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LETTERS

Supercooled Liquids and Polyamorphism†

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We have discovered a solid, apparently amorphous phase of triphenyl phosphite to which the supercooled liquid converts, a phase distinct from both the glass and the crystal. To date, this is the clearest and best identified case of a first-order transition from a liquid to another apparently amorphous condensed phase. We discuss this phenomenon in terms of a recently formulated theory of supercooled liquids that predicts and naturally incorporates the existence of such low-temperature phases, thereby suggesting that its existence is a general phenomenon intimately connected with the existence and properties of supercooled liquids. In accord with the theory, we also suggest that although the X-ray scans do not indicate any lattice structure, these apparently amorphous phases may in fact be defect-ordered structures with large unit cells.

Introduction

This is a study of what has been called[1] "polyamorphism", the existence of two or more "apparently amorphous condensed phases" in one-component systems, especially the liquid plus another "apparently amorphous" low-pressure phase. It has long been known that below a temperature T_g, which lies well below the melting temperature T_m, structural relaxations in a supercooled liquid (a metastable liquid below T_m) become too slow to allow local equilibration in the experimental times, the consequence being the formation of an amorphous solid or glass;[1,2] the glass is therefore merely the liquid (supercooled) phase which is unable to equilibrate. We have identified a formerly unknown, rigid, "apparently amorphous phase" to which at least one single-component supercooled liquid (triphenyl phosphite denoted as TPP) converts by way of a first-order transition. We tentatively denote this phase the "glacial phase", thereby suggesting amorphous, vitreous properties while still distinguishing it from the glass. We believe this study to be the most direct analysis to date of a first-order transition between condensed amorphous states. For TPP there is a range of temperatures between T_m and T_g where the supercooled liquid converts to the glacial phase, a metastable phase which, over our experimental times, is stable unless heated and which upon heating converts to the crystal at a temperature well below T_m. This glacial phase is distinct from both the normal crystal and, though apparently amorphous, distinct from the glass as well. Our preliminary experiments on other liquids, as well as comparison with the results of others, lead us to believe that this "glacial phase" is not restricted to TPP or to a small group of "fragile" glass-forming materials but is a "supercooled phase" associated with supercooled materials in general and that the understanding of this phase is closely tied to understanding of supercooled liquids and glasses. In this article we summarize our experimental results, and secondarily we interpret them in terms of a recently formulated theoretical model of supercooled liquids,[3,4] the only existing model that we have identified that incorporates the possibility of the observed low-temperature phase changes.

Brief Summary of Results. The characteristic temperatures associated with TPP are given in Figure 1. If the liquid is supercooled slowly, it crystallizes at about $T_{uf} \approx 245$ K, but if it is quick-quenched below $T_{lf} \approx 225$ K, it can remain liquid without crystallization for long periods of time. However, if

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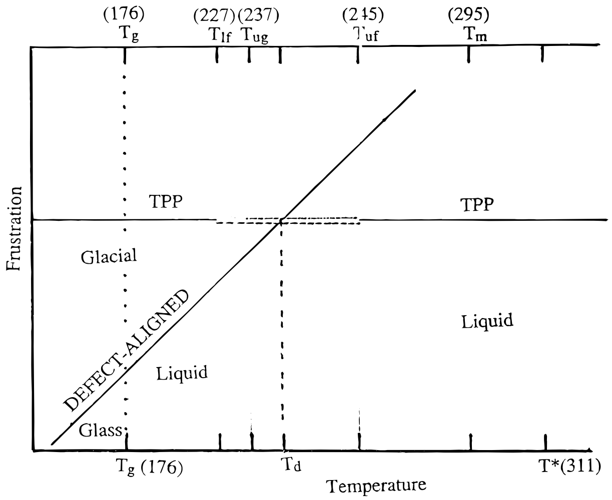

Figure 1. Schematic frustration versus temperature diagram. Broken and horizontal lines indicate regions where crystallization dominates. Each liquid has its specific frustration. Numbers given are for TPP. T_g is taken as temperature at which viscosity equals 10^{13} P, based on data and extrapolation with eq 10 of: Zhao, X.; Kivelson, D. *J. Phys. Chem.* **1995**, *99*, 6721. T^* is also obtained from this reference.

