Molecular Dynamics Simulations of Silicate Glasses and Melts

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Abstract

The application of molecular dynamics to the modelling of silicate glasses and melts is reviewed. Several examples are used to illustrate the value of these computer simulations in advancing our understanding of the structure of polycomponent silicate glasses.   In addition to structure, transport properties, in particular alkali ion migration, emerge naturally from the simulations.   It becomes possible to relate transport properties to structure.   The mixed alkali effect is explained in terms of structural variations in going from single alkali to mixed alkali glasses that lead to distinct environments for each type of alkali ion and also result in the smaller alkali ion becoming more tightly bound to the network.   Some recent results on the structure of silicate melts are presented and the relationship between the structures of glass and melt is discussed.

Introduction

Glasses and melts are of considerable importance to a wide range of technologies, as diverse as fibre optics and traditional container glass, and also to mineralogists because of the role they play in mantle processes [1].   They also attract the attention of metallurgists because of their occurrence in refining processes.   The main differences lie in the details of the compositions of the glasses and melts.   Because the high temperatures of the melts were not easily accessible experimentally, until recently one looked to the lower temperature solid state material for insight into the way the melt would behave.   Glasses are thus not only of intrinsic interest.

However, the application of traditional structural analysis tools to glassy materials is somewhat more difficult than for crystalline materials, leading to incentives to develop other ways of probing the structure of non-crystalline solids.   In this presentation, we will discuss the application of molecular dynamics (MD) to the structure of silicate, and related, glasses.   Some aspects of the simulations of melts will also be presented.

Molecular Dynamics

Molecular dynamics (MD) is a computational approach to modelling of solids, which includes the effects of both temperature and time. It has been used with some considerable success to probe the structures and the dynamics of ion migration in glasses.

In the present context, the objectives of molecular dynamics may be defined as providing an atomic scale picture of the structure of glasses, an understanding of composition- (atomic) structure relationships, and an insight into the atomic migration mechanisms that operate in the glasses. Since these latter will be determined by the structure, one may also infer how compositional changes will affect the transport of ions in the glasses.

The principle of MD is simple: the evolution of an ensemble of atoms is followed as a function of time. The positions and velocities of each of the atoms in the simulation are determined from classical mechanics, using Newton s second law and forces (acting on each atom) that are obtained from an interatomic potential model. Usually, the Born model of the solid is used: atoms are treated as point charges with short-range forces acting on them.
The equations of motion are solved in an iterative process: the positions and velocities are updated in small increments of time, known as timesteps. Each timestep corresponds to a Δt of the order of 10^{-15} s. The structure of the glass is obtained by averaging over a large number of timesteps, of the order of thousands.

There are some technical issues that complicate the apparently simplicity of MD simulations. The most important one concerns the interatomic potential model, on which rests the validity of the simulation. A variety of means of determining the potentials is possible; a detailed discussion is outside the scope of this paper. In our work, the potential model is imported from other, crystalline, systems. These are usually the binary oxides, which comprise the components of the glass. This assumes that the potentials are transferable; although this is an approximation, experience suggests that it is an acceptable one; however, more detailed studies may require more accurate potentials. Given that ion polarisability is not included in most models used in MD simulations, the limitations in transferring potentials are probably not, in themselves, that severe.

One consequence of the limited accuracy of the potential model concerns the Boltzmann relation between energy and temperature: $\Delta E = k_b \Delta T$. In this case, uncertainty in the energy of the simulation leads to an uncertainty in the absolute temperature of the simulation. Unfortunately, relatively small errors or uncertainties in energy result in large uncertainties in the absolute temperature: $0.025 eV = 300 k_b$. Quantitative temperature dependencies thus may not be possible.

Two other facets of the simulation govern the effective temperature of the simulation. The first relates to the size of the simulation, which is relatively small. Simulation boxes typically contain around 1600 atoms, although they may range from a low of around 400 to 10,000 or more. Only the available computational resources limit the size: Vashista and colleagues [2] have run simulations containing more than1 million atoms, for example.

The temperature of the simulation is affected by the ability of the atoms in the simulation box to reach their equilibrium configuration. If equilibrium cannot be achieved then the fictive temperature will be higher. The periodic boundary conditions used to create an infinite solid also prevent the structure from reaching complete equilibrium, because of

the need for structural coherence across the boundaries. Larger simulation sizes would seem to be the way around this limitation, but it is not yet completely clear how the effective temperature depends on the size of the simulation. One consequence of larger simulation sizes would appear to be the need for longer simulation runs, but again information on this topic is scant.

The second aspect of the simulation which influences the effective temperature concerns glass formation procedures, that is, how the glass is created in the computer. The key property here is the so-called cooling rate , that is how the thermal energy is removed from the glass. Many procedures, which involve taking a simulation from a high temperature, in which the system is in a molten, highly disordered, state to a temperature below the glass transition temperature, do so in stages. Others adopt a nominally continuous procedure. However, even in the case of very slow rates of cooling, only nominal rates of 1K/ps can be practically achieved. These are considerably faster than actual physical rates experienced in the laboratory (or the field). However, there are questions whether the direct comparison between the simulated and physical cooling rates is appropriate. One reason for this is the fact that the simulations are on an infinite solid, which is effectively superheated (on melting) and supercooled on forming the glass. Notwithstanding this issue, the effect of different cooling rates on the simulated structure of silica has been examined by Vollmeyr et al. [3], as well as the present author s group. Small differences in structures obtained with the different cooling rates were observed. However, how these differences relate to differences in density was not clearly established.

Basic Glass Properties

Glass properties may be divided into two aspects, structural and transport-related. One of the roles of MD is to relate the microscopic properties resulting from the simulations to the macroscopic properties that are accessed experimentally. Points of contact between theory and experiment provide a means of validating the simulations so that one has some confidence in the additional details available from the simulations.

Probably the most important aspect of the structure of glass is the spatial distribution of different chemical species. This can be seen directly in the simulated structures. A related property is the tetrahedral ring size distribution; although this cannot be measured directly, it provides a different way of characterising the glass structure, as will be seen later. The Q_n distribution, that is, how the non-bridging oxygens are distributed, may be probed by solid state NMR techniques [4]. Also of interest is the co-ordination number, especially of the network modifying ions.

The macroscopic description of the structure is embodied in the radial distribution functions. The most popular way of measuring them nowadays is neutron scattering [5]. From the scattered intensity, the total distribution function, T(r), is obtained. T(r) is also the sum of the individual pair distribution functions. If the experimental T(r) could be deconvoluted into the individual pdfs, then we would have a reasonably detailed idea of the structure of the glass. Unfortunately, this cannot be done, for a couple of reasons.

