"DIFFUSION IN AMORPHOUS SOLIDS: SOME GENERAL FEATURES"

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Abstract

We examine the process of diffusion in amorphous media using a combination of computer simulation and experimental studies of glassy, molten, and polymeric media. The emphasis is on the understanding of how structural and interaction factors determine whether the ions of interest can diffuse independently of their neighbors (decoupled motion) or in concert with them and how this relationship is affected by changes of temperature relative to the glass transition temperature. Cases of diffusion of ions in molecular and ionic chain polymer systems are discussed. We identify an anharmonicity criterion for predicting the occurrence of observable diffusivity of a given species in the glassy state, and suggest experiments which probe site harmonicity characteristics as novel probes of such diffusion-related phenomena as the mixed alkali effect.
Introduction

Diffusion in amorphous solids is a phenomenon of very wide occurrence and importance, controlling such diverse processes as rehydration and germination of seeds, the loss of CO$_2$ from carbonated beverage plastic containers, the encoding of age in archaeological glasses, and the hardening of plastic car upholstery. It is of such frequent occurrence that it’s easy to overlook the fact that, viewed from the conventional liquid dynamics standpoint, it is a somewhat unexpected phenomenon. According to the Stokes-Einstein equation, which seems to hold very well for the majority of liquids and solutions, the frictional force impeding the motion of a particle $i$ of radius $r_i$ is accurately given by the viscosity of the liquid in which it moves. In this case the rigorous Einstein equation for diffusivity $D$

$$D = \frac{k_B T}{\zeta}$$

(1)

where $\zeta$ is the friction coefficient becomes the Stokes-Einstein equation

$$D_i = \frac{k_B T}{4\pi \eta r_i}$$

(2)

Argument has been focussed more on the question of whether the numerical factor $A$ should be 6 ("stick" boundary conditions) or 4 ("slip" boundary conditions), than on whether or not the use of the macroscopic viscosity in the equation is appropriate. While there has not yet developed any satisfactory molecular level explanation for the success of Eq.(2) (which was derived a macroscopic sphere moving steadily through a viscous fluid) the general feeling has become that the equation has broad validity. There is nothing in the theoretical literature on fluid dynamics to prepare one for the massive failure of Eq. 2 which is needed to explain the existence of measurable diffusion in brittle amorphous, i.e. glassy solids. Thus we devote an initial section of this paper to the need to recognize and understand the decoupling of motions of specific components of the original fluid (from which the amorphous solid formed) from the viscous (or modes during cooling to the glassy state).
Relation of diffusion in glasses to decoupling in liquids

In a glassforming liquid containing more than one diffusing species the diffusion coefficient of any particle which is constrained to move on the same timescale as the majority of other particles, must be less than $10^{-18}$ cm$^2$s$^{-1}$ in the glassy state. This can easily be demonstrated using Eq.(2) and the fact that viscosity changes by 15 orders of magnitude between normal temperatures where diffusivity is of order $10^{-5}$ cm$^2$s$^{-1}$ and the glass transition temperature $T_g$. We note that for molecular liquids like the classical glassformer glycerol, the Stokes-Einstein equation has been proven valid over the entire temperature range from near the boiling point to $T_g$, $(\eta(T_g) = 10^{12}$ Pa.s).$^{(1)}$ Since D values of $10^{-16}$ cm$^2$s$^{-1}$ are beyond the ability of most techniques to measure, the existence of easily measurable diffusion coefficients in many multi-component amorphous solids implies that some major breakdown in the simple laws of particle mobility in liquids must have occurred during cooling. Furthermore, since diffusion coefficients for different species have been measured in members of all the different classes of glassy materials ranging from molecular through metallic to ionic materials, it is clear that the breakdown of the simple liquid laws, for at least some types of particles, is a general phenomenon. The purpose of this short paper is to review the conditions under which such breakdowns occur, and to characterize the structure/energetic factors responsible in certain instances.