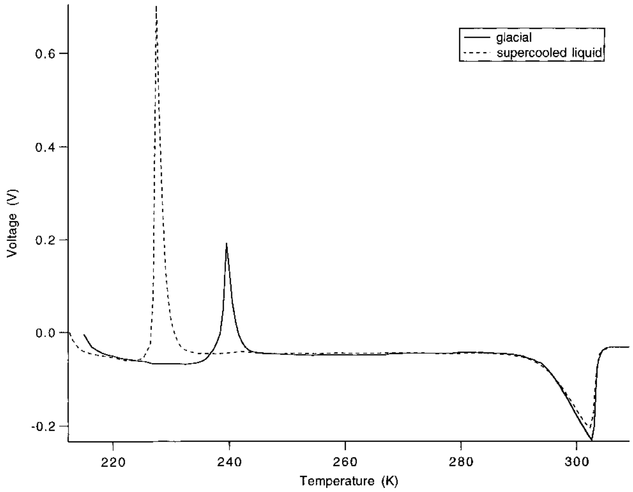

Figure 2. Differential scanning calorimetric curves for glacial (—) and supercooled liquid (- - -) TPP.

kept at a fixed temperature between 213 and 225 K, the supercooled liquid converts, in a matter of hours, to the rigid, amorphous glacial phase which seems to be stable for indefinite times. If the supercooled liquid is heated, it turns to crystal in a matter of minutes at about $T_{lf} \approx 227$ K, while if the glacial phase is heated it turns to crystal in a matter of minutes at a somewhat higher temperature, $T_{ug} \approx 237$ K. The time required for the supercooled liquid to convert to glacial phase increases as the temperature is lowered, and below about 213 K the time needed exceeds that available to us; thus at temperatures below 213 K, we were unable to convert supercooled liquid to glacial phase, but, of course, the glacial phase formed at higher temperature can be brought down below 213 K, in fact below the glass temperature $T_g \approx 176$ K, so that the glacial and glass phases can be compared at low temperatures.

Experimental Section

Validation of the picture given above comes from a number of experiments presented in detail elsewhere.[5] If a liquid sample of TPP is quick-quenched (in a matter of minutes) to a temperature in the range 225−213 K and held at that temperature, the sample gradually becomes turbid, then nearly opaque (in a matter of hours), and then clear again (in a time about twice the time to maximum opacity). Whereas the initial liquid form has a moderate viscosity (in the range 10^4−10^5 P), the final form is rigid (with an immeasurably high viscosity), has visible cracks (presumably due to strain), and has a smaller volume (higher density). The final rigid form is what we denote the "glacial phase". Differential scanning calorimetric measurements (with the bath temperature rising at about 1 K/min) indicate first-order transitions from liquid to crystal and from glacial phase to crystal at $T_{lf} \approx 227$ K and $T_{ug} \approx 237$ K, respectively, the enthalpy change in both cases being negative. See Figure 2. The X-ray powder patterns of the supercooled liquid at 218 and 200 K (where it has become very viscous) are quite similar and much like what would be expected for an amorphous material (e.g., it is not unlike the background signal from the capillary used as a sample holder). The X-ray scans of the glacial phase at these temperatures are very similar to those of the liquid, and it is for this reason that we classify the glacial phase as "apparently amorphous"; whether the small observed differences will ultimately prove to be significant, or whether low-angle or high-resolution experiments will detect differences is uncertain. The X-ray scan of the crystal is quite different and has a series of Bragg peaks. Therefore, on the molecular level, the X-ray scans exhibit marked differences between the glacial and crystalline phases, but we turn to ^{31}P spin−lattice relaxation times, T_1, to exhibit molecular differences between the glacial and supercooled liquid (glass) phases: the T_1's for the liquid, glacial phase, and crystal, all at 200 K, are 17.5, 28.4, and 83.9 s, respectively. Although we have not measured densities directly, it is readily seen, as indicated above, that the glacial phase is denser than the liquid at the same temperature; because upon slow heating many of our glass sample holders broke during the transition from glacial phase to crystal, it is clear that the glacial phase is also denser than the crystal.

