

From vibrations to diffusion in amorphous materials

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Summary

Simulation of amorphous materials is hampered both by the lack of symmetry, which necessitates large samples, and by the slow evolution with time. Despite this, combining first-principle calculations, molecular dynamics and physical modeling considerable insight can be gained. This will be illustrated for the atomic dynamics by examples from covalent and metallic systems.

Introduction

Amorphous materials pose a twofold challenge to computer simulations. First, the lack of long range order and symmetry necessitates large samples in simulations. In first-principle electronic calculations only a few hundred atoms can be treated for a limited number of possible configurations which forces one to resort to effective interatomic interactions. Secondly, amorphous materials are not in thermal equilibrium and, therefore, evolve over long times from ns to years and longer, depending on temperature. This again rules out first-principle calculations since they are limited to short times of order ps. On the other hand methods such as Monte Carlo, which have no inherent time scale, are hampered by the absence of an underlying lattice and consequently the uncertainty in defining a suitable elementary process.

Despite these difficulties, by combining different methods, e.g. first principle electronic calculations, classical molecular dynamics and physical models, considerable progress, both concerning general and material specific properties, has been made over the last few years. We will illustrate this on three examples concentrating on classical molecular dynamics. First we illustrate the problem of long times on the example of the quench rate dependence of the structure of amorphous Se. As second a example we look at general properties of the low energy excitations and finally take a glimpse at diffusion.

Quench rate dependence

Amorphous selenium is one of the few elementary glasses. Its glass transition temperature, $T_g \approx 305$ K, is near room temperature which facilitates experiments. It has been studied extensively in experiments on both structural and dynamical properties. Se is covalently bound and prefers a coordination number of two. The most stable crystalline (trigonal) phase consists of parallel helical chains. Two monoclinic forms are composed of rings of eight atoms. The polymorphs are distinguished by the correlation between neighboring dihedral angles: a trans- (chains) or a cis-configuration (rings). The energy difference between these was estimated as only 0.03 eV. From a first-principles molecular dynamics simulation Hohl and Jones [1] conclude that both amorphous and liquid selenium are built from branched chains which include rings of different length.

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For a classical simulation, this immediately leads to the difficulty of simultaneously having to describe the covalent binding in the chains and rings and the van-der-Waals like interaction between the rings, as well as possible branching and bond breaking. One possibility is to disregard the last two, and to use different interactions for atoms in the same chain and in different chains, respectively. One then considers a glass or a liquid of chains of a predefined length. This fragmented chain method has been employed both for electronic structure calculations and for classical molecular dynamics simulations. Another possibility is to use a more simple description of the electronic properties, such as tight binding models. We follow a different line. As done before by Stillinger *et al.* in their study of liquid sulfur [2], we use one effective inter-atomic three-body potential for both, the intra-chain and the inter-chain interactions. This potential was constructed to reproduce the different Se_n structures found in a first-principle simulation [1] and crystalline data. Despite its simplicity this interaction model leads to realistic results for the structure and dynamics [4].

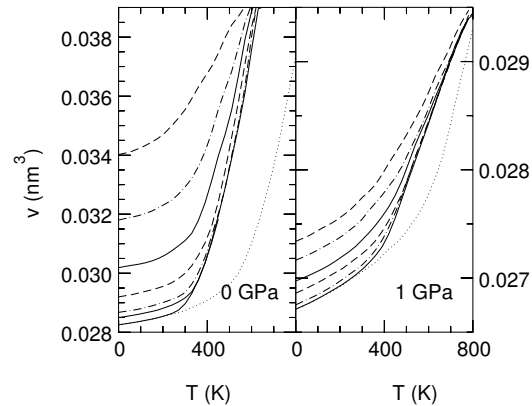


Figure 1: Evolution of the specific volume per atom as function of temperature for different applied pressures ($p = 0.0$ GPa left, $p = 1$ GPa right) and different quench rates (from top to bottom: $Q_r = 10^{14}$, $3 \cdot 10^{13}$, 10^{13} , $3 \cdot 10^{12}$, 10^{12} , $3 \cdot 10^{11}$ K/s and $1 \cdot 10^{11}$ K/s ($p = 0$ only) [5]. The dotted lines show the volume evolution upon rapidly heating the samples with the lowest quench rate.

