Structure of Oxide Glasses through the First Principles Simulation of Vibrational Spectra

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Using a density-functional framework, we investigate the vibrational spectra of disordered oxides to determine to what extent these spectra provide information about their structure. Our approach benefits from a recently developed technique which allows one to apply finite electric fields in periodic density-functional calculations [1]. Through this approach, it becomes possible to calculate the otherwise computationally expensive coupling factors which are required to access infrared, Raman, and hyper-Raman spectra. We illustrate this scheme through applications on disordered oxides, such as SiO2 [2,3], GeO2 [4,5], and B2O3 [6]. We find that, among the vibrational spectra, the Raman spectra are most sensitive to medium-range structural properties through their strong dependence on the O bond-angle distribution. This dependence allows us to estimate the concentrations of small ring structures in these glasses through comparisons between calculated and measured spectra [2-6].

Nature of Vibrational Modes in simple Silicate Glasses

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The vibrational properties of silica glass have been intensively studied experimentally and theoretically during the last four decades. However, only few investigations have explored the evolution of the vibrational features of simple alkali glasses or silica under compression. In this contribution, we will present a mode analysis of two simple (Li/Na) alkali glass models obtained by combined classical and Car-Parrinello molecular dynamics. In particular we will discuss how the presence of the network modifier influences the relevant vibrational parameters: positions, shapes and intensities of the main peaks in the vibrational density of states (VDOS) and IR spectra. We will also show the decomposition of the VDOS on symmetry-adapted modes of the basic structural units of our models networks: SiO$_4$ tetrahedra and SiOSi bridges. The same analysis will be carried out in the case of few silica glass models at normal density as well as at higher density generated by Car-Parrinello molecular dynamics simulations.

Structure and mixing properties in soda and alkaline-earth silicate glasses and melts.

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Configurational entropy has been linked with the structure of Na$_2$O-MO-SiO$_2$ (M=Mg, Ca, Sr, Ba) glasses and melts, based on combined viscosimetry and Raman spectroscopic investigations. From viscosity measurements at low and high temperatures, we have obtained the configurational entropy, $S_{conf}$ (using $\log h = A_e + B_e/T S_{conf}$, where $h$ is the viscosity, $T$ the temperature and $A_e$, $B_e$ two constants). Using Raman spectroscopy, we obtained structural information from the $Q$ speciation and from the variation of the boson peak with chemical composition.

A rapid decrease in the viscosity at low temperature was observed in M-silicate melts with addition of Na$_2$O. At high temperature, the viscosity is almost the same for the M-and Na-silicate liquids. The configurational entropy calculated from the viscosity measurements for M/Na mixing shows a non-ideal variation, which can be interpreted in term of non random distribution of Na and M in the silicate network. The addition of Na$_2$O to the M silicate melts produces a decrease of the fragility of the liquid and an increase of the $Q^3/Q^2$ ratio observed with Raman spectroscopy.
Infrared spectroscopy of borate glasses in bulk and thin film forms

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Infrared spectroscopy is an effective tool for investigating the structure of glasses. This presentation reviews some applications for the characterization of alkali borate glasses in bulk and thin film forms. Infrared reflectance spectra of bulk glasses are analyzed to study the effect of alkali content and type on the short-range order of the borate network and on the interactions of alkali ions with their sites in glass. Infrared spectroscopy of thin films requires proper consideration of optical effects before it can reveal compositional and/or thermal history effects relative to bulk glasses having the same nominal composition with films.

Vibrations and Glass Structure

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The talk summarizes Hyper-Raman and Raman scattering experiments performed in simple oxide glasses. The first part will be devoted to the description of the vibrations in the glass formers SiO₂ and B₂O₃. Here, the inelastic light scattering results are compared to literature IR-absorption data, and a “normal modes” analysis is performed using a simple structural model which considers a randomly connected network of well defined elementary structural units (SiO₄ tetrahedra for silica, and BO₃ triangles and B₃O₃ rings in boron oxide). Simple Raman-spectra analyses relating the vibrations to quantitative structural information will be describe in a second part. The structural quantities that can be accessed are for example, the concentration of small rings (permanently densified silica), the Si-O-Si angle (silica and silicates), and the role (modifier or compensator) in silica-based glasses.