The increasing turbidity observed as the glacial phase begins to develop is attributed to the formation and growth of clusters of glacial phase floating in the supercooled liquid; the size and number of these clusters as a function of time has been studied by light scattering.[5] After some time, multiple scattering becomes too significant for our light-scattering studies to be effective, and at this stage the turbidity is quite high. We attribute the decrease of turbidity at still longer times to the dominance of the glacial phase, the scattering during these times coming primarily from small pools of liquid within the solid, and ultimately, when full conversion to the glacial phase has occurred, the system is homogeneous and scatters little. The time τ_{op} to maximum opacity (i.e., minimum transmitted light) increases with decreasing temperature, a not unexpected phenomenon since the higher viscosity at lower temperature is indicative of slower dynamics. The viscosity itself changes imperceptibly during the early stages of glacial phase growth but ultimately increases very rapidly to immeasurably high values consistent with the presence of a rigid phase. Note that in our experiments, crystals were prepared in the temperature range 245−240 K, and glacial-phase samples were prepared by allowing supercooled liquid to sit for several hours at constant temperature in the range 225−213 K. Once prepared, the systems can be cooled and maintained indefinitely at temperatures below 213 K. However, studies of supercooled liquid in the range 225−213 K must be carried out rather quickly because of the onset of the glacial phase: viscosity, opacity, and X-ray studies were all carried out at various stages of glacial-phase development. When cooled down to 77 K, both the glacial and glass phases exhibit extensive cracking, a phenomenon that we have not yet studied. In the temperature range 225−227 K the nature of the phases is somewhat uncertain, this being a range where the rates of crystal and glacial formation are competitive; the rate of heterogeneous crystallization is somewhat irreproducible.

How General Is This Phenomenon? Supercooled water and two low-temperature amorphous forms of H_2O have been extensively studied.[6−16] One of these is a low-density amorphous material (called LDA ice, or ASW for amorphous solid water, or water II) which can be prepared by vapor deposition or hyperquenching at 77 K; the other is a distinct high density amorphous form (HDA ice) which can be prepared by compressing LDA ice at 77 K, and which persists even when the pressure at 77 K is lowered to 1 atm but can be converted to the LDA form by heating above 120 K. Because it crystallizes readily at about $T_{uf} \approx 236$ K where its viscosity is only 10^{-1} P,[6] it is not easy to study deeply supercooled water much below its melting point $T_m = 273$ K, but studies by Speedy[7] suggest that the LDA cannot evolve continuously by supercooling water, i.e., that the LDA must be an amorphous phase that is distinct from water (and hence from the ordinary glass). Whether or not this is so, various studies have led to a glass temperature $T_g \approx 139$ K[6,7,11,12] for the LDA, and to a crystallization temperature upon heating at temperatures between $T_{lf} \approx 152$ and 160 K.[6,7,14] Although H_2O has been studied with focus on its specific and unique properties,[6,7,11] here we would like to seek elements of generality by tying the data to the properties we have presented for TPP. In particular, we propose that the LDA ice may be associated with the glacial phase of TPP. The viscosity of the LDA form has not been directly measured, but it has been estimated as being very high.[6] We conclude that there is at least the interesting possibility of meaningful analogies between the H_2O and the TPP systems.

Polyamorphism of various kinds have recently been discussed by Angell.[1,17] Our somewhat different perspective on the problem nevertheless draws from his analysis. It has been proposed that in at least some of the systems discussed in ref 1, i.e., H_2O,[15] $Y_2O_3-Al_2O_3$,[18] and Si,[19,20] first-order transitions from supercooled liquid to an amorphous rigid or at least to a highly viscous phase may be taking place. However, in none of these examples has a one-component first-order transition from one amorphous condensed phase to another been so explicitly displayed. Whereas the low-temperature glacial phase in TPP has a "high" density, the low-pressure, low-temperature amorphous, rigid phases in these other systems have low densities. (The fact that crystalline ice and amorphous SiO_2 under compression convert to higher density forms[21−23] is also presumably related to tetrahedral coordination.)