Due to the combination of van-der-Waals and covalent bonding, in Se properties, such as the atomic volume or the glass transition temperature, depend particularly strongly on the production history and in particular on the quench rate, as illustrated in Fig. 1[5]. The glass transition temperature, T_g , can be derived from the $v(T)$ -curves as the crossover between the extrapolated high temperature (liquid) curves and low temperature (glassy) curves. Experimental quench rates are of the order 1 K/s, about ten orders of magnitude smaller than the one obtainable with reasonable computational effort. Arguing that the glass transition occurs when the relaxation time increases upon cooling to the inverse of the quench rate,

the dependence of T_g on Q_r can be fitted by a Vogel-Fulcher law

$$T_g = T_0 + \frac{B}{\ln A Q_r}, \quad (1)$$

where A and B are two parameters and T_0 is the glass transition temperature corresponding to $Q_r \rightarrow 0$ K/s. Applying these data to the data of Fig. 1 one finds for zero pressure and $Q_r = 1$ K/s $T_g = 253$ K about 20% below the experimental value. Increasing the pressure we find an increase of T_g by 13.5% compared to an experimental estimate of about 20%.

The atomic volume for a given pressure, p , depends linearly on the quench rate dependent glass transition temperature:

$$v(p, Q_r) = v_0(p) + \alpha(p)T_g(p, Q_r). \quad (2)$$

The resulting value for $Q_r = 1$ K/s is $v = 0.027$ nm³ which is about 10% too low compared with experiment.

Considering the simplicity of the interaction model these results are encouraging but also show that there is scope for improvement. In fact, it is within the accuracy of the original fit to scale the parameters so that the simulation results come close to the experimental error margins. This is then a first step in an iterative scheme to improve the description of the Se-interaction.

Fig. 1 clearly illustrates that great care has to be taken when transferring results from the ns-times of simulation to experimental times. One has to make sure that artifacts from the simulation, such as quenched in voids, do not influence the investigated property too strongly or are properly accounted for.

Comparing the curves for different pressures one also sees that applying pressure during the quench reduces the number of voids considerably. This indicates a possible path to reduce the number of unwanted voids, namely to quench under pressure and release the pressure only below the glass transition.

Vibrations

At a first view glasses behave like crystalline solids. They can carry sound waves, their elastic constants are similar to the ones of their crystalline counterparts (albeit isotropic) and the vibrational spectra are similar. At low temperatures, however, qualitative differences are observed.

At the lowest temperatures, below ≈ 1 K, the dynamics in glasses is dominated by two-level systems which can be described by the tunneling model which was formulated nearly thirty years ago. In addition to these tunneling states, one observes in glasses local relaxations and an excess of vibrations over the Debye value (given by the sound waves)

which culminates in the so called boson peak in the inelastic scattering intensity. To describe these low energy excitations, the tunneling model was extended to the soft potential model [6][7]. From this model “universal” temperature dependencies can be derived for temperatures of some 10 K. Comparing the model to experiment, one finds that the excess low energy excitations are collective motions with cores of 10 to 100 atoms [8]. This claim of the model cannot be verified experimentally. Structure factor measurements are not accurate enough.

In molecular dynamics simulations of a soft sphere glass [9], a simple model for metallic glasses, and later for a number of different materials (e.g. Se [11] or SiO₂ [10]) it was found that glasses have a whole spectrum of low frequency quasi-localized (resonant) vibrations (QLV) whose cores extend over 10 and more atoms. The atomic structure reflects the underlying local order of the material. In dense metallic glasses the QLV are chain like. As assumed in the model QLV and atomic hopping motion are closely related. The latter consists of a coherent motion of chains of atoms where a single atom moves only a fraction of the nearest neighbor distance [12], see Fig. 2, left.