Firstly, the scattering intensity is isotropic and so T(r) is one dimensional. Secondly, measurements may only be made over a finite region of reciprocal space, thus broadening the experimental peaks and making deconvolution even harder. On the other hand, the pdfs are available from the simulations, so T(r) can be calculated. Concordance between measured and calculated T(r) implies that the simulated structure reflects the details of the actual glass structure. One should bear in mind, however, that there may not be a unique structure giving rise to a particular T(r). How well the current models reproduce the measured T(r) may be gauged from figure 1 which compares, for vitreous silica, the latest data of Wright with T(r) calculated from a simulation by Yuan and Cormack, using a slightly modified BKS potential. The Wright reliability index [6] is 8%, which is amongst the lowest obtained so far.

Ion transport processes underlie a number of technologically important properties, such as chemical durability. Probably the most interesting aspect involving ion transport is one that has engaged the attention of virtually all glass scientists (and others) at some time or another, namely the Mixed Alkali Effect. This is a topic to which we shall return later.

In the next section, we will review some of the details of the structure of glasses that have emerged from the simulations.

Silicate glass structures: what does the computer tell us?

There have been a number of proposals for the structure of glasses, the most widely accepted being based on Zachariasen s random network model for silica. Whilst Zachariasen s model is generally accepted for silica (and vitreous B_2O_3), how the picture changes when the network is disrupted by the addition of network modifiers, such as alkali or alkaline earth ions, is not so clear. On the one hand, one might postulate that the alkalis would be randomly, but homogeneously, distributed throughout the glass, along with their associated non-bridging oxygen ions [7]. On the other hand, however, is the suggestion that the alkalis (and NBO) are spatially aggregated, so that NBO ions are shared between more than one alkali ion, since this occurs in comparable crystalline compounds. This picture is represented by the Modified Random Network Model proposed by Greaves [8], and depicted in Figure 2. We note, however, that many importance slag compositions are much poorer in silica than those encountered in traditional glass science and engineering. Slag structures may thus be better described in other terms.

MD simulations, by us, as well as others, indicate that alkali silicates have a Modified Random Network like structure, rather than being described by a simple extension to Zachariasen s model. The simulations show that the alkalis and NBO are spatially segregated, forming alkali/NBO rich regions. An example of this is given in figure 3, for a 5mol%Li_2O•95mol%SiO_2 glass. Increasing the amount of alkali generally causes the alkali/NBO rich regions to get larger. At the kind of alkali loadings used commercially, however, the simple picture is hard to visualise, because the sizes of the alkali-rich and silica rich regions must be rather small. Yuan [9] has developed a way to estimate the

sizes of these regions, which turn out to be of the order of 10-15 , similar in magnitude to the anionic cages proposed for the structure of silicate melts by Bokris and colleagues [10] thirty years ago.   Tetrahedral ring-size distribution calculations also indicate that there are silica rich regions in alkali silicates.   Figure 4 shows that as Na_2O is added, the peak representing the distribution in silica decrease, but does not disappear completely. The larger sized rings are those associated with the sodium ions, which have broken up the original silica network.

Now, it is known that the addition of Al reduces the number of NBO in the structure, for the same reasons that NBO are created by alkali addition (as long as the Al acts as a network former, of course).   The work of Cao [11] indicates that the addition of Al promotes a Zachariasen like structure: Al prefers Q_4 sites and thus causes a redistribution of the alkali ions. The prediction that Al will occupy Q_4 sites is now being confirmed by O^{17} solid state NMR studies [12].   As the amount of Al increases, so that the ratio of Al to alkali approaches unity, the number of NBO decreases, reaching zero at that ratio. Further addition of Al must lead to a change in co-ordination.   Although there has been some suggestion that the Al moves into octahedral sites, this has not been observed in the simulations.   Instead, some of the oxygens become three fold co-ordinated, resulting in a change to the network topology.   These tri-clusters have been invoked to account for viscosity changes in alumino-silicate melts of geological significance.

The addition of Al leads to a re-polymerising of the tetrahedral network structure, making a Zachariasen picture more appropriate.   LaCourse [13] has introduced the term transitional structures to describe the structures of those compositions for which small changes in composition result in large changes in properties.   Many commercial glass compositions behave this way, and it is thought that the small compositional changes cause a (significant) change from a modified random network to a Zachariasen like network.

The Mixed Alkali Effect

The mixed alkali effect (MAE) was first observed about a hundred years ago, but, in spite of a great deal of attention, has still no commonly accepted explanation, even of its most basic aspects.   Most suggestions which have been put forward invoke an interaction, usually (but not always) between the two different alkali species, which would be absent in the single alkali glasses.   There is often an energy associated with this interaction. However, different theories generally propose different kinds of interaction.

The general feature of the effect, sometimes also known as the Mixed Mobile Ion Effect, since it is not confined exclusively to alkali ions, but also occurs in systems with non-alkali modifiers (e.g. silver), is as follows.   In an alkali containing glass, if some of the alkali is replaced by a different alkali species, then the diffusion coefficients of both species are lowered from the single alkali composition.   This is nicely illustrated by the data of Lapp and Shelby [14] in figure 5.

A remarkable feature of the MAE is its non-linear behaviour. The change in diffusion coefficients, or related property such as ionic conductivity, is highly non-linear, and can be several orders of magnitude. In the alkali silicates, the addition of aluminium also has a marked influence. The deviation from additivity (Vegard s Law) is greater in systems containing Al, and increases with increasing Al content, as shown in figure 5.

The MAE offers an excellent example of a compositionally dependent phenomenon. Not only is there the change in alkali ratio, but there is also the aluminium dependence. Since the transport of alkali ions (or other mobile ions, or, indeed, other modifiers) is ultimately governed by the structure of the glass, a simulated structure, which reproduces the mixed alkali effect, must contain the essential factors underlying the effect.   The challenge for computer simulations is to reproduce these compositional dependencies.

The first simulations to show the mixed alkali effect were those of Huang [15], who also found that there were small, but significant, differences between the alkali ion sites in the single and mixed alkali glasses. Subsequent studies by Balasubramanian. and Rao [16] and Smith et al. [17] also reproduced the effect. Figure 6 shows the deviation from additivity calculated by Cormack and Cao [18] for $R_2O.3SiO_2$ and $R_2O.Al_2O3.2SiO_2$ glasses. They also found that the effect was greater in the alumino-silicates.