We also believe that there may be a connection between the glacial phase we have detected in TPP and the low-temperature clusters that Fischer and co-workers reported in deeply supercooled orthoterphenyl[24] and other systems.[25] In fact, in the early stages of glacial-phase development TPP appears identical with the cluster systems reported by Fischer and co-workers. (A preliminary analysis of TPP clusters is given elsewhere.[26] However, the clusters reported by Fischer and co-workers did not develop into a new phase; whether they would do so if kept supercooled sufficiently long, whether the phenomenon should be considered some sort of polymer equilibrium rather than a true phase change, or whether the Fischer clusters are a totally different phenomenon is not yet clear.

Theoretical Implications. In accord with many, if not most, models of supercooled liquids, we envisage them as composed of molecular clusters or domains rather than of individual molecules.[3,27,28] The size of such domains provides a larger than molecular length scale which grows with decreasing temperature and can provide a rationalization of the very slow relaxation observed as the temperature of a supercooled liquid is reduced toward T_g. In the supercooled liquid, these domains presumbly have a distribution of sizes (which corresponds to a distribution of relaxation times) and are arranged randomly. We believe that at some temperature, well below T_m, but sometimes well above T_g, these domains can themselves form a crystal, a state of matter sometimes known as a defect-ordered crystal,[29−33] such as those observed in Frank−Kasper phases and cholesteric blue phases.[29,30] Such a phase, in which the unit cells are themselves large collections of molecules, should be quite general and not too dependent upon the specific molecular characteristics of the material. We believe that the glacial phase may be such a defect-ordered crystal. If so, although glacial phases may be ubiquitous, we may still have been fortunate to find a supercooled liquid that formed such a phase in a finite time at a temperature in a range well above T_g and where crystallization did not intrude. Below we outline some theoretical justification for this picture.

The fact that the characteristic length scale, i.e., domain size, associated with the salient properties of supercooled liquids are larger than molecular, suggests that the supercooled liquid, as well as the glacial phase, might be described by a mesoscopic thermodynamic theory, in particular a critical theory. On the other hand, in contrast to usual critical behavior, there does not seem to be any critical point that can be approached arbitrarily closely; quite the contrary, it would seem that if there is an underlying critical point, it is inherently *inaccessible* for dynamic reasons or *avoided* for structural reasons. These concepts are intrinsic to many theories, theories that differ, among other features, on their placements of the critical point.

We follow a model[3] that envisages a *narrowly avoided critical point* at a temperature T^* near or slightly above the melting point T_m, a crossover temperature above which the liquid is molecular and below which it is collective, i.e., clustered into domains. The physical picture that we associate with this theory is one in which the preferred local structure could give rise to continuous crystallization at T^* were it not for the fact that it is not possible to tile space with this local structure; consequently, spatial extension of the preferred local structure is accompanied by geometric frustration (weak frustration in the case of fragile supercooled liquids) and increasing strain. Therefore, frustration aborts critical crystallization at T^*, and although the preferred local structure may extend somewhat, it will become more and more strained as it grows. Ultimately, the free energy increase due to strain overcomes the reduction obtained by extending the preferred local structure, and the system then breaks up into domains (*frustration-limited domains*) or forms defect-ordered phases.[32] If the critical point is truly "avoided", then at temperatures just below T^* it is the breakup into domains that takes place, and only at still lower temperatures, T_d, does the system crystallize into a defect-ordered phase. See Figure 1. In this picture, the supercooled liquid, with its high viscosity, is a system of randomly distributed domains whose behavior is determined by its proximity to the avoided critical point T^*, and not, as in some theories,[30,34] to its approach to the defect aligned transition at T_d, the latter very possibly being first order. We interpret our TPP data in this manner and associate the glacial phase with the defect-aligned phase. We know of no other theoretical model for the transition between low-temperature condensed, apparently amorphous, phases, let alone one that connects this phenomenon to the behavior of supercooled liquids.

