters at low temperature. After a time (30 min or so), at temperatures about 218 K, the cluster concentration in TPP became so high and the scattering so intense that multiple scattering dominated, and we could no longer carry out meaningful dynamic light-scattering experiments; we then resorted to measurements of transmitted light, *i.e.*, to the opacity measurements discussed above.

Reliable intensity measurements are difficult to effect without an internal standard, which we do not have. But the Landau–

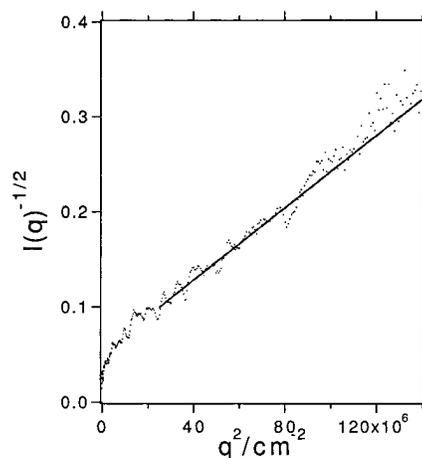


Figure 9. $I(q)^{-1/2}$ as a function of q^2 for TPP at 223 K, 49 min after having been quenched from 313 K. The curves are fits that have been made with the formula $I(q)^{-1/2} = (N_c \xi^3)^{-1/2} (1 + q^2 \xi^2)^{-1/2}$, N_c and ξ being adjustable parameters.

Placzek ratio, while exhibiting much the same behavior in the presence of clusters as the total integrated intensity, can be more dependably measured. The Landau–Placzek ratio for equilibrated (unclustered) liquid TPP above 313 K is about 1 ± 0.5 , the uncertainty (irreproducibility) presumably being due to dust, other impurities, and stray light. For supercooled TPP in which clusters were given time to develop, ratios exceeding 100 were measured, after which the sample became too opaque for light-scattering experiments.

Fischer and co-workers⁸ found that the q dependence of the integrated intensity, $I(q)$, of the light scattered from cluster-containing *o*-terphenyl was given by $N_c \xi^3 [1 + \xi^2 q^2]^{-2}$, where the correlation length ξ and the concentration of clusters N_c are both determined by fits to the data. This intensity corresponds to a Debye spatial (r) correlation function of the form $\exp(-r/\xi)$. On the other hand, for other systems they found¹⁰ that the intensity varies as $N_c \xi^2 [1 + \xi^2 q^2]^{-1}$; this intensity corresponds to an Ornstein–Zernicke correlation function of the form $r^{-1} \exp(-r/\xi)$. Our data fit well to the Debye function, which for large q yields the Porod q^{-4} law; this suggests that the density falloff at the edge of the cluster is reasonably sharp. See Figure 9.

We have used the formula $I(q) = I_0 [1 + \xi^2 q^2]^{-2}$, where $I_0 = N_c \xi^3$, to determine the relative concentration N_c of clusters and the correlation length ξ associated with the clusters, both as functions of temperature and of time. See Figures 10–12. The curves in Figure 11 suggest that the number, N_c , of clusters increases exponentially, *i.e.*, as $\exp(k_n t)$, with a “nucleation rate constant” k_n which decreases with decreasing T . A $\log[k_n(T)]$ versus $\log[\eta(T)]$ plot suggests $k_n \propto \eta^{-1/3}$, a very approximate result that we do not yet understand. In contrast to the rapid rate of “nucleation”, the rate of cluster growth, *i.e.*, $d\xi/dt$, is, as indicated in Figure 12, slow. Although the conclusions are not definitive, the data in Figure 12 suggest that the correlation length ξ grows as $k_c \log[t]$, which indicates a rate of cluster growth of the form $k_c t^{-1}$. The quantity k_c seems to decrease with decreasing T . *The salient feature of this study is that both the “nucleation rate” and the “growth rate” decrease with decreasing T .* Our data on the early stages of glacial phase growth do not seem compatible with homogeneous nucleation theory.¹²

Fischer and co-workers⁸ reported that supercooled cluster-containing *o*-terphenyl shows no perceptible increase of viscosity over that of the unclustered supercooled liquid at the same temperature. Although Fischer and co-workers did not actually

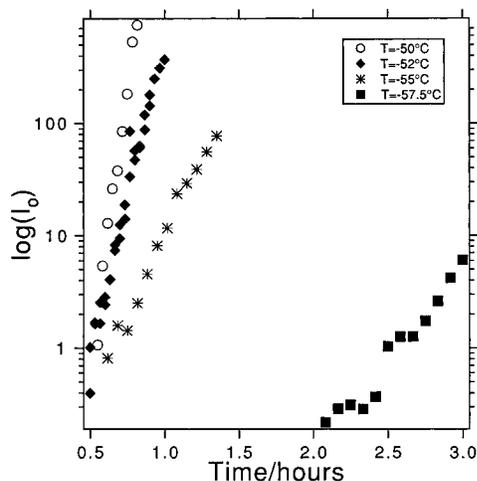


Figure 10. Light-scattering intensity (I_0) at $q \rightarrow 0$ as a function of time at various temperatures that have been reached by quenching from 313 K (I_0 in arbitrary units).