Decoupling of motions of particles in mixtures can occur in systems as simple as binary Leonard Jones systems. A recent study by Kob and Andersen$^{(2)}$ has shown that the smaller of two Leonard Jones particles in a mixture can exhibit a temperature dependance of diffusivity which is entirely different from that of the larger diameter component and that at least for a fraction of these particles, diffusion can continue freely in the configurationally arrested, or glassy state$^{(2)}$. Our own experience has been principally in systems with electrically charged particles, i.e. molten salts or glassforming quasi-network liquids such as the alkali silicates. Accordingly, we will use examples from systems to illustrate the decoupling and to discuss the magnitude of the resulting glassy state diffusivity of mobile species.

Ionic systems are particularly useful for illustrating the phenomenology of decoupled diffusional motion in solids because their motions can be followed simply and precisely by electrical conductivity studies. When
such decoupling occurs in glassforming ionic systems, the conductivity can become entirely determined by the mobile ion component since the difference in mobilities can become enormous, up to 14 orders of magnitude\(^{(3)}\). We therefore use conductivity data on glassforming ionic liquids to present the full range of decouplings which may be observed.

Fig. 1 shows the conductivities of a variety of ionic systems in which the conductivity (reflecting the mobile ion diffusion coefficient at the glass transition temperature) is seen to vary by 14 orders of magnitude. In order to make the decoupling behavior clearer, the data are replotted in Fig. 1b using a \(T_g\)-scaled temperature axis, so that the range of conductivities at the temperatures \(T_g\) - at which the structural relaxation time has a common value \(\sim 10^2\) sec - can be seen\(^{(3b)}\).

The pattern of behavior in these cases is clear and is believed by us to be general for decoupled processes in liquids and glasses. In the temperature range above the glass transition temperature the particle mobilities \(\mu_i\) of individual species \(i\) follow a non-Arrhenius expression conveniently approximated by the empirical Vogel-Fulcher equation

\[
\mu_i = \mu_0 \exp \left[ \Delta_i T_0/(T - T_0) \right].
\]  

in which the \(\Delta_i\) parameter is the parameter mainly responsible for the differences in mobilities. For the least mobile particles, \(\Delta_i\) is close to the value describing the fluidity of the solution, (fluidity = viscosity\(^{-1}\)) and is known as the "strength" parameter of the "strong/fragile" liquids classification\(^{(4)}\). \(\mu_i\) may be either an Einstein diffusive mobility, \(\mu_i = \xi^{-1} = D_i/k_BT\), or an ionic mobility related to equivalent ionic conductivity \(\lambda_i\) by \(\mu_i = \lambda_i/F\) where \(F\) is the Faraday.

Eq.(3) has been given various theoretical interpretations. Those given most attention have invoked the concepts of free volume control of mobility\(^{(5,6)}\) or alternatively configurational entropy control of mobility\(^{(7,8)}\). The latter has the advantage that it does not require the concept of negative free volume to explain diffusion in certain anomalous cases in which the glass transition temperature has a negative pressure dependence\(^{(9)}\) due to a decrease in expansivity above \(T_g\). It has been
Figure 1 (a) Arrhenius plots for ionic conductivity of glassforming systems in liquid and/or vitreous states. For vitreous cases only highest and lowest T data points are shown. The conductivity at 25° (sometimes obtained by extrapolation) is seen to vary by some twelve orders of magnitude. In a few cases, additional data have been obtained in the liquid state. They do not follow an Arrhenius Law. Dotted lines extrapolating low temperature data indicate that a pre-exponent of about \((10^{-2} - 10^{-3} \text{ } \Omega^{-1}\text{cm}^{-1})\) is common to both excellent and poor conductors. Note the proton conducting glass indicated by dashed line: plot appears Arrhenius but the Arrhenius law pre-exponent \(\sigma_0\) value is unphysical. Dot-dashed line at \(10^{-14} \text{ } \Omega^{-1}\text{cm}^{-1}\) is conductivity expected for glasses at their \(T_g\) according to classical solution law expectations.

Fig. 1(b) The same data with temperatures scaled by the glass transition temperatures, \(T_g\). Note the great spread of conductivity values at \(T_g\), where liquid viscosity has common value of \(~10^{12} \text{ Pa}.s\).
observed that in some cases Eq.(3) ceases to describe the temperature dependence before the glass transition is reached and the Arrhenius Law again applies, though with an unphysical pre-exponent. A modified version of free volume theory(6) accounts for such behavior.