The SiO₂-GeO₂ and alkali-GeO₂ binaries at ambient and high T

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Raman spectra are extremely sensitive to changes in the structure of glasses, not just at the local short range scale but also at longer length scales such as the median range structure. However, the observed spectra are often unable to be fully interpreted due to a lack of understanding of the origin of vibrational features, as well as, an inability to quantify these features. Here I will discuss the vibrational spectra of glasses along the SiO₂-GeO₂ binary and the alkali-GeO₂ binaries, with respect to what is observed at ambient and high T (including the melt phase), emphasizing the spectral changes we see but don’t fully understand due to our lack of knowledge noted above. Finally, I will briefly discuss some recent findings on Na₂O-SiO₂
glasses and their relevance to our understanding of glass structure theories such as the modified random network model.

Disorder-induced vibrational anomalies and random-matrix statistics

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The enhancement of the Density of states of disordered solids with respect to the Debye expectation ("boson peak") is discussed in terms of symmetry arguments. It is pointed out that at low frequencies the vibrational spectrum consists of eigenstates, which are plane waves due to the global translational and rotational invariance of the material. Above a certain frequency the vibrational states become more and more affected by the fact that locally these symmetries do not hold. The strong degeneracy of the plane-wave states becomes lifted and the states exhibit level repulsion due to the random-matrix character of the dynamical matrix. The boson peak arises as a result of a crossover from the plane-wave regime to the random-matrix regime. This argument is independent of specific mechanisms and models of disorder.

Quasi-Localized Vibrations: Boson Peak and Phonons

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Quasi-localized modes provide a unified picture for tunneling, hopping diffusion and an excess in low frequency vibrations, leading to the boson peak. The quasi-localized vibrations can be pictured as local vibrations hybridized with the sound waves. The structure of the localized modes depends on the material. They can also be taken as fragments of low frequency optic vibrations. The soft potential model and its later extensions provides a tool to calculate with few experimental parameters the boson peak or the related damping of the phonons. It also makes predictions on the variation under changed external parameters such as pressure which have been verified experimentally. The underlying physical picture assumes a strong disorder as opposed to many q-space discussions where a mere distortion of crystalline-like phonons is assumed.

Computer simulations of low-frequency modes in glasses: application to far-IR absorption

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Dynamics of silica glass — are glasses more like crystals than we imagine?

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We approach glasses and liquids from the perspective of our studies of crystalline materials, with a strong focus on network materials such as phases of silica, and more recently metal-organic framework structures. Our starting point was Mike Thorpe's and Jim Phillips's ideas of network rigidity/flexibility based on constraint counting. In the case of crystalline silica, the standard counting methods suggest that silica is exactly balanced between being over-constrained and under-constrained, yet because of crystalline symmetry the number of independent constraints is reduced and the balance is lost. This additional flexibility is responsible for phenomena such as phase transitions, negative thermal expansion, and zeolite flexibility. When we applied our tools to silica glass, we found more flexibility that the standard counting methods would suggest, even to the extent of some crystalline network structures. Moreover, neutron scattering experiments suggest close similarities in both structure and dynamics between amorphous silica and polycrystalline cristobalite. My talk with review these results, and I will suggest that the approach from crystalline materials can offer useful insights.

Evidence from the Dynamic Structure Factor at the Boson Peak

Uli Buchenau

This is a review of old, but essentially forgotten work: Comparing the prediction $Q^2 S(Q)$ for the dynamic structure factor of long-wavelength phonons to the measured structure factor in silica, boron trioxide and polybutadiene, one can determine a sound wave fraction and its development with increasing frequency. One finds a maximum below the boson peak, which is even higher than the Debye prediction.