The model outlined above has a theoretical base in that spin hamiltonians do exist in which weak, long-range frustration gives rise to avoided (not merely shifted) critical points with defect-ordered phases arising at distinct, lower temperatures T_d. (See ref 4 which discusses a frustrated spherical model.) Unfortunately no spin model with any obvious direct connection to the actual physical systems has as yet been solved; thus full quantitative comparison between theory and experiment is still not possible. However, it has been shown that merely with the postulate of a critical point narrowly avoided due to weak frustration (as in the frustrated spherical model), one can obtain a variety of physically significant results,[3] in particular, a very successful expression for the temperature dependence of the viscosity and relaxation times of supercooled liquids.[3,35]

It should be noted that the apparently amorphous glacial phase is structurally distinct from both the ordinary crystal and the glass and that whereas the glass exists only at temperatures below T_g, the glacial phase exists at temperatures above T_g. Furthermore, as understood by our model, the glass is "out-of-equilibrium", whereas the glacial phase is at equilibrium, in fact, it is a stabler state than the supercooled liquid itself. (Of course, as in all such thermodynamic equilibrium theories, the crystalline part of phase space is excised.)

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References and Notes

(1) Angell, C. A. *Science* **1995**, *276*, 1924.

(2) Angell, C. A. J. *Non-Cryst. Solids* **1991**, *131−133*, 13. This article gives a good summary of supercooled liquids including a discussion of "fragile" and "strong" liquids.

(3) Kivelson, D.; Kivelson, S. A.; Zhao, X.-L.; Nussimov, Z.; Tarjus, G. *Physica A* **1995**, *219*, 27.

(4) Chayes, L.; Emery, V. J.; Kivelson, S. A.; Nussinov, Z.; Tarjus, G. *Physica A*, in press.

(5) Cohen, I.; Zhao, X.-L.; Ha, A.; Lee, M.; Fischer, T.; Kivelson, D. *J. Phys. Chem*., submitted.

(6) Angell, C. A. *J. Phys. Chem.* **1993**, *97*, 6339.

(7) Speedy, R. J. *J. Phys. Chem.* **1992**, *96*, 2322.

(8) Angell, C. A.; Sare, E. J. *J. Chem. Phys.* **1970**, *52*, 1058.

(9) Mayer, E. J. *J. Phys. Chem.* **1983**, *89*, 3474.

(10) Mishima, D.; Calvert, L. E.; Whalley, E. *Nature* **1984**, *319*, 393.

(11) Johari, J. P.; Hallbrucker, A.; Mayer, E. *Nature* **1987**, *330*, 552. Hallbrucker, A.; Mayer, E.; Johari, G. P. *J. Phys. Chem.* **1989**, *93*, 4986. Johari, G. P.; Fleissner, G.; Hallbrucker, A.; Mayer, E. *J. Phys. Chem.* **1994**, *98*, 4719.

(12) Johari, G. P.; Astl, G.; Mayer, E. J. *J. Chem. Phys.* **1990**, *92*, 809.

(13) Burton, E. F.; Oliver, W. F. *Proc. R. Soc. London, A* **1935**, *153*, 166.

(14) MacFarlane, D. R.; Angell, C. A. *J. Phys. Chem.* **1984**, *88*, 759.

(15) Mishima, D.; Calvert, L. E.; Whalley, E. *Nature* **1985**, *314*, 76.

(16) Poole, P. H.; Essmann, U.; Sciortino, F.; Stanley, H. E. *Phys. Rev. E* **1993**, *48*, 4605, *Nature* **1992**, *360*, 324.

(17) Poole, P. H.; Grande, T.; Sciortino, F.; Stanley, H. E.; Angell, C. A. *Comput. Mater. Sci.* **1995**, *223*, 1.

(18) Aasland, A.; McMillan, P. F. *Nature* **1994**, *369*, 633.

(19) Spaepen, F.; Turnbull, D. *AIP Proc.* **1979**, *50*, 73.

(20) Thompson, M. O.; Galvin, G. J.; Mayer, J. W. *Phys. Rev. Lett.* **1984**, *52*, 2360.

