The vibrational dynamics of vitreous silica: Classical force fields vs. first-principles

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Abstract. – We compare the vibrational properties of model SiO$_2$ glasses generated by molecular-dynamics simulations using the effective force field of van Beest et al. (BKS) with those obtained when the BKS structure is relaxed using an ab initio calculation in the framework of the density functional theory. We find that this relaxation significantly improves the agreement of the density of states with the experimental result. For frequencies between 14 and 26 THz the nature of the vibrational modes as determined from the BKS model is very different from the one from the ab initio calculation, showing that the interpretation of the vibrational spectra in terms of calculations using effective potentials can be very misleading.

Motivation. – Understanding the microscopic properties of vibrational excitations in disordered systems is a long standing challenge in basic physics as well as in material science since the lack of positional order makes both the experimental study and the theoretical interpretations of the results very difficult. For instance the mechanism leading to the existence of the so-called boson peak present in many glasses is the subject of a long standing debate, and the reason for the presence of the $D_1$ and $D_2$ lines in the Raman spectra of amorphous SiO$_2$ has remained unclear for a long time [1–8].

In principle molecular dynamics (MD) computer simulations overcome these difficulties since one has direct access to all the necessary microscopic information. Therefore in recent years many studies of this kind have been carried out with the aim of shedding some light on the nature of these vibrational excitations, in particular for the case of silica, the paradigm of network forming glasses [9–19]. Due to the large computational costs of such simulations the vast majority of them were done with effective classical force fields, i.e. potentials which were optimized to reproduce certain (somewhat arbitrarily chosen) experimental features of SiO$_2$. It is clear that the reliability of the results of these investigations depends crucially on whether or not the interactions used are sufficiently accurate to allow a faithful description of the real material. Hence a considerable effort has been made to check that the models used do reproduce the salient structural and dynamical features of real silica. In these studies it has been shown that the classical force fields employed are indeed able to give a good description of quantities like the structure factor, the diffusion constant or viscosity, etc. [11, 20–24], so their use in investigations of the vibrational properties also appears a reasonable undertaking. Nevertheless, it was found that certain features of the vibrational density of states (DOS) are not well reproduced by these models and more sophisticated calculations, such as the numerical studies based on first-principles, seem to be required [25], in agreement with conclusions drawn for the case of liquids [26]. Pasquarello et al. showed that using an ab initio scheme it is possible to reproduce many structural, electronic and vibrational properties.
of real silica \[9, 10, 12, 13\]. However this approach suffers from its heavy computational cost which restricts this type of calculation to the study of very small systems with a rather low statistical accuracy.

One possibility to overcome this limitation, at least partially, is to use a combined approach which consists in generating a glass using an effective potential and subsequently refining the structure obtained by means of first-principles \[27\]. In previous work we showed that the structure of vitreous SiO\(_2\) generated using the effective force field by van Beest, Kramer and van Santen (BKS) \[28\] is only modified weakly by a first-principles calculation, thus validating the structural model generated with this potential.

In contrast to this we show in this letter that the DOS of a SiO\(_2\) glass generated by classical MD simulations using the BKS potential is strongly modified by using an \textit{ab initio} treatment of the forces, and that this treatment leads to a much better agreement with experimental results. Moreover, in a large frequency range, the nature of the excitations as determined from the effective potential differs significantly from the one determined from the \textit{ab initio} forces thus raising doubts as to the detailed analysis of the nature of the vibrational excitations determined from the BKS force field.