Structure and vibrations in disordered systems: an inelastic x-ray scattering perspective

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1. Structure and vibrations
It is largely accepted that disordered systems are characterized by a short range order usually very similar to that of the corresponding crystalline phase at the same density. It is less clear to what extent dynamic properties of disordered systems and crystals can be compared. In particular, high-frequency collective excitations reminiscent of phonons in solids exist as well in disordered systems. They are traditionally discussed in terms of relaxation processes characteristic of the disordered state [1]. We discuss here a quantitative comparison of the collective excitations in liquid and polycrystalline sodium [2]. We show that liquid sodium exhibits acoustic excitations of both longitudinal and transverse polarization at frequencies...
strictly related to those of the corresponding crystal. The only relevant difference between the liquid and the polycrystal appears in the broadening of the excitations: an additional disorder-induced contribution comes into play in the case of the liquid, which we show to be related to the distribution of local structures around the average one. This result establishes a close connection between structure and vibrations on the lengthscale characteristic of the short range order.

2. Boson peak
On the opposite side of the lengthscale, in the macroscopic regime, the dynamic properties of a disordered system can be described treating it as an isotropic continuum. This regime is well known in many details. It is clear that the macroscopic and microscopic regimes must be separated by an intermediate regime: the mesoscopic one. We present here an experimental [3,4] and numerical [5] study of this mesoscopic regime looking at the acoustic dynamics of glasses. We study in particular how, on decreasing the acoustic wavelength, the continuum, Debye approximation for the acoustic dynamics breaks down. In crystals, this takes place when the wavelength approaches the interatomic distance. We show here that in glasses this instead takes place on the larger lengthscale characteristic of the medium range order. Specifically, we find that the acoustic excitations with nanometer wavelengths show the clear signature of being strongly scattered. This crossover region is accompanied by a characteristic softening of the acoustic excitations that marks the breakdown of the Debye approximation.


Acoustic Damping and the Boson Peak of Glasses

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Sound attenuation in glasses exhibits a rich variety of phenomena which depend on the frequency and temperature. Typically above 10 K, the thermally activated relaxations of defects which can be modelled by two-well potentials are the major source of attenuation. At higher temperatures, the anharmonic interaction of sound waves with the thermal phonon bath becomes important. This initially varies with the square of the frequency, making it the dominant source of attenuation at high frequencies, typically above 10 GHz in the case of vitreous silica. How the attenuation evolves at still higher frequencies remains currently debated. Picosecond optical techniques now offer a possible approach to access sub-THz sound properties. We report recent accurate measurements of attenuation of longitudinal acoustic phonons up to frequencies near 300 GHz in vitreous silica. At very high frequencies, in the THz range, sound changes in nature, loosing its wave-like character. This Ioffe-Regel crossover nearly coincides with the excess of vibrational modes manifested by the boson peak.
Questions to the Boson Peak From Nuclear Scattering

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The talk will provide an attempt to outline several (three experimental and one theoretical) directions of studies, which seem to be crucial for understanding of glass anomalies:
1. What are (are any) anomalies in the density of vibrational states of glasses relative to their crystalline counterparts?
2. Are there any additional vibrational states in glasses at zero-energy extreme, i.e., well below the boson peak?
3. What is the functional dependence of the density of states in glasses at high energy region, i.e., well above the boson peak?
4. What is the wave-number dependence of the energy positions of the peaks in the dynamic structure factors?

"The Boson Peak through a model system of monohydroxy alcohols"

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Earlier and recent experiments performed on simple aliphatic glass-forming monohydroxy alcohols at low temperatures are reviewed and discussed. By doing this, one finds an interesting model system to explore different relevant issues concerning the properties of glasses—and the glass transition itself. Among other findings, a very similar boson peak was observed for the amorphous (i.e. structural glass) and orientationally-disordered crystal (i.e. glassy crystal) states of ethanol. On the other hand, a very strong influence of the location of the hydrogen bond on lattice dynamics and hence on the boson peak has been found when comparing the different positional isomers in propanol and in butanol. The complementary assessment of the acoustic and elastic coefficients of those glasses, is basic to investigate the nature of the vibrational excitations producing the so-called boson peak in glasses.