What structural features may be identified as underlying the effect?   Figure 7 shows the alkali-oxygen pair distribution functions from Na/Li silicate and alumino-silicate glasses. It is observed that the alkali ions retain very similar environments in both single and mixed alkali glasses.   Broadly speaking, this means that in the mixed alkali systems, a set of sites becomes inaccessible to one of the alkali species, since the sites occupied by the smaller ions will not be large enough for the larger alkali species.   On the other hand, the larger ion sites are not energetically attractive to the smaller ion, a phenomenon familiar to crystal chemists as the no-rattling rule. Ion migration will largely be confined to a subset of the total available alkali ion sites in the glass.   This is illustrated in Figure 8, which shows the dynamic alkali-alkali pair distribution function. This function is basically a measure of how often an ion jumps from a site of one character to a site of the same, or different, character. The figure clearly shows that alkali ions will predominantly jump to sites of the same character: jumps between different ion sites are very rare.   Thus Li-Li jumps are much more common than Li-Na jumps. Balasubramanian. and Rao reported a similar observation.

At the same time, however, the co-ordination of the alkali ions differs slightly in the mixed alkali systems, compared to those in the single alkali glasses.   This is manifested in a change in average site potential.   The site potential (similar, say, to the Madelung site potential in crystals) for the smaller ion decreases, in a non-linear manner, as the concentration of the larger ion increases.   In mixed alkali silicates, the site potential of the larger species increase slightly, but at a slower rate than the decrease in the site potential of the smaller species.   In the alumino-silicates, the site potential of both alkali species decreases.   The effect of the decrease in site potential is to increase the activation energy of migration: the alkali ions are more tightly bound to the silicate network.

These observations can be related to ion — ion interactions, which are a common feature of many theories of the mixed alkali effect. In the present case, the interactions are between the different kinds of alkali ions, and are mediated through the oxygen ions in the network. The excess interaction energy may be expressed as

$$\varepsilon_{int} = \varepsilon_{ab} - (\varepsilon_{aa} + \varepsilon_{bb})/2,$$

where ε_{ij} is the energy of the interaction between i and j.

The site potential may be used to relate the structural and energetic aspects of the interaction. We may write

$$\varepsilon_{int} = (V_a - V'_a + V_b - V'_b)/2,$$

where V_i and V'_i are the site potentials of species i in the single and mixed alkali glasses, respectively. The values for the interaction energy obtained in this way compare well with those extracted from experimental data, as may be seen from the table.

glass	ε_{int} (eV)
experimental: Ag: $Na_2O.4SiO_2$ (Inman et al.)	-0.063
calculated: $(Na,K)_2O.3SiO_2$	-0.021
calculated: $(Na,Li)_2O.3SiO_2$	-0.075
calculated: $(Na,Li)_2O.Al_2O_3.2SiO_2$	-0.181

The interaction between the different alkali species may be understood in terms of how the tetrahedral network packs around the alkalis. In a single alkali silicate, all of the alkalis compete equally for the attention of the network oxgyens, resulting in a particular distribution of alkali-oxgyen bond lengths. In the mixed alkali glass, the two different species compete differently for the framework oxygens, because their field strengths are not the same (their radii are different). The packing of the coordinating oxygens around the alkalis becomes more efficient, especially for the smaller species. The alkali-oxygen bond length distribution narrows, and the site potential becomes more negative. The interaction, which may be considered an alkali-alkali interaction, nevertheless involves ions in the tetrahedral framework and is really an indirect sort of interaction.

Diffusion processes

The mechanisms by which the alkali ions migrate in the glass structure may be seen in the simulations. The mechanisms are, by and large, correlated, jump and reside mechanisms, similar to those found in crystalline materials, rather than fluid-like motion. The correlations are apparent in the observation that the alkali ions predominantly jump into sites which were previously occupied by other alkali ions. Single ion processes, such as simple vacancy or interstitial mechanisms were not frequently observed, but presumably must occur. The mixed alkali glass simulations also suggest that ions jump between well-defined sites, in that case between sites of a similar character. The alkalis are found to migrate predominantly within NBO rich regions in the structure.

Recent work of Park and Cormack [19], from analyses of mixed Li-K silicates, have described jump mechanisms which have a number of features in common with atomic jump processes in crystalline materials.

In one mechanism involving potassium ions (shown in Figure 9), one cation was seen to jump into an adjacent, neighbouring site, displacing the K ion from that site.   The displaced cation jumped into a vacant position, and the site from which the first cation moved became vacant.   The neighbouring sites were found to share co-ordinating oxygen ions.   This is essentially a vacancy mechanism, although the sites are not as ordered as in crystalline materials.   The unusual feature of this mechanism is that it involves the co-operative migration of two cations, so that the net displacement of the vacancy is more than a single K — K distance, in contrast to that expected for a vacancy jump in a crystal. We note, however, that in some fast-ion conductors, similar co-operative motions of ions have been observed.

In the same simulations, the direct exchange of two Li ions was observed (see figure 10). Again, it was found that the Li ion sites shared co-ordinating oxygen ions, just as they would in a crystalline structure. Direct exchange mechanisms are not commonly reported in oxide systems, but are considered to be important mechanisms for diffusion in metals.

Silicate Melts

There has not been much work on the atomic structure of silicate melts.   However, the higher temperature of the melts should, in fact, provide for more accurate simulations. This is because the relaxations leading to thermal equilibration are easier at these temperatures, and the stereochemical constraints of the periodic boundary conditions ought to be absent, or at least much less pronounced.

Figure 11 compares $T(r)$ of a $30mol\%Na_2O.70mol\%SiO_2$, calculated at 1700K and 300K. As expected, the peaks in the melt $T(r)$ are broadened because of the additional thermal motions at that temperature.   Although not much detailed structural information can be obtained directly from the $T(r)$, it does appear that the melt retains a substantial degree of the structural features seen in the glass: The SiO_4 tetrahedra are clearly still present.   On the other hand, the ring size distribution is somewhat more revealing.   It, too, suggests that there are features common to both the glass and the melt, in addition to the tetrahedra.   In particular, the peaks that represent the smaller-sized rings typical of silica-like structural units are very similar in both distributions.
   This implies that the concept of the MRN model may also be extended to include melt structures, an idea that is consistent with the proposal of Bokris and colleagues.   More than forty years ago, they suggested that there were, in the melts, anionic cages which were small aggregates of SiO_4 tetrahedra.   These would correspond to the silica-rich regions of the MRN model.

Note that both $T(r)$ and the ring size distribution are really time-averaged properties, and do not reflect the significantly different dynamical behaviour experienced by the melt.

Thus one may expect that oxygen ions may switch between bridging and non-bridging character on a fairly rapid timescale. There have been indications of this from NMR experiments, but more work needs to be done in this respect.

Summary and conclusions

We have endeavoured to illustrate the usefulness of molecular dynamics simulations in probing the structure of silicate glasses and, to a lesser extent, melts. In addition, atomic migration mechanisms, which are controlled by the atomic structure, may also be examined. The technique is not confined to silicates, however; any inorganic system for which a suitable interatomic potential model can be found, is amenable to this approach.