\textit{Simulation details}. – Molecular-dynamics simulations were done using the BKS potential on systems containing 26 SiO\(_2\) units at the experimental density (2.2 g/cm\(^3\)). For this we used the velocity form of the Verlet algorithm with a time step of 1.63 fs. Three different samples were generated by quenching liquids well-equilibrated at 3500 K to 300 K, using three different cooling rates: \(5 \times 10^{12}\) K/s, \(3 \times 10^{11}\) K/s, and \(7 \times 10^{10}\) K/s. The glasses obtained this way (which are non-equilibrium structures) were annealing for 70 ps at 300 K, and subsequently quenched to 0 K, at which their dynamical matrices were evaluated and diagonalized in order to obtain the vibrational frequencies and the corresponding (normalized) eigenmodes. In parallel the final atomic coordinates and velocities after the annealing at 300 K were used as initial coordinates and velocities for short (\(\approx 0.12\) ps) \textit{ab initio} molecular-dynamics simulations of the Car-Parrinello type \[29\], using the CPMD code \[30\]. The technical details of these simulations were identical to the ones described in Ref. \[27\]. At the end of these simulations the structures of the three glasses were relaxed to 0 K and the dynamical matrices were computed by evaluating the second derivatives of the total energy with respect to atomic displacements by taking finite differences of the atomic forces. Subsequently the vibrational frequencies and the corresponding eigenmodes were obtained from these matrices. Hence we obtained \(g(\omega)\), the \textit{true} DOS for this system. Note that although the cooling rates are high and the system size is small, the DOS depends only weakly on these parameters \[20\].

In the following, the quantities computed by means of classical molecular-dynamics simulations using the BKS potential and the CPMD code will be labeled “BKS” and “CP”, respectively.

\textit{Results}. – Since we found that the DOS from the three different cooling rates are identical to within the statistical error - which is relatively large due to the small system size - we decided to treat the three glasses as independent statistical samples and analyzed the three sets of vibrational frequencies/modes together. The resulting vibrational DOS was used to compute an \textit{effective} neutron scattering cross section \(G(\omega) = C(\omega)g(\omega)\). This was done by using the incoherent approximation and by calculating \(C(\omega)\) as in Ref. \[16\]. We note that the correction functions \(C(\omega)\) for the BKS and CP are very similar and hence differences in the respective \(G(\omega)\) are mainly due to differences in the respective \(g(\omega)\). In Fig. 1 we compare the \(G(\omega)\) obtained and we see that at intermediate frequencies the two curves are very different. In particular we see that the CP curve has a pronounced peak at around 12 THz and a smaller one at around 24 THz. Finally there is a small peak at 18 THz, the so-called D\(_2\)
Fig. 1 – Frequency dependence of the effective density of states $G(\omega)$ calculated from ab initio (solid line) and classical (dashed line) molecular dynamics simulations and compared to neutron scattering experiments from Ref. [31] (filled circles). The calculated $G(\omega)$ have been obtained using the experimental values for the neutron scattering length factors $b_{\text{Si}} = 4.149 \text{ fm}$ and $b_{\text{O}} = 5.803 \text{ fm}$ and a Gaussian broadening of width $2 \sigma = 1.05 \text{ THz}$.

line, which is due to a ring of size three. Overall the CP curve is in very good agreement with previous investigations [13]. All these features are missing in the BKS curve, despite the good agreement between CPMD and BKS with regard to structural properties. Also included is the result of a neutron scattering experiment by Carpenter and Price [31] and from the reasonable agreement between this curve and the one from the CP calculation we conclude that the latter is reliable. [ Note that i) there is no fit parameter whatsoever, and ii) the lack of a small peak at around 4 THz in the experimental data is related to the insufficient experimental resolution [7]. ] Hence we conclude from this figure that the DOS as calculated from the BKS model is not very reliable at intermediate frequencies, in agreement with Ref. [11]. Note that similar discrepancies between experiments and simulations with various effective interactions have already been observed in previous studies [11, 16, 17, 20, 22] and hence we conclude that many other types of force fields also lead to a density of states which is not trustworthy and that most probably the conclusions drawn in this paper hold for these other potentials as well. However, the good agreement between the CP and the experimental DOS clearly shows that a simple refinement of the BKS model glass by a first-principles calculation is sufficient to significantly improve the vibrational density of states.