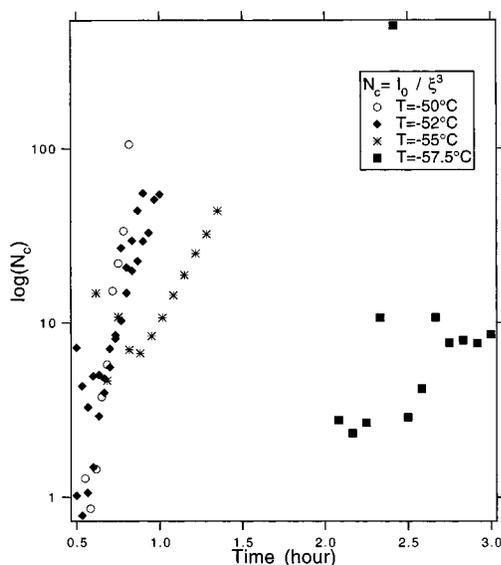


Figure 11. Cluster concentration N_c as a function of time at various temperatures that have been reached by quenching from 313 K (N_c in arbitrary units).

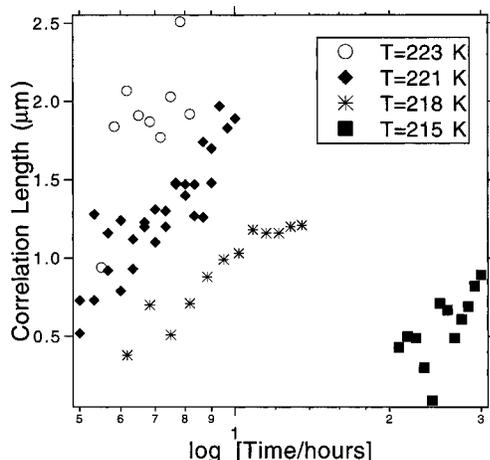


Figure 12. Correlation length ξ as a function of time for TPP at various temperatures that have been reached by quenching from 313 K.

measure viscosity, but rotational relaxation, and these measurements may have been heavily weighted by those molecules not in clusters, their results are consistent with our viscosity results for the early stages of glacial phase growth. See Figure 4.

Samples and Procedures. The triphenyl phosphite (TPP), purchased from Fisher Scientific, was examined by both ^{31}P and ^1H NMR. The samples from the bottle (which we denote as “pure”) contained about 0.5% impurity, which we characterized by NMR as mainly phosphoric acid and phenol. With time and exposure the samples develop a slightly yellowish cast which can be eliminated by distillation. Doubly distilled samples seem to have about double the phosphoric acid concentration as does the material taken directly from the bottle. Many samples were filtered in order to remove dust. Due to degradation of TPP, the phosphoric acid content in some of the older samples was as high as 10%, but the results reported here were carried out on samples with phosphoric acid content well below 1%.

The slow relaxations in the systems studied led to hysteresis and made the results history dependent. Impurities seem to inhibit both glaciation and heterogeneous crystallization, and so the results are sometimes sample dependent. In particular, we have found that phosphoric acid can inhibit glaciation very strongly. The phenomenon of large cluster growth in one-component systems is sufficiently unexpected that one might suspect that a major role is played by rogue impurities, bubbles, strange nucleation leading to microcrystals, or critical fluctuations about some unsuspected critical point. We believe that we have either ruled out or learned to control most of these intrusive effects, exercising care in the analysis of the data. Although there is still a level of irreproducibility and uncontrollability in these studies, particularly due to impurities and heterogeneous nucleation leading to crystallization, we believe all the results reported here to be robust.

Polyamorphism

Recently, there has been considerable interest in the phenomenon of polyamorphism,⁴ the ability of a given system to exist in more than one amorphous state.¹³ We have shown that TPP can exist, actually coexist, in two “apparently” amorphous phases; this observation may well fit into these studies.