In a multi-component system it is possible in principle to have as many \( \Delta_i \) parameters as there are components though, in Coulomb systems, correlations among the motions may force guest (minority) species to follow the host behavior.\(^{(10)}\) The departure from Arrhenius behavior is caused principally by the fact that above \( T_g \) the structure through which the particles are diffusing is different at each temperature due to the "liquid-like" expansion of the system. In most cases this leads to more open structures at higher temperatures. (In unusual cases like water and certain aqueous solutions, the liquid shrinks with increasing temperature). Below the glass transition temperature the structure is fixed, and so the mobility follows an Arrhenius law in the general case. The activation energy of this Arrhenius process is determined by the degree of decoupling of the particles at the glass transition temperature, and by the thermal history - e.g. the rate of passage through \( T_g \), or the amount of annealing which has been permitted after the initial vitrification. Annealing always increases the activation energy, the effect being smaller the smaller the activation energy, i.e. the more decoupled the diffusing species.

Structures responsible for decoupling in ionic systems

To appreciate the types of structures which lead to decoupling we quote three examples from computer simulations in which all details of the motion can be followed. These examples have been studied separately for different reasons,\(^{(11), (12)}\) but in fact they form a sequence in which we can see different stages in the depolymerization of what was originally a tetrahedrally coordinated polymeric structure. In this structure a Lewis acid (highly charged) species, e.g. \( \text{Si}^{4+} \) or \( \text{Al}^{3+} \), which is tetrahedrally coordinated, is being reacted with a Lewis base. The reaction leaves a mobile cation \( \text{Na}^+ \) or \( \text{Li}^+ \), (which was introduced with the Lewis base), free to migrate through the partly or wholly depolymerized structure.

In the first case\(^{(11)}\) the base is the oxide ion \( \text{O}^{2-} \) which is added to liquid silica, \( \text{SiO}_2 \), and the sodium ion is the decoupled species. In the second case\(^{(3)}\) the base being added is sulfide and the mobile species is lithium.
In this case the simulation has been carried out at a composition where the depolymerization is much more extensive than in the first case. Finally there is the third case (12) in which aluminum is the four-coordinated species and the depolymerization has been taken to the limit where every negatively charged species is an individual AlCl$_4^-$ anion. Again the mobile species is lithium, though in this case the decoupling is found to be much weaker than in the previous cases.

The results are depicted in two different manners. The first is a projection of the trajectories of the mobile species on to one side of the computational box in order that the manner in which the ion migrates can be appreciated, (see Fig. 2(a) and (b)). The second depiction is by the standard mean square displacement vs. time plot (which accumulates all the motions seen in Fig. 2(a) and (b)). From this plot the numerical diffusion coefficient may be determined via the relation

$$D = \lim_{t \to \infty} \frac{\langle \Delta r^2 \rangle}{6t} \quad (4)$$

Fig. 2(a) shows the trajectories of all the sodium ions in a standard sodium trisilicate system in which the temperature is fixed at a value, 1500K, where the system is a glass (on the computation time scale) insofar as the diffusivities of the silicon and oxygen species are zero within calculation error. Fig. 2(b) shows the trajectories of lithium ions under similar computation conditions in the system Li$_2$S-SiS$_2$ at the mole ratio 2Li$_2$S:SiS$_2$. Fig. 2(c) shows how the decoupled motions of the mobile species depicted in part (a) lead to a linear mean square displacement time plot for the mobile species (the case of the sodium disilicate studied at 1500 K). The decoupling in the case of LiAlCl$_4$ is only seen clearly by plotting the results of liquid state diffusivities over a range of temperatures in an Arrhenius plot for the liquid. These are shown in Fig. 2(d). If pure LiCl is studied the plot corresponding to Fig. 4(d) shows two parallel lines implying no decoupling at all.