Having shown that the effective DOS from the BKS differs significantly from the one from the CP we now investigate this difference in more detail by comparing the corresponding eigenmodes. Since the number of eigenmodes for the BKS and CP cases is the same, Fig. 1 implies that there is a considerable reshuffling of the modes from one frequency to another if the force field is switched. In order to check whether at a given frequency $\omega^\text{BKS}_\nu$ ($\nu = 1, \ldots, 3 \times 3N$, and $N$ is the number of atoms in each of the three samples) the nature of a given mode $e^{\text{BKS}}(\omega^\text{BKS}_\nu)$ from the BKS system is similar to one of the CP modes we calculated
the projections of the latter onto the former modes:

\[ H(\omega_{\nu}^{BKS}, \omega_{\mu}^{CP}) = |E^{BKS}(\omega_{\nu}^{BKS}) \cdot E^{CP}(\omega_{\mu}^{CP})| \quad \text{with} \quad \nu, \mu = 1, \ldots, 3 \times 3N. \] (1)

Here \( E^{CP}(\omega_{\mu}^{CP}) \) is the eigenvector for the CP system at frequency \( \omega_{\mu}^{CP} \). With this definition, \( H \) varies between 0 and 1, since \( |E^{BKS}(\omega_{\nu}^{BKS})| = |E^{CP}(\omega_{\mu}^{CP})| = 1 \). If the nature of the modes in the BKS system were identical to the ones of the CP system, \( H \) would be a line of \( \delta \)–functions along the diagonal in the \((\omega_{\nu}^{BKS}, \omega_{\mu}^{CP})\) plane. The frequency dependence of \( H(\omega_{\nu}^{BKS}, \omega_{\mu}^{CP}) \) is shown in Fig. 2 as a contour plot.

This plot shows a well-defined ridge close to the diagonal of the graph up to \( \approx 7 \) THz and between \( \approx 28 \) and \( 39 \) THz. This means that the overlap between the BKS and the CP vibrational modes is significant in these frequency ranges, i.e. that at a given frequency the nature of the mode is very similar. For \( 7 \) THz \( \leq \omega^{CP} \leq 13 \) THz we still find a well defined ridge, but its location is above the diagonal. Hence we see that although the BKS modes can still be well represented by the CP ones, they are shifted to slightly higher frequencies. Since the interval \( 7 \) THz \( \leq \omega^{BKS} \leq 21 \) THz is compressed into the range \( 7 \) THz \( \leq \omega^{CP} \leq 14 \) THz this leads to a significant larger \( g^{CP}(\omega) \) in this range, in agreement with Fig. 1.

In the range \( 16 \) THz \( \leq \omega^{BKS} \leq 28 \) THz we find that the BKS modes have a significant overlap with CP modes that cover a large range in \( \omega^{CP} \). This implies that in this frequency range the vibrational dynamics of the BKS system is no longer realistic and that hence care must be taken if one draws conclusions from the analysis of the modes in this range.

In order to investigate whether in this frequency range the CP eigenmodes can at least be written as a sum of only a few BKS modes, we ordered for each frequency \( \omega_{\mu}^{CP} \) the overlaps \( H(\omega_{\nu}^{BKS}, \omega_{\mu}^{CP}) \) in descending order, i.e. \( [H(\omega_{1}^{BKS}, \omega_{\mu}^{CP})]^{2} \geq [H(\omega_{2}^{BKS}, \omega_{\mu}^{CP})]^{2} \geq \ldots \), and
calculated the sum

\[ S_J(\omega^{CP}_\mu) = \sum_{\nu'=1}^{J} \left| H(\omega^{BKS}_{\nu'}, \omega^{CP}_\mu) \right|^2. \]  

(Note that the sum of such eigenmodes is in general no longer an eigenmode.) The resulting \( S_J \) as a function of the CP vibrational frequencies \( \omega^{CP}_\mu \) are presented in Fig. 3 for \( J = 1, 2, 10, \) and 20. This figure demonstrates that in general the CP modes are not well represented until the sum extends over at least 10 BKS eigenmodes. The only exceptions are modes at very low frequency (\( \leq 3 \) THz) and around 27, 29, and 38 THz. These latter modes show already a prominent peak in \( S_1(\omega^{CP}_\mu) \) and are at band edges and hence are localized. Note that even for \( 3 \) THz \( \leq \omega^{CP} \leq 13 \) THz, i.e. the frequency range where we find a strong correlation in Fig. 2 the BKS modes do not describe well the CP modes. In the range 13 THz \( \leq \omega^{CP} \leq 26 \) THz one needs on the order of 20 BKS modes in order to describe a CP mode, which shows that the former have not much in common with the latter.