(21) Bondot, P. *C. R. Hebd. Seanc. Acad, Sci., Paris B* **1969**, *268*, 933.

(22) Venkatesh, C. C.; Rice, S. A.; Bates, J. B. *J. Chem. Phys.* **1975**, *63*, 1065.

(23) Shao, J.; Angell, C. A., to be published.

(24) Fischer, E. W.; Meier, G.; Rabinau, T.; Patkowski, A.; Steffen, W.; Thonnes, W. *J. Non-Cryst. Solids* **1991**, *131−133*, 134.

(25) Fischer, E. W.; Becker, C.; Hagenah, J.-U.; Meier, G. *Prog. Colloid. Polym. Sci.* **1989**, *80*, 198. Gerhartz, B.; Meier, G.; Fischer, E. W. *J. Chem. Phys.* **1990**, *92*, 7110. Fischer, E. W. *Physica A* **1993**, *201*, 183. Patkowski, A.; Fischer, E. W.; Glaser, H.; Meier, G.; Nilgens, H.; Steffen, W. *Prog. Colloidal Polym. Sci.* **1993**, *91*, 35. Kanaya, T.; Patkowski, A.; Fischer, E. W.; Seils, J.; Glaser, H.; Kaji, K. *Acta Polym.* **1994**, *45*, 137.

(26) Kivelson, S. A.; Zhao, X.-L.; Kivelson, D.; Fischer, T.; Knobler, C. M. *J. Chem. Phys.* **1994**, *101*, 2391.

(27) For theories that depend upon structural collectivity, see, for example: Adam, G.; Gibbs, J. H. *J. Chem. Phys.* **1965**, *43*, 139. Anderson, P. W. In *Ill Condensed Matter*; Les Houches Lectures, 1978. Cohen, M. H.; Grest, G. S. *Phys. Rev. B* **1979**, *20*, 1077. Weber, T. A.; Stillinger, F. H. *Phys. Rev. B* **1987**, *36*, 7043. Sethna, J. P. *Europhys. Lett.* **1988**, *6*, 529. Wolynes, P. G. In *Proceedings of the International Symposium on Frontiers in Science*; AIP Conference proceedings No. 180; Chan, S. S., Debrunner, P. G., Eds.; 1988; p 39. Kirkpatrick, T. R.; Thirumulai, D.; Wolynes, P. G. *Phys. Rev. A* **1989**, *40*, 1045. Sethna, J. P.; Shore, J. D.; Huang, M. *Phys. Rev. B* **1991**, *44*, 4943. Mountain, R. D.; Thirumulai, D. *Phys. Rev. A* **1992**, *45*, R3380. Chamberlin, R. V. *Phys. Rev. B* **1993**, *48*, 15638.

(28) For a theory that depends exclusively on dynamical collectivity see: Götze, W. In *Liquids, Freezing and Glass Transition*; Hansen, J. P., Levesque, D., Zinn-Justin, Eds.; Elsevier: New York, 1991; p 287. These theories are strictly dynamical and do not depend upon structural collectivity.

(29) Kleman, M.; Sadoc, J. F. *J. Phys. (Paris) Lett.* **1979**, *40*, L569.

(30) Nelson, D. R. *Phys. Rev. Lett.* **1983**, *50*, 982; *Phys. Rev. B* **1983**, *28*, 5515.

(31) Sethna, J. P. *Phys. Rev. Lett. 51*, **1983**, 2198; *Phys. Rev. B* **1985**, *31*, 6278.

(32) Low, U.; Emery, V. J.; Fabricus, K.; Kivelson, S. A. *Phys. Rev. Lett.* **1994**, *72*, 1918.

(33) Wu, D.; Chandler, D.; Smit, B. *J. Phys. Chem.* **1992**, *96*, 4077.

(34) Sachdev, S. In *Bond Orientational Order in Condensed Matter Systems*; Standburg, K. J., Ed.; Springer-Verlag: New York, 1992.

(35) Kivelson, D.; Tarjus, G.; Zhao, X.-l.; Kivelson, S. A. *Phys. Rev. E.*, in press.

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