Acknowedgements

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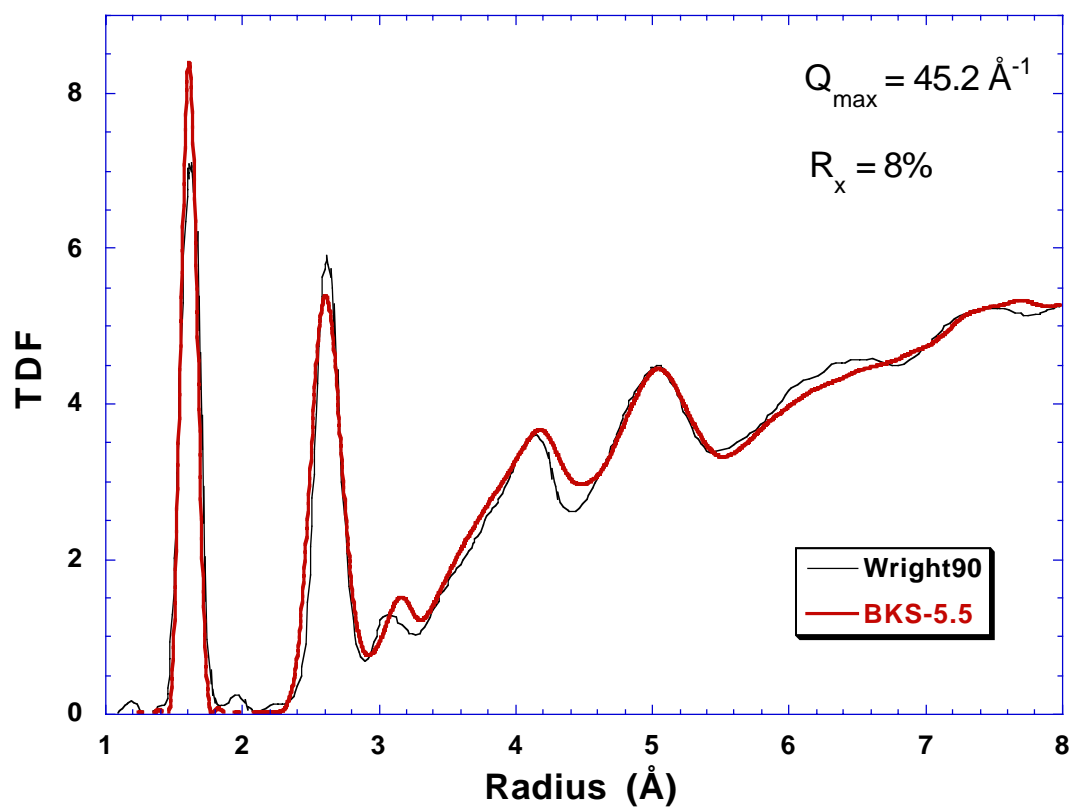19. B. Park and A.N. Cormack, J. Non-Cryst. Solids, (1999) in press.