It is well known that the vibrational excitations of silica include modes that are very localized as well as ones that are collective. In order to see whether there is a difference in the ability of the BKS potential to describe the one or the other type we have defined the following quantities:

\[ X^{CP}_J(\omega^{CP}_\mu) = \sum_{\alpha'=1}^{J} \sum_{i=1}^{3} \left| e^{CP}_{\alpha',i}(\omega^{CP}_\mu) \right|^2 \quad \text{and} \quad X^{BKS}_J(\omega^{BKS}_\nu) = \sum_{\alpha'=1}^{J} \sum_{i=1}^{3} \left| e^{BKS}_{\alpha',i}(\omega^{BKS}_\nu) \right|^2 \]  

where \( \alpha' \) is the atomic index, \( i = x, y, z \) and the prime in the sum (\( \alpha' \)) indicates that we have made the ordering: \( \sum_{i=1}^{3} |e_{1,i}|^2 \geq \sum_{i=1}^{3} |e_{2,i}|^2 \geq \cdots \). Thus \( X^{CP}_J(\omega^{CP}_\mu) \) is the sum of the \( J \) largest atomic displacements for that eigenvector. The resulting \( X^{BKS}_J \) and \( X^{CP}_J \) are shown in Figure 4 for values of \( J = 1, 4, 20 \) and 50. (Note that for the sake of clarity the quantity is only shown for one sample. The other two samples look qualitatively similar.)
Fig. 4 – Sum of the $J$ largest components of an eigenvector with frequency $\omega$ (see Eq. (3)) for $J = 1, 4, 20$ and 50. Left panel: $X^\text{CP}_J$; Right panel: $X^\text{BKS}_J$.

Using this quantity, we can estimate the number of atoms participating in a given vibrational mode. Firstly, we note that most of the modes with frequencies below $\approx 22$ THz have a “collective” nature since around 20 eigenvectors are needed to make 60% of $X$, independent of the model used. Exceptions are CP modes at 14 and 18 THz which show a pronounced peak with a height larger than 0.4 even for $J = 4$. These modes correspond to the D$_1$ and D$_2$ lines in the Raman spectrum of vitreous SiO$_2$ that have been attributed to breathing modes of 3 and 4-membered rings [13,19]. From the curves it becomes clear that these modes are not present in the BKS description, thus raising the problem of the interpretation of the Raman spectrum of glassy SiO$_2$ using this model potential (see also [25]). For frequencies higher than $\approx 22$ THz the nature of the modes becomes more localized for the case of the CP model as well as the BKS model. However, we note a clear difference in the $X^\text{BKS}_J$ and $X^\text{CP}_J$ between 22 and 29 THz, where the BKS modes seem to be more collective than the CP ones. Finally we mention that one sees a strong localization of the modes near the gap of the DOS and at around 39 THz, in agreement with the comment made in context of Fig. 3.

Conclusion. – We have shown that for the case of silica the DOS as predicted by an effective force field can be improved considerably by relaxing the configuration by means of an \textit{ab initio} simulation, without a significant change in the structural properties. For intermediate frequencies the nature of the modes in the BKS system is very different from the one in the CP system. In particular the effective force field is not able to reproduce the nature of the modes attributed to the D$_1$ and D$_2$ lines in the Raman spectra. In view of the fact that the BKS model was obtained by an \textit{ab initio} calculation of a single tetrahedron and a lattice dynamic simulation of a crystal to optimize the elastic constants [28], it is not surprising that the model does well at very high and very low frequencies, but is not reliable at intermediate
frequencies. Hence we conclude that despite the reliability of effective potentials with regard to structural properties, it might be that if one wants to investigate vibrational features in the whole frequency range one would need an effective potential which is more accurate, or a full \textit{ab initio} calculation.

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