All of these two component cases have in common the feature that the interaction between the lithium and the basic species, viz., Si-O$, S^-$, or Cl$^{(1/4-)}$ is weaker than the interaction between the basic species and the other positively charged entity in the simulation, Si$^{4+}$, Al$^{3+}$. This situation has the effect of simultaneously trapping the highly charged cation and detrapping the monovalent cation.
Figure 2 (a) Trajectories of all sodium ions in a sodium trisilicate glass projected onto one face of the cubic simulation box. Note how the sodium ions move in channels which are known to be formed by the non-bridging oxygens in the broken-down silica network.

(b) Trajectories of all lithium ions in the more dipolymerized case of Li₄Si₂S₇ glass. In this case, all network character has been removed and the system is more correctly viewed as a vitrified molten salt.

(c) Mean square displacement of Na⁺ and O²⁻ particles from points of origin in sodium-trisilicate glass at 1500K, showing decoupled motion of Na⁺ ions, through stationary O²⁻ anions.

(d) Mean square displacement vs. time plots for Li and Cl species in the liquid state of the fully dipolymerized system, LiAlCl₄ at 650K. The decoupling of the Li⁺ motion from that of the AlCl₄⁻ ions in this case is rather weak, and diffusion of the chloride can also be observed.

(e) Arrhenius plot of diffusivities of Li⁺ and Cl⁻ species in LiAlCl₄ melt, showing progressive decoupling of Li⁺ with decreasing T.
The conditions necessary for detrapping of a species, which we emphasize are the conditions essential for the measurement of diffusivity in glassy solids to be possible, are rather delicate since it is found that quite small changes can drastically affect the diffusivity of the species of interest. For instance, if only a second alkali cation, Cs+, is included in a sodium trisilicate glass then, at constant total alkali content, the mobility of the sodium ion decreases by almost 3 orders of magnitude (when measured at 400°C, ~150° below Tg). The decrease is much larger at lower temperature according to conductivity measurements. Nevertheless both cations remain mobile relative to their silicon and oxide ion neighbors.

Even greater changes in alkali ion mobilities in the glassy state may be observed if the balance of interactions is inverted. By this we mean making an alkali cation-to-anion interaction the strongest interaction in the system. To achieve this we must remove any highly charged cationic species. For instance if we pass from a system like LiAlCl4 (obtained by mixing LiCl and AlCl3) to a system like LiCl + KCl (or more extremely, lithium chloride + some tetraalkyl ammonium chloride in which the tetraalkyl ammonium cation is large and electrostatically non-competitive), then Li+ becomes the winner rather than the loser in the electrostatic tug-of-war, and the lithium ion motion becomes severely restricted. It is then able to move only when its environment moves so its diffusivity at the glass transition temperature must fall to the order 10^{-18} cm^2/s, and would not be measurable below Tg.

While this latter case has not yet been specifically studied in computer simulation "experiments", it may be illustrated by the electrical conductivity experiments performed on mixtures of lithium iodide and a trialkyl alkoxy ammonium iodide by Cooper and Angell. Their studies showed that the conductivity of the salt mixture at Tg, relative to that at Tg in highly decoupled cases (such as the system Li6Si2S7 illustrated in Fig. 2(b)) fell by some 10 orders of magnitude to reach the almost-insulating value of 10^{-12} Scm^{-1} at the glass transition. Thus the ability of a given particle to diffuse in a glassy medium is a delicate function of the interactions it experiences with its immediate environment and, in the case of cation diffusion in ionic systems, depends on the balance in the competition with the next nearest neighbor cations.
Diffusion in chain polymer systems