Figure 1. Comparison between experimental and calculated T(r) for vitreous silica.
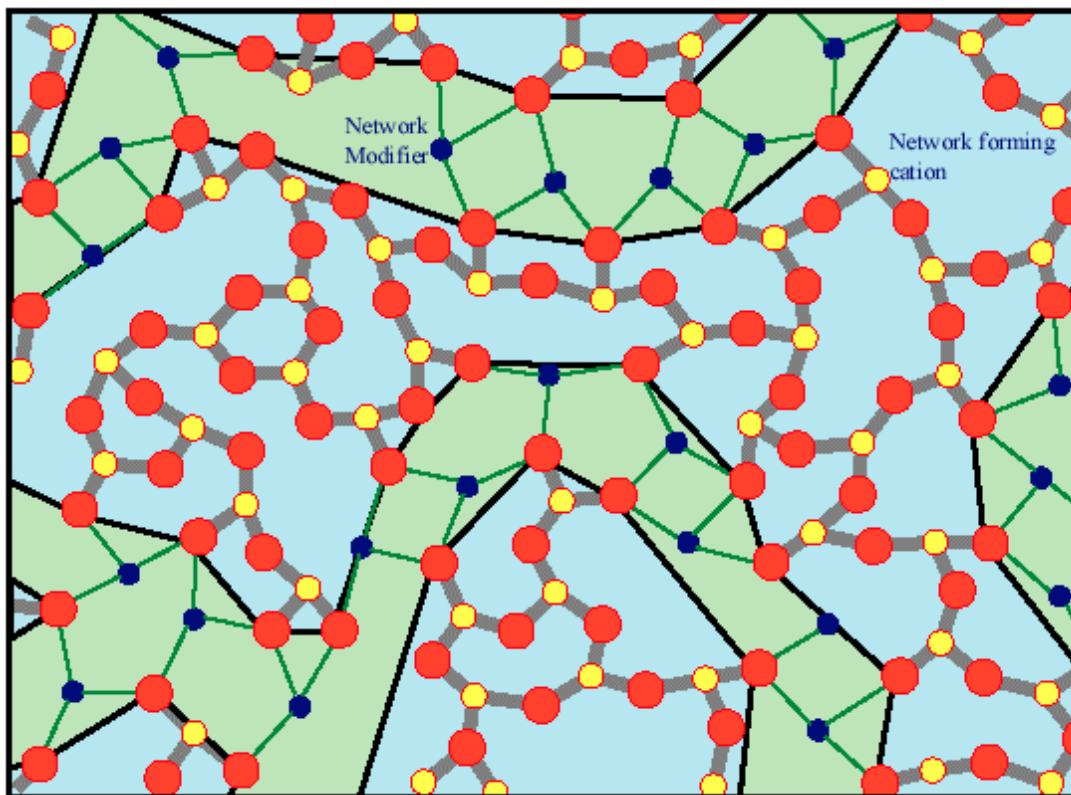
Figure 2. Schematic representation of the Modified Random Network Model of glass structure. (After Greaves [9])
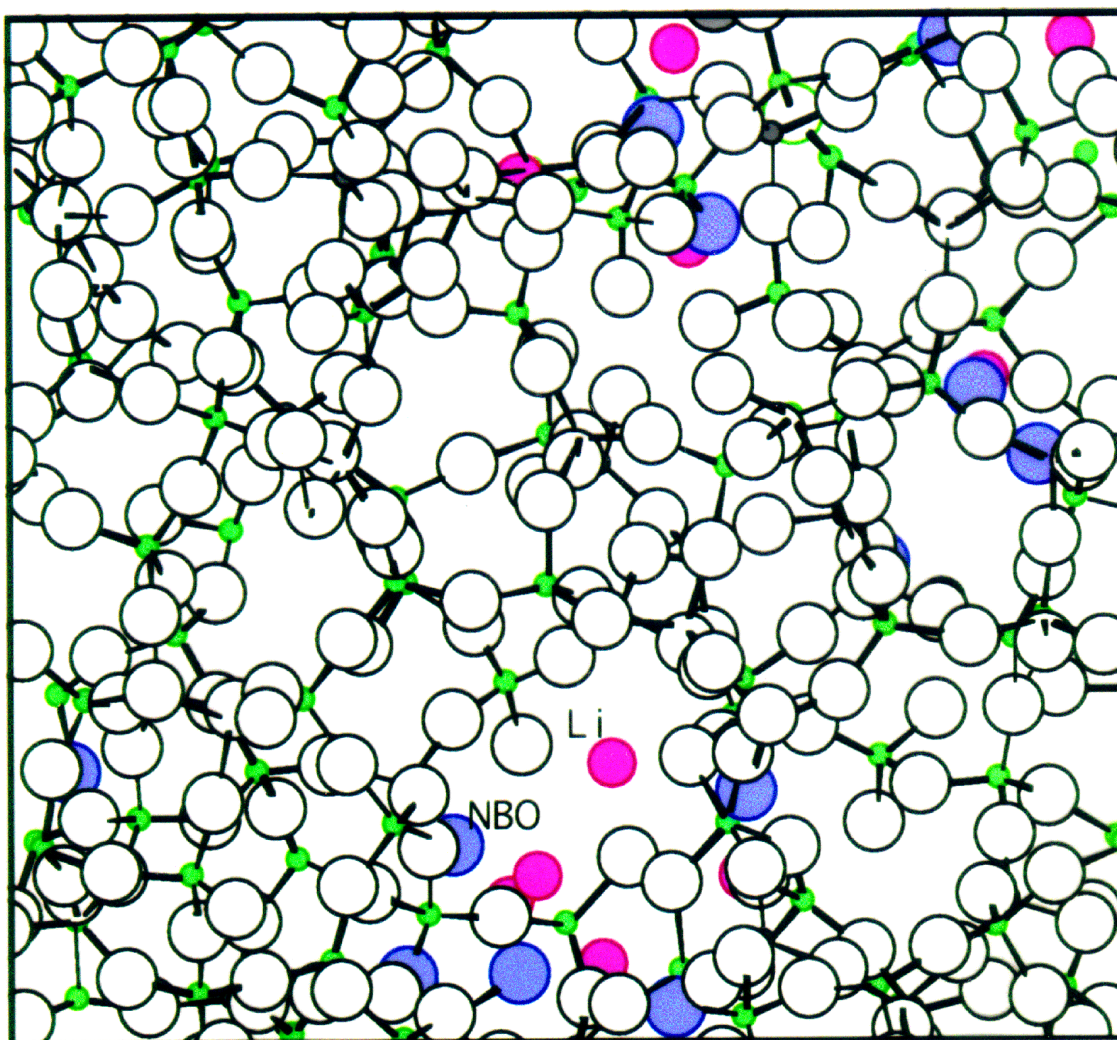
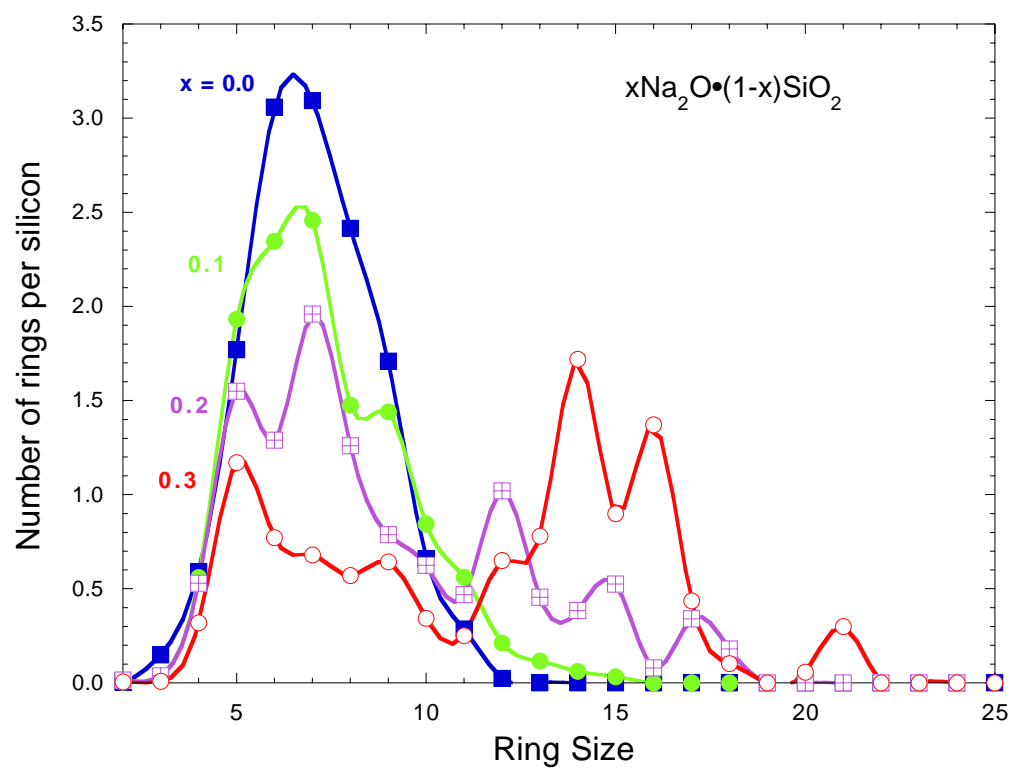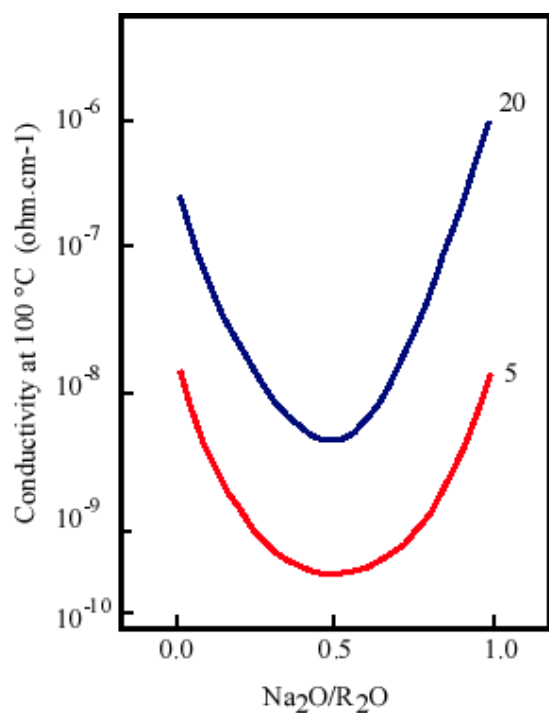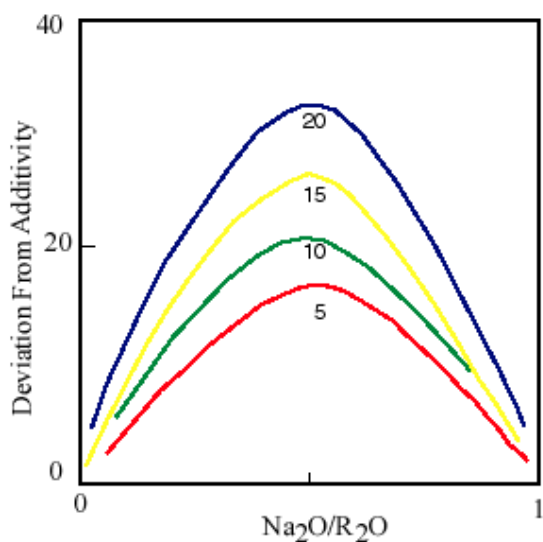Figure 3.   Segregation of Li and NBO in a silicate glass containing 5mol% lithia.