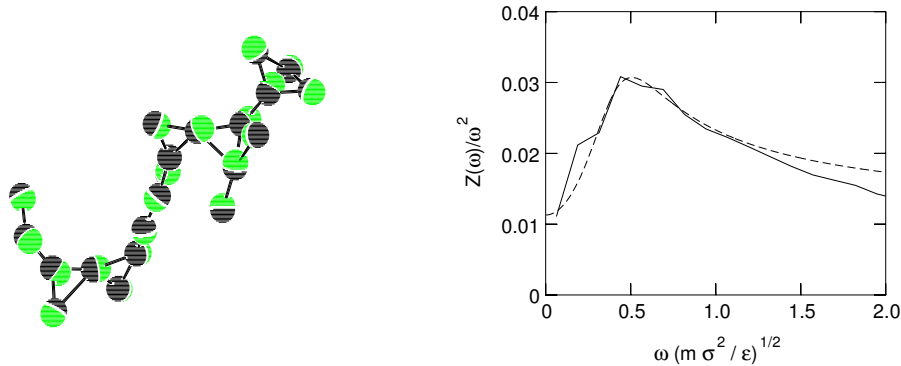


Figure 2: Left: Collective jump in a soft sphere glass at $T = 0.15T_g$. The initial positions of the atoms are shown by the dark spheres and the final ones by the shaded spheres. The bonds connect nearest neighbors. Shown are all atoms with more than 40% of the maximal atomic displacement [12]. Right: Vibrational spectrum divided by ω^2 versus ω [14]. The solid line gives the simulation results, corrected by a Debye contribution at the lowest frequencies. The dashed line is a fit with the model of Ref. [13].

In an extension of the soft potential model it was shown that the interaction of the QLV leads, due to the always present anharmonicity, to a universal shape of the boson peak [13]. Anharmonicity is important in creating the boson peak; the vibrations themselves are harmonic. Again simulation confirms these results, Fig. 2, right.

Diffusion

For temperatures well below the glass transition, computer simulation cannot distinguish between local hopping between a few local minima and hopping leading to long range diffusion. From experiment it was concluded that in metallic glasses the collective hopping is indeed the elementary step in diffusion [15]. A central piece of evidence is the vanishing of the isotope effect in diffusion, i.e. there is no measurable difference in the diffusion constant of different isotopes.

Diffusion can be measured directly in molecular dynamics in the glass at temperatures close to T_g and in the melt. Such simulations have shown that upon quenching to the glass transition collectivity of diffusive motion sets in well above the glass transition. The isotope effect vanishes for temperatures some 10% above T_g .

In accordance with the picture of collective jumps, there is, different from crystalline matter no preferred distance an atom jumps in a single hop. This is shown in Fig. 3 for glassy and undercooled liquid $\text{Cu}_{33}\text{Zr}_{67}$ ($T_g \approx 1000$ K).

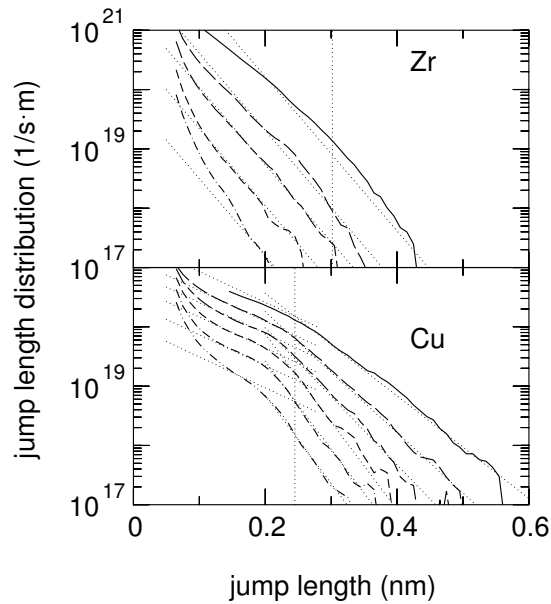


Figure 3: Distribution of jumps/second over jump length for Zr (top) and Cu (bottom). Temperatures from top to bottom: 1400, 1200, 1100, 1000 and 900 K. The dotted lines indicate the fits by exponential jump length distributions, see text. The respective nearest neighbor distances for the two components are indicated by the vertical dotted lines.

This collectivity of motion can be shown to be intimately connected with another typical property of amorphous materials and undercooled melts, namely the so called dynamic

heterogeneity: again different from crystalline materials one has at a given time groups of mobile and immobile atoms. Only for times comparable to typical diffusion times this heterogeneity disappears.

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