Polyamorphism in H_2O has been extensively studied, but the interpretation of the data remains controversial.^{13–22} Amorphous solid water (ASW) or water II can be formed in a number of different ways such as vapor deposition, liquid hyperquenching,¹⁸ or pressure-induced amorphization¹⁹ followed by annealing at about 130 K; this phase has a higher density than ordinary ice but a lower one than water. This form, when heated, may undergo a weak “glass transition” to “liquid” at about 136 K,^{16,20} but the transition is at most very weak, and although the viscosity of this material has not been measured, it has been estimated to be very high.¹⁴ At a temperature of about $T_{\text{UG}} \approx 160$ K the ASW crystallizes to ice.^{14,23} The ASW is not thought to be the glass one would obtain by quick quenching water to very low temperatures;¹⁵ such deep quenching is difficult because even at the fastest quenching rates water tends to crystallize at about $T_{\text{uf}} \approx 235$ K, where its viscosity is only about 10^{-1} P.¹⁴ Nevertheless, it has been estimated that $T_{\text{g}} \approx 139$ K, and upon heating it appears that crystallization of the liquid takes place at about $T_{\text{if}} \approx 152$ K.¹⁴ Note the analogies between the behavior of supercooled water and TPP, as well as those between ASW and glacial TPP. See Figure 1.

Other examples of polyamorphism have been observed.⁴ Under pressure, the “strong” liquid SiO_2 can be converted to what appears to be a denser,²⁴ “fragile” liquid. When $\text{Y}_2\text{O}_3\text{—Al}_2\text{O}_3$ is fast temperature quenched, the fragile high-temperature liquid is partially vitrified and partially transformed to a low-temperature, low-density amorphous phase with the same density.^{4,25} Amorphous solid Si “melts” to a liquid via a first-

order transition,^{4,26,27} a phenomenon which might be considered the reverse of that which we have observed for TPP, *i.e.*, the transformation of the liquid to the glacial phase. We list these examples here merely to suggest a possible tie-in of our observations on TPP with a broader class of polyamorphous phenomena.

Theory

Overview. No general theory of the glacial phase and of the larger class of amorphous rigid phases exists, and there is much controversy concerning theories of supercooled liquids themselves. Here we outline a model, the only extant model, we believe, that purports to describe and connect supercooled liquids and the glacial phase. The model is, we believe, reasonable and intriguing and has a theoretical foundation; at this point, at least, it is not demonstrably wrong.

Most theories^{28,29} of supercooled liquids attribute the salient properties of these systems to collective effects. We concur, and we look to descriptions that associate both the supercooled liquid and the glacial phases with collective long-range (relative to molecular size) correlations. Many, even most, theories envisage a supercooled liquid as a heterogeneous mixture of clusters or domains, or possibly of slow, large fluctuations, the nature of these domains varying from model to model but quite generally polydisperse in a significant characterizing property (such as size, fluidity, order) that grows in “importance” as the temperature is lowered. There is a good deal of indirect, mostly dynamic evidence supporting this picture^{30,31} and growing, but not yet conclusive, direct structural evidence.^{32,33} We shall pursue a picture in which the characterizing property of the domains is their volume.³⁴

Although low-resolution X-ray studies indicate that the glacial phase is amorphous, *i.e.*, very similar to the liquid and glass, the striking differences in properties and the first-order transition between them suggest that there may be more to the structure of the glacial phase than first meets the X-eye. There is the possibility that some “apparently” amorphous phases may, in fact, be crystalline. If the unit cells in these apparently amorphous materials are large, consisting of many molecules in rather loose order, and if, in addition, the microcrystals are not sufficiently large, direct confirmation by means of scattering experiments may be a nontrivial task; consequently, although in principle such structures should be detectable in high-resolution, high-intensity, low-angle scattering, the difficulties are such that a negative result cannot be taken as evidence against the existence of such structures. With these considerations in mind, we hypothesize that the glacial phase may be a defect-ordered crystal, one in which the domains characteristic of a supercooled liquid arrange themselves into a crystal array, where the organization within a domain may or may not be identical from domain to domain. Such defect-ordered phases have been studied, *e.g.*, the Frank–Kasper phases in bimetallic systems,⁵ the blue phases of cholesteric liquid crystals,⁶ and various striped phases.³⁵ In support of this hypothesis we offer “physical reasonableness” and the results of model calculations described below.