Figure 4.   Tetrahedral ring size distribution in sodium silicate glasses.

The deviation from additivity increases with increasing alumina content.

Electrical Conductivity for samples

Figure 5. Experimental data on Li/Na aluminosilicates, from Lapp and Shelby [15].
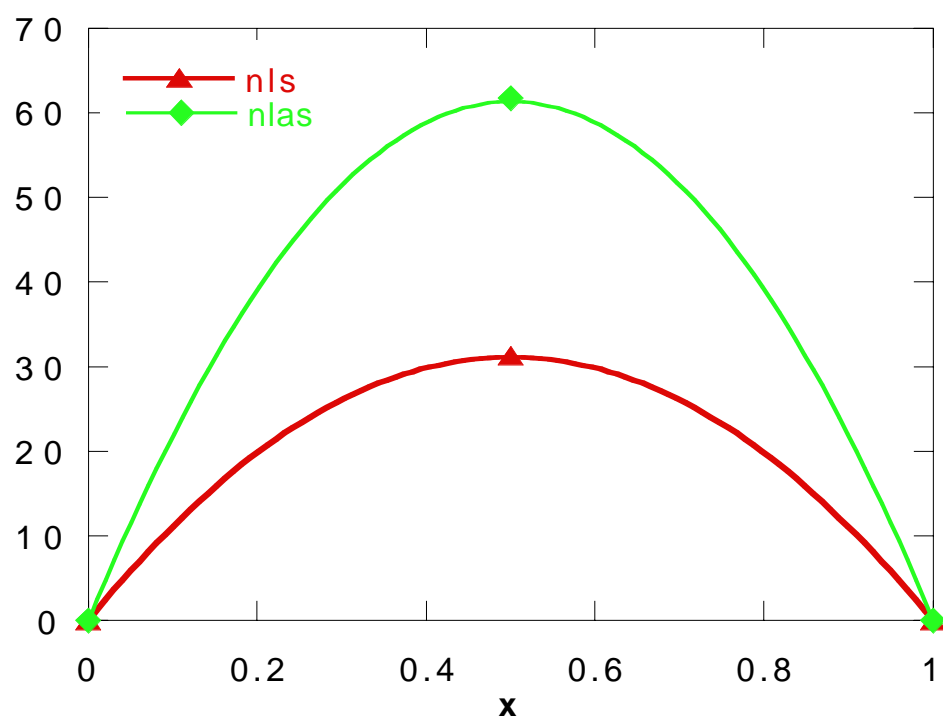
Figure 6.   Calculated deviation from additivity for mixed alkali silicates and alumino-silicate glasses (from Cao and Cormack).
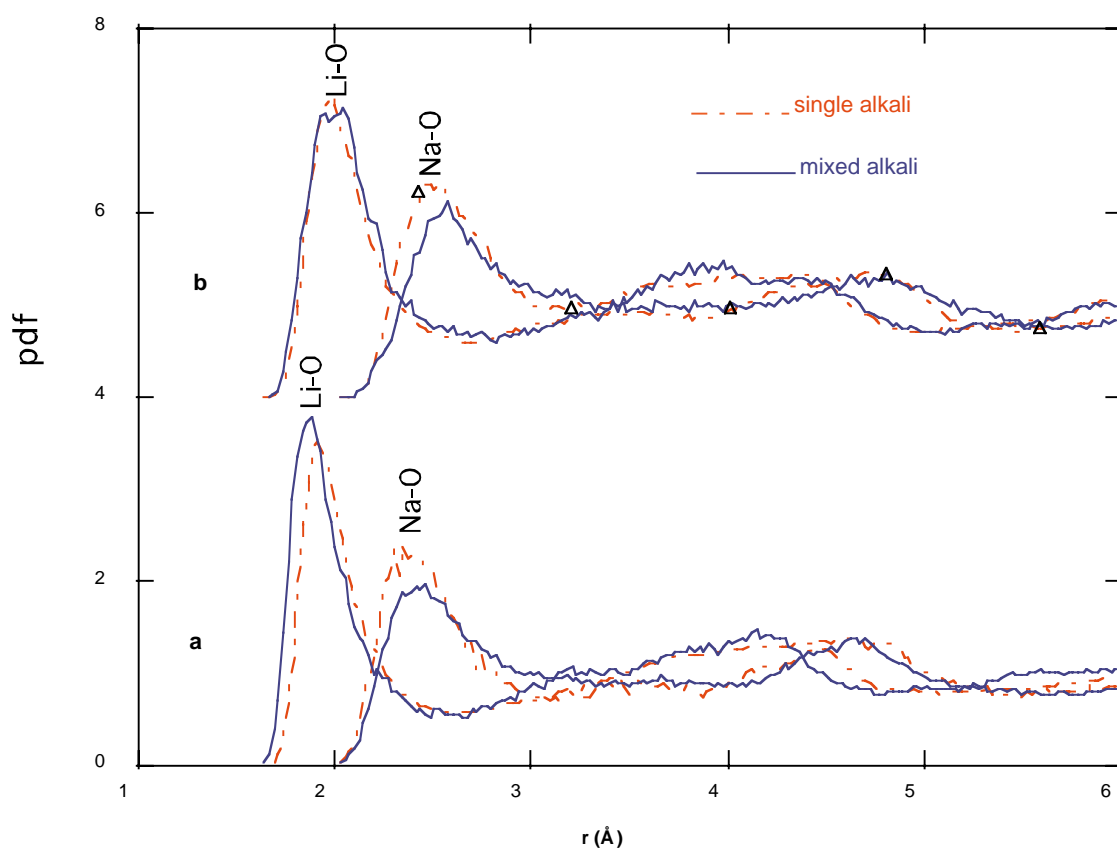
