1 Silicate glasses

Silicate glasses of various composition are an important class of materials with many practical applications in the chemical industry, optics, optoelectronics and the atomic industry. Amorphous silica doped with alkali and alkaline-earth ions is a basis for a wide range of commercially available products, including utensils in the kitchen, window glasses, solid electrolytes and nuclear waste forms. These ions affect the structural, dynamic and transport properties of the host silica glass and, thus, enable tailoring of its characteristics to a diverse range of applications.

2 Molecular Dynamics

Molecular dynamics (MD) is a powerful computational method to the modeling of solids, liquids and gases, which includes the effects of both temperature and time. Though a very modern method, requiring electronic computers, it would not have appeared strange to Isaac Newton, the founder of modern physical science. The principle of the 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.

$$\vec{F}_i = m \times \vec{a}_i$$

MD has been used with some considerable success to probe structural properties (e.g. crystal structure, predicted x-ray and neutron diffraction patterns), thermodynamical properties (e.g. enthalpy, temperature, pressure) and transport properties (e.g. thermal conductivity, viscosity, diffusion). In addition, the application of MD to glass may provide an atomic scale picture of the structure and an insight into the atomic migration mechanisms active in the glasses and compare them with theory. It is a valuable bridge between experiment and theory.

3 Calculating diffusion

The motion of an individual molecule does not follow a simple path. As it travels, the molecule is jostled by collisions with other molecules which prevent it from following a straight line. If the path is examined in close detail, it will be seen to be a good approximation to a random walk. Mathematically, a random walk is a series of steps, one after another, where each step is taken in a completely random direction from the one before. In MD we can describe the mobility of atoms through the mean square displacement. The mean square displacement (MSD) contains information about the atomic diffusivity of the individual species in the glass structure. It is a measurable quantity which relates directly to the underlying motion of the molecules. The MSD measures the average distance an atom of the jth species moves:

$$MSD = \frac{1}{N_j}\sum_{i=1}^{N_j}\langle \Delta r^2(t)\rangle = \frac{1}{N_j}\sum_{i=1}^{N_j}[\vec{r_i}(t)) - \vec{r_i}(t=0)]^2$$

where $\vec{r_i}(t)) - \vec{r_i}(t=0)$ is the distance travelled by an atom i over some time intervals of length t and the squared magnitude of this vector is averaged over many such time intervals and over all the atoms of the jth species in the MD model.

This kind of path was famously analysed by Albert Einstein (in his PhD thesis in 1905) in a study of Brownian motion and he showed that the mean square of the distance travelled by particle following a random walk is proportional to the time elapsed. This relationship can be written as:

$$\langle r^2\rangle = 6Dt + C$$

where $\langle r^2\rangle$ is the mean square distance and t is time. D and C are constants. The constant D is the most important of these and defines the diffusion rate. It is called the diffusion coefficient. This expression relates macroscopic transport coefficient D with microscopic information of the mean square distance of molecular migration. The slope of the linear regime of the MSD plotted as a function of the simulation time will give us an estimation of the diffusion coefficient and consequently a picture about the mobility of the ions withing the structure.

4 Why diffusion is important?

The mobility of the cations affects important properties of the silicate glasses. Many glass properties, such as the electrical and thermal conductivity, chemical durability and viscosity are governed by the diffusion of the cations. The ion dynamics of all the components are important to prevent defects during the production of the glass. The ionic transport to the surface also affects the process of dissolution of the glass in an aqueous environment, which has deep implications for advanced technological applications where the glass durability is a major issue. For instance, the rate of initial dissolution in a biological (aqueous) medium determines the possible use of soda-lime phosphosilicate glasses as implants for tissue repair and regeneration. A fast release of Na and Ca ions, which accompanies the glass dissolution, is in fact a key requirement for the effective integration of the implant through interfacial bonding.

Diffusion is a process that became important in the early days of the semi-conductor industry. The diffusion process was one of the most significant early developments in the manufacture and commercial use of semiconductor devices, such as transistors and diodes. Semiconductor devices are made by introducing small amounts of specific dopants at explicit locations and in carefully controlled concentrations. Such dopants give the semi-conductor the electrical properties required. Historically, the control and reproducibility of the fabrication process was a real problem. Diffusion afforded a relatively well controlled method of introducing dopants precisely and at shallow depths. Diffusion could be combined with certain masking procedures, using photolithography, to minimise the size of the devices, ultimately leading to the complex integrated circuits of today. For the semiconductor industry, diffusion consists of the dopant atoms migrating into the host semiconductor crystal lattice from a source, usually at the surface, by "stepping" through vacant lattice sites, that is, by a substitutional mode.