We can use the latter line of thought to discuss the case of diffusion of atomically small species in polymer systems, and to provide a contrast with the case of gas and plasticizer diffusion in polymers. Consider the small species Li$^+$ in a polyether chain polymer solvent. This is typical of the salt-in-polymer type of system which has been so actively researched in the past two decades for possible lithium battery electrolyte applications. Although the Li$^+$ species is smaller than any gas molecule, it turns out that it does not diffuse freely at all. In fact, in these systems the trapping of the alkali is even more complete than in the example cited in the previous section since the conductivity falls two decades below $10^{-14}$ Scm$^{-1}$ at the glass transition. Obviously the diffusivity in the glass would be unmeasurable and again this is because the lithium-to-polyether oxygen interaction is the strongest interaction in the system (except of course for the interaction between the in-chain atoms). This contrasts with the rapid diffusion of small gas molecules such as He, Ne in glassy chain polymer matrices. The latter diffuse quite readily, i.e. exhibit highly decoupled motion, because their interactions with the chain species are comparable to or weaker than those for the interchain interactions. Accordingly, diffusion coefficients have been easily and widely studied in polymer matrices particularly in the rubbery state above $T_g$ where even larger gas molecules such as CO$_2$ diffuse readily. Here the volume of the diffusing molecule relative to the volume of the chain atoms is the critical factor deciding the particle mobility and free volume theories have been usefully applied. For such small diffusing molecule volume, the Eq.(3) $\Delta_1$ parameter for the diffusing species would be small, the condition for decoupled motion.

Naturally it would be interesting from the electrolyte synthesist's point of view to design a chain polymer system containing Li$^+$, in which the Li motion would be decoupled as in the superionic conducting glass case but in which the system would remain rubbery at ambient temperature. A start in this direction can be made by reducing the cohesive energy of the silicate, phosphate or borate chain-type glasses (the formulae are Li$_2$SiO$_3$, LiPO$_3$, or LiBO$_2$) by reducing the Coulomb charge density. For instance Lucas and co-workers recently reported the neutral chain polymer BOF based on the $\text{B-[O-B]_n-O}$ chain in which there is an $\text{F}$ on every boron. Addition of LiF to this chain gives LiBOF$_2$ in which every $\text{B}$ is four-coordinated. Intermediate compositions are also possible.
We show in Fig. 3, the extent to which Li diffuses uncoupled from the remaining ions in this system. Unfortunately, the total cohesive energy is still rather high and its $T_g$ is therefore found above room temperature. For this reason it does not give the possibility of rubbery electrolytes, nevertheless it provides a starting point, and a contrast with the sodium trisilicate case of Fig. 2.

To illustrate the manner in which Li$^+$ executes its diffusion in this type of chain polymer system, we provide, in Fig. 4, a different type of trajectory plot in which several individual Li$^+$ cations are traced in their motion through the 3-dimensional box. One observes a rather long "flight" in the case of one of the Li ions, resulting in a displacement of several ionic diameters, while the others illustrated spend most of their time oscillating within a single trap. Such observations are not inconsistent with the Gaussian distribution functions which describe diffusional motion a given direction, but are helpful in visualizing as well as in characterizing the diffusion process in these media.

**Dynamical origin of decoupled motion**

In this final section we make some comments on the fundamental requirements for diffusion in a system in which the decoupled motion is a possibility. Any diffusion process requires that vibrational motions which are, at very low temperatures, randomized oscillations within

![Graph](image)

**Fig. 3** Mean square displacement vs. time curves for the more highly decoupled case of LiF-2BOF glass.
Fig. 4 3-D trajectory plots for a selection of ions in the LiF-2BOF glass showing different types of trajectories followed by the mobile ions.

harmonic wells, become not only anharmonic, but anharmonic to a degree which permits the passage of particles over barriers. The motion of a particle at the top of a barrier is of course that of an infinitely anharmonic vibrator. The onset of anharmonicity can be judged from the onset of an anomalous Debye-Waller factor.

The Debye-Waller factor is a short time measure of the mean square displacement of the particle from its point of origin, and under conditions of harmonic oscillations, is known to increase linearly with temperature. It is a quantity which is easily evaluated from computer simulations of small systems. The "anomalous" Debye-Waller factor refers to the behavior at higher temperatures where the value of $<r^2>$ increases superlinearly, i.e. more rapidly than expected for a harmonic system. The source of the anomalous behavior is a subject of current discussion and controversy$^{(21-23)}$ but at least part of it is assignable to the onset of strong anharmonic character in the vibrations. Fortunately it can be simply investigated by computer simulation, as it is in neutron scattering.
or in Mössbauer spectroscopy, by a plot of the mean square displacement of the particles as a function of increasing temperature. The onset of anharmonicity is, obviously, detected by a departure from linearity in the $\langle r^2 \rangle$ vs. $T$ plot.