Figure 7. The alkali-oxygen pair distribution functions, for (a) alkali silicates and (b) alkali alumino-silicates.
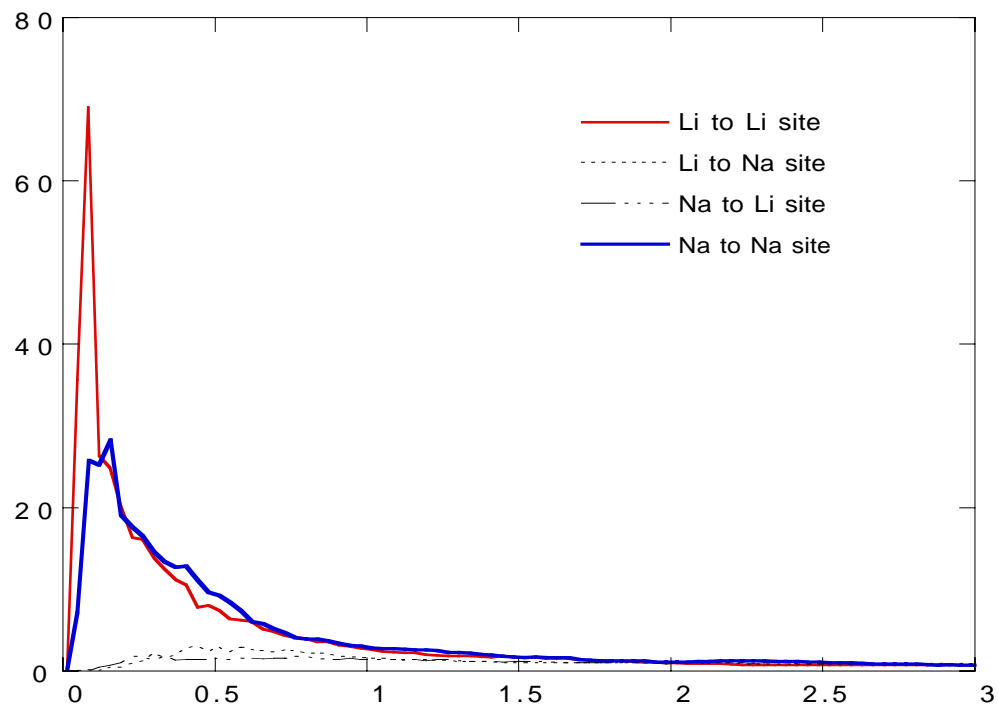
Figure 8. **Dynamic Structure factor, showing the preference for ions to jump between sites of similar character.**
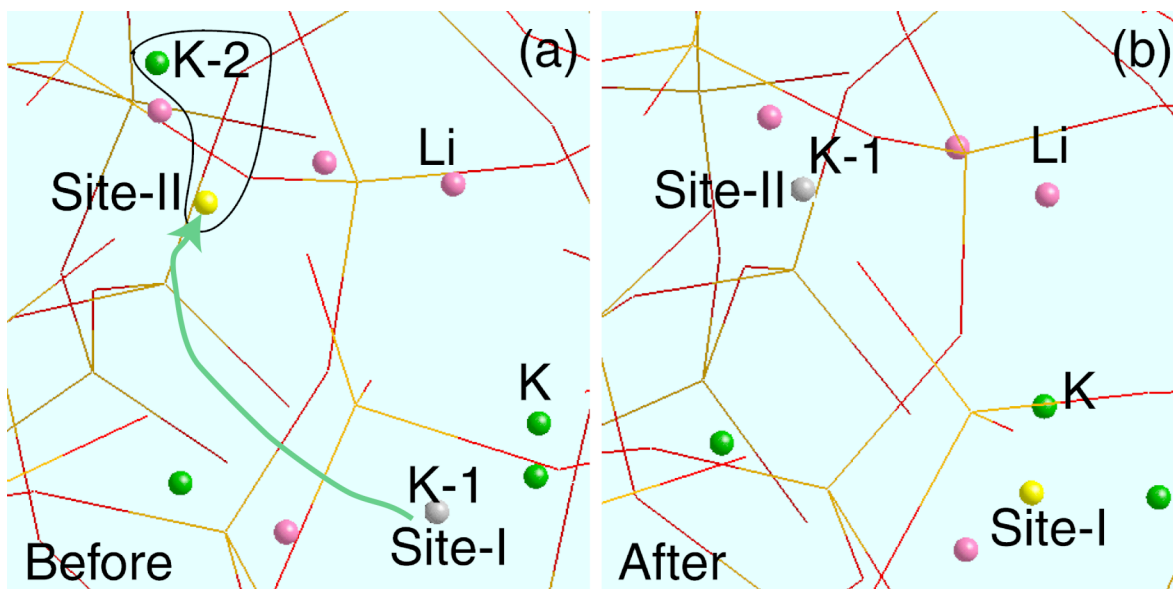
Figure 9. Schematic depiction of correlated potassium ion movements. K-1 displaces K-2 into a vacant site, leaving behind a vacant site. The "vacancy" has effectively moved by two K jump distances. K-1 and K-2 sites share common co-ordinating oxygen ions.