Frustration-Limited Domains. The theory of “frustration-limited domains” has been developed and discussed elsewhere.^{11,34,36} It envisages a liquid as consisting of small groups of neighboring molecules grouped in *locally preferred structures*.^{11,34} As the temperature is lowered, these structures are more favored. If it were possible to tile space with this structure, at some temperature T^* one would expect the system to crystallize continuously with this locally preferred structure; since this hypothetical or reference crystal would minimize the

free energy both globally (as does the real crystal) and locally (in contrast to the real crystal), it would be more stable⁴⁵ than the real crystal, and one would expect $T^* > T_m$.^{11,34,37} However, because of geometric frustration, one cannot tile space with this locally preferred structure; consequently, as the temperature decreases, the extension of the locally preferred structure is accompanied by increasing strain. The strain ultimately limits the growth of the locally preferred structure, and frustration-limited domains are formed, each domain consisting of many molecules; these domains themselves can either distribute themselves randomly or, alternatively, organize themselves into crystals with very large unit cells. In our picture both these structures occur: below a temperature T^* collective effects lead to a random distribution of domains; at a temperature T_d , which is *strictly* below T^* , there is a transition from the system composed of frustration-limited domains (supercooled liquid) to a defect-ordered crystal. See Figure 1.

(1) Below T^* , the break up into randomly distributed frustration-limited domains is our picture for a supercooled liquid.³⁴ The slow relaxation times characteristic of supercooled liquids are associated with the restructuring of individual domains, a process that is expected to have an activation energy proportional to the cross section of the domain. The nonexponential relaxation observed^{30,38} in supercooled liquids is then associated with the distribution of domain sizes.

(2) Below T_d , the organization of the domains into crystals with enormous unit cells can be denoted as “defect-ordered crystals” because one can envisage such a crystal as arising from the ordering of the defect lines between domains.^{5,6,39}

Avoided Critical Point. The theory of frustration-limited domains^{11,34} is built about an “avoided critical point” at T^* , the crossover temperature between molecular and collective behavior. In the absence of frustration the system would undergo a critical transition at T^* and would have an order parameter below T^* . In the presence of weak frustration, the situation actually encountered, the system is weakly perturbed, and the critical point is narrowly avoided; *i.e.*, in the presence of even vanishingly small frustration, there is no critical point that connects continuously to that at T^* . See Figure 1. But if the frustration is weak, the nearby, or avoided, critical point strongly affects the behavior of the real system. In particular, it can be *proved* that, because of the avoided critical point, below T^* there is a second macroscopic length (in addition to the usual critical correlation length), and this length has been associated with domain size, *i.e.*, with a region over which an order parameter can be specified.³⁴

One can postulate a spin Hamiltonian that has the desired behavior, one that has a short-range ferromagnetic term plus a weak, long-range (r^{-1}) antiferromagnetic perturbation. The first term represents the reference critical system and the second term the effect of frustration. Although the mapping of the molecular Hamiltonian upon this spin Hamiltonian has not yet worked out, it is often the case that strain enters with r^{-1} range; the fact that we are interested in collective, *i.e.*, long-range, phenomena makes the details of the mapping less essential. A *perturbative approximation* yields a second macroscopic length that grows, as anticipated, with decreasing temperature; we associate this length with domain size.³⁴

The theory of frustration-limited domains³⁴ has had success in describing the temperature dependence of the viscosity and relaxation times of supercooled liquids.³⁶ And we are finding that it is also capable of quantitatively describing other phenomena associated with supercooled liquids. The theory is, in essence, a scaling theory which has been applied over a wide temperature range from the avoided critical point T^* , which lies

near, but usually somewhat above⁴⁵ T_m ,³⁶ down to T_g . It is always difficult to establish theoretically the valid range of critical scaling, but there is comfort to be gained by the fact that the resulting expression seems to be validated by experiment.

To date, the only frustration-avoided critical-point models that have been solved are those for the frustrated spherical and $O(N)$ models, the latter in a $1/N$ expansion.⁴⁰ Although these are not likely to have physically realistic symmetries, they do exhibit, and therefore validate, a number of properties that have been inferred in the theory of frustration-limited domains. In particular, they yield an avoided critical point at T^* and a phase transition to a defect-ordered phase at a temperature $T_d < T^*$. The latter is, of course, the feature most pertinent to the present study since it is this predicted defect-ordered phase that we tentatively associate with the observed glacial phase.

We conclude that *our picture of supercooled liquids and the glacial state is compatible with the present state of the theory of frustration-limited domains.*

Comparison with Other Theories. We comment briefly on the connection of this theory with other relevant ones. In the theory of frustration-limited domains the characteristic temperatures are T^* and T_d . The first, T^* , is the avoided (due to frustration) critical point (in a physically unattainable reference, unfrustrated system) which represents the crossover from molecular to collective behavior and which also corresponds to the crossover from “normal” to supercooled liquid. (T^* should not be confused with T_m .) The second characteristic temperature, T_d , corresponds to a first-order transition (also associated with frustration) from supercooled liquid to defect-ordered crystal. We expect $T^* \geq T_m > T_d$, and whereas $T_m > T_g$, T_d may be greater or less than T_g . (We note that in the spherical model the transition at T_d is continuous⁴⁰ and not first order.) In this picture the high viscosity of the supercooled liquid is associated with the proximity of the high- T avoided critical point T^* , and *not* by the approach from above to the transition at T_d .