To illustrate this behavior, we again take the classical case of sodium trisilicate glass, and plot in Fig. 5 the mean square displacements of Na$^+$ and O$^{2-}$ particles vs. $T$ in the range 0-800K in which no long range diffusion such as seen in Fig. 2(c) or Fig. 3 occurs on the computation time scale i.e. up to 100 ps. For the Na$^+$ species, we note the onset of departures from harmonic (linear) behavior above about 300K. This is close to the temperature at which internal friction losses on time scales of seconds due to Na$^+$ jumping, are detected by torsion pendulum techniques.(24) The diffusion coefficient of Na$^+$ at this temperature would be about $10^{-12}$ cm$^2$sec$^{-1}$ according to extrapolation of data from higher temperatures.(13-15)

![Graph showing $\langle r^2 \rangle$ vs. temperature for sodium trisilicate glass, Na$_2$O-3SiO$_2$, showing onset of anomalous Debye-Waller Factor at about 350K. This is comparable to the temperature ~250K at which a mechanical relaxation peak due to sodium ion jumping is observed in 0.4 Hz torsion pendulum studies of this system (see ref. 24). Insert shows values of diffusivity measured at higher temperatures. It is seen that diffusivity becomes unmeasurably small by computer simulation at temperatures 3 times higher than that of anharmonicity onset.]

Fig. 5: Pre-diffusion mean square displacement vs. temperature for sodium trisilicate glass, Na$_2$O-3SiO$_2$, showing onset of anomalous Debye-Waller Factor at about 350K. This is comparable to the temperature ~250K at which a mechanical relaxation peak due to sodium ion jumping is observed in 0.4 Hz torsion pendulum studies of this system (see ref. 24). Insert shows values of diffusivity measured at higher temperatures. It is seen that diffusivity becomes unmeasurably small by computer simulation at temperatures 3 times higher than that of anharmonicity onset.
It is obvious from Fig. 5 that the sodium ion motions become anharmonic at a much lower temperature than do those of the oxygen particles. A comparable onset of anomalous $<r^2>$ vs. $T$ for oxygen only sets in at the glass transition temperature at ~700K, indeed we are currently reporting an interpretation of the glass transition phenomenon in these terms.(25) This then provides a criterion for decoupled diffusive motion in glassy solids: the vibrational motions of the mobile subset of particles must become strongly anharmonic while those of the remainder remain harmonic. While this in turn must reflect the relatively flat potentials at the sites in which the mobile particles reside, it provides a quantitatively characterizable observable which predicts the onset of diffusion with D values of ~10^{-18} cm-s^{-1}. From this the approximate diffusivity at any other temperature could be obtained by use of the Arrhenius Law with a pre-exponent of 10^{-3} cm^2 sec^{-1}. We are unaware of any studies of anomalous Debye-Waller factors for mobile ions in glasses, though this should be achievable for ions with favorable scattering cross sections, and should be straightforward for protonic fast-ion conductors of which two examples were provided in Fig. 1. It would be interesting to see how such phenomena as the mixed alkali effect show up in the anomalous Debye-Waller factor.

Concluding Remarks

We have discussed diffusivity in amorphous solids in terms of interaction and trapping effects which modulate the extent to which individual species translational motions may be decoupled from those of the host matrix. Finally we have linked those phenomena to the nature of the potential well in which the microscopic rattling motions occur and identified a key characteristic of that site, viz. the temperature at which the particle motions in the well begin to explore the anharmonic part of the potential. We have suggested that it is at this temperature that diffusivity becomes possible at a level of about one escape per $10^{15}$ attempts ($\sim$10^{-13} cm^2 s^{-1}) and that the temperature can be identified via (short time scale) measurement of the anomalous Debye-Waller factor, or related probes of anharmonicity such as vibrational phonon echo studies.(26) Such phenomena as the mixed alkali effect should therefore be investigated through studies of the effect of a second alkali on the anomalous Debye-Waller factor for the first, and then interpretable directly in terms of changes in site harmonicity due to changes in the second nearest neighbor.
Acknowledgments

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