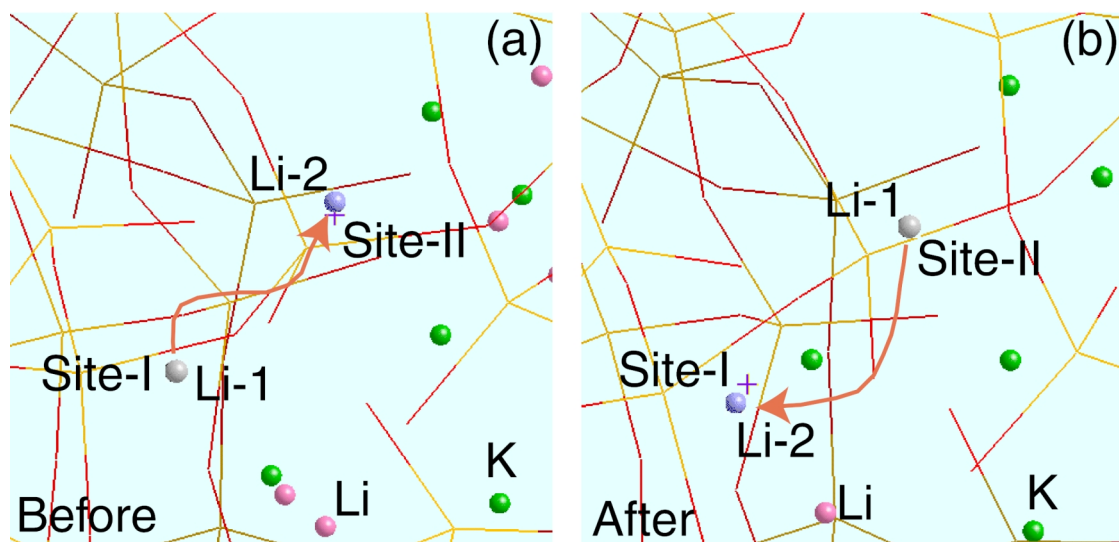
Figure 10. An exchange mechanism involving two Li ions which switch sites. The two sites share co-ordinating oxygen ions.
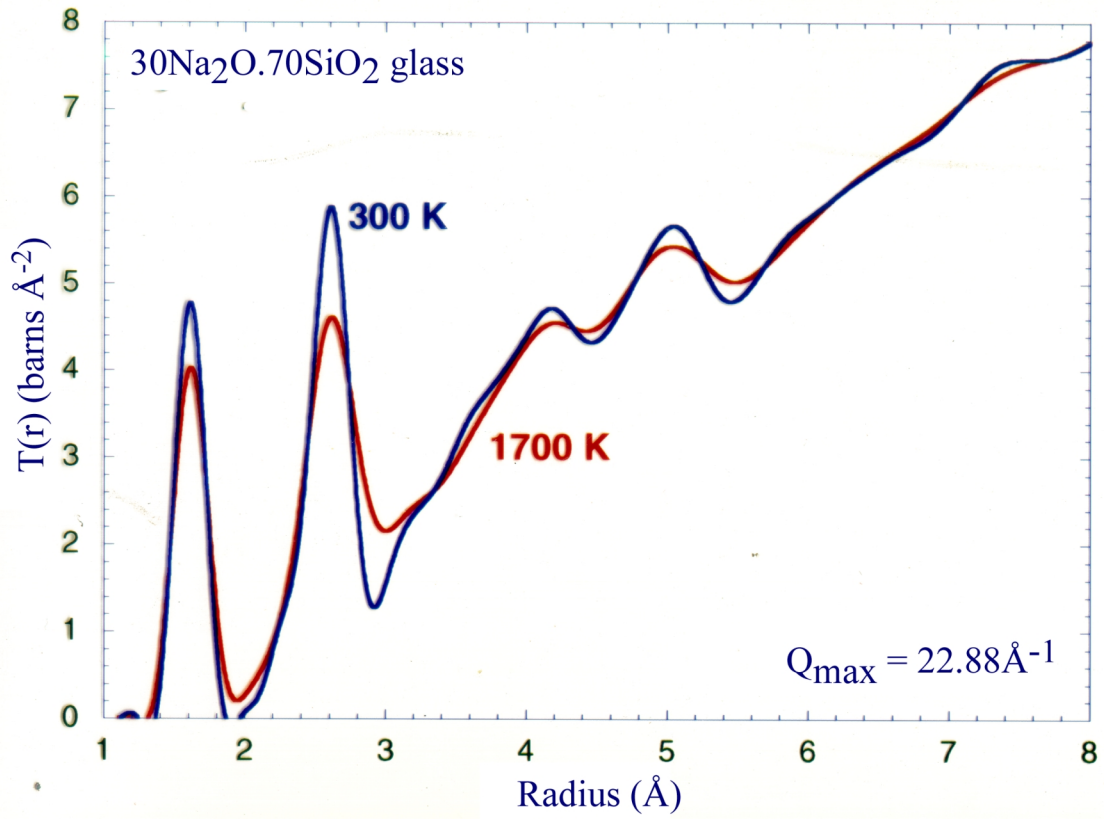
Figure 11. Comparison of T(r), calculated for the melt at 1700K and at 300K.
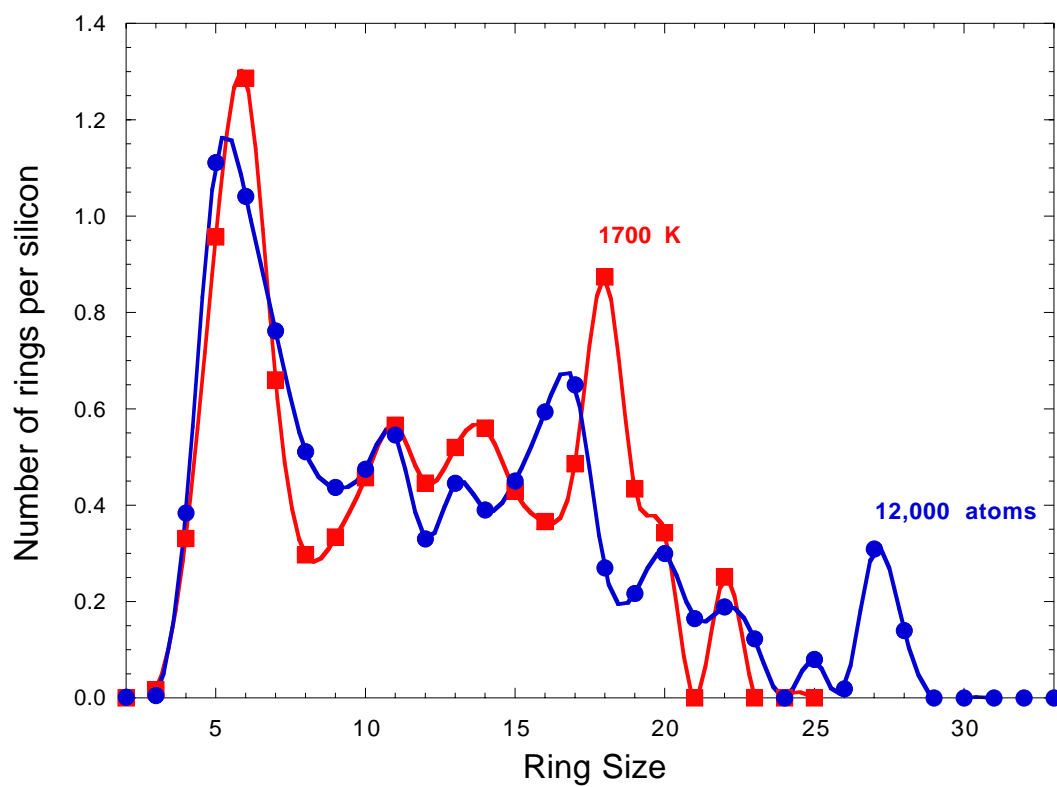
Figure 12. Calculated ring size distributions calculated for the melt at 1700K, compared with that of a glass. The melt simulation contained only 1500 atoms.