In contrast, most previous theories of supercooled liquids envisage a low-temperature transition temperature T_0 which lies below T_g , and it is the approach to this dynamically inaccessible transition from above that is responsible for the salient properties of supercooled liquids.^{5,28,42,43} This transition at T_0 is sometimes denoted as the transition to an “ideal glass”. In one class of such theories,^{5,42,43} similar in some ways to the theory of frustration-limited domains, it is the defect-ordered crystal that represents the ideal glass, and T_0 is the transition temperature $T_d < T_g$; in these theories, the critical point at T^* is not “avoided” but because of frustration is shifted down to T_d . In these theories the defect-ordered phase should be inaccessible because it should always occur below T_g . The theory of frustration-limited domains thus differs greatly from all those in which the properties of supercooled liquids are based on the approach to a low-temperature transition; among extant theories, only the theory of frustration-limited domains can accommodate an accessible associated defect-ordered phase. We believe it to be possible that the glacial phase is such a phase, but this interpretation as well as other apparently successful applications of the theory of frustration-limited domains has still to be tested.^{43,44}

Liquid–Glacial Viscosity Percolation Limit. We seek a phenomenological explanation of our observation that the threshold time, τ_η , for viscous arrest during the transition from supercooled liquid to glacial phase decreases with decreasing temperature, even though the time, τ_{op} , for transformation to the glacial phase increases. See Figures 2–4. As the glacial

phase starts to develop, islands of rigid material form in the liquid, but when the transformation is nearly complete, one has puddles of liquid in the solid material. Above some concentration of solid material, channels of “sufficient” width within the solid no longer interconnect adequately to allow the fluid material to percolate through the system. “Sufficient” width means width that can accommodate the diffusing units, in this case, presumably domains of supercooled liquid. Since the domain size increases with decreasing temperature, so too does the required “sufficient” width of the channels. We propose that the critical concentration of solid material at which channels of a given width no longer interconnect is smaller for wider channels; therefore, the critical concentration of solid material at which percolation of supercooled liquid domains is arrested decreases with decreasing temperature. However, we have seen that the time required to obtain any given concentration of solid (glacial) material increases with decreasing temperature. In summary, we conclude that the time necessary to break connectivity of channels of a given width increases as the temperature decreases, that as the temperature decreases wider channels are needed to permit percolation of the larger supercooled liquid domains, and that it takes less time to break connectivity of wider channels. If the last two effects dominate, then, as observed, the time τ_η should decrease with decreasing temperature even though τ_{op} increases.

This explanation for the opposite temperature trends for τ_{op} and τ_η is simple and intuitive but certainly not quantitative or definitive. It does, however, provide further indirect evidence of the domain or clusterlike structure of supercooled liquids.

Comments

We have detected the glacial phase for TPP. This phase is rigid, “apparently” amorphous, and denser than either the crystal or the liquid (*i.e.*, than the supercooled liquid and glass). By amorphous we mean that its low-resolution X-ray scattering is nearly indistinguishable from that of the supercooled liquid and glass. At sufficiently low temperatures, the glacial phase is stable relative to the supercooled liquid and glass, but presumably metastable relative to the crystal. We have studied the slow, first-order transformation of supercooled liquid to glacial phase.

A degree of serendipity is required for study of the onset of the glacial phase. Crystallization must be sufficiently inhibited, the transition to the glacial phase must occur at a temperature T_d that lies above T_g , and the times for transforming from supercooled liquid to glacial phase must be experimentally accessible. All these requirements are met by TPP, but the relevant range of temperatures is somewhat difficult to attain and maintain. It is not clear yet for which other glass-forming liquids these conditions are met.

We identify several basic unresolved questions concerning the glacial phase. Is the glacial phase a property of many, or even all, supercooled systems, or is it a peculiarity of TPP? We believe it is a general property, because of both the analogous properties with other system and the occurrence of Fischer clusters in a number of systems. Is the glacial phase truly amorphous, or is it a defect-ordered phase? We believe that it is possible that it is a defect-ordered phase because of both the results of model calculations and the fact that the structure of such a phase may not be readily detectable in low-resolution X-ray scattering. Is such a defect-ordered glacial phase an inherent property of supercooled systems as suggested by the model calculation? We believe that it is possibly so.

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