Disordered SiO$_2$ Systems: A First-Principles Investigation

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Ladies and Gentlemen,

It is a great honour for me to be awarded the Latsis Prize and to have the opportunity to present the principal results of my research activity to this audience today. On this occasion, I would like to thank once more the Latsis family and their foundation for making this possible.

1. Introduction

The tremendous impact of disordered forms of SiO_2 on everyday life have made of these materials one of the most actively studied aereas of research during several decades [1, 2]. Two major industrial sectors such as the electronic and the glass manufacturing industries critically rely on disordered SiO_2 materials. Soon after the discovery of the transistor, the particular properties of the interface between silicon and its amorphous oxide have emerged as the most suitable for electronic device applications. During the years, the combination of performance and cost-effectiveness of this silicon based technology has repeatedly outrun all alternative solutions and has grown into one of the most flourishing industrial successes of all times. Still today there are no signatures of a decline of this technology and its potential is expected to remain unmatched at least for another decade. Similarly, the high transmission of optical wavelengths in fibers and their low production cost are at the origin of the success of the glass technology. The increasing demand for rapid transfer of information in modern societies is spurring the massive installation of optical fiber networks, making of glass manufacturing a highly competitive industrial field. Besides the use of SiO_2 materials in industrial programs, silicates are also found as one of the primary constituants of the earth's mantle. This confers to disordered forms of SiO_2 also a geophysical relevance.

The fundamental interest in vitreous silica derives from the fact that it constitutes a prototypical example of a network-forming disordered material. The atomic structure is characterized by a network of corner-sharing tetrahedra. An individual tetrahedron is composed of a central Si atom with four oxygen atoms at its corners. Whereas the structure within a tetrahedron is very rigid, a large flexibility is observed in the

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angles at the shared corners. This combination gives rise to a structure in which the disorder is essentially determined by a distribution of Si-O-Si angles, with a strong preservation of the local order within the tetrahedra. Furthermore, the structure presents an extremely low density of defects, and this is certainly one of the most relevant properties which underlie its success in so many applications.

The remarkable characteristic of SiO_2 to exist in a multitude of allotropic forms is related to the peculiar mixture of ionic and covalent contributions to the Si-O bond. Hence the explicit treatment of the electronic structure, which depends on the structural environment, is expected to be an essential ingredient to an accurate description of disordered forms of SiO_2. Furthermore, access to the electronic structure appears also critical to interpret results obtained by experimental techniques which directly probe electronic properties.

However most investigations of disordered SiO_2 systems have so far relied on empirical classical potentials. The high computational cost of quantum mechanical schemes has prevented their application in systems sufficiently large to reproduce the properties of a disordered material. Although classical approaches have provided an adequate description of structural properties their accuracy in treating properties in which the electronic structure plays a more subtle role is limited. Therefore, in spite of more than three decades of research on disordered SiO_2 materials, a series of problems related to the electronic properties in these systems have remained unclear and ill-understood.

2. Theoretical approach

The aim of this work is to address such problems within a theoretical scheme of improved accuracy, in which the electronic structure is treated in a quantum mechanical way. First-principles approaches based on density functional theory serve this purpose. An important feature of such approaches is that their application does not rely on parameters extracted from experiment. Thus, the degree of bias inherent to empirical approaches is greatly reduced. Furthermore, a great deal

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of research, mostly on crystalline systems, shows that in many cases first-principles approaches yield results in excellent agreement with experiment.

The application of such techniques to disordered forms of SiO_2 has long been precluded by several difficulties, related to the size of the problem and to the presence of oxygen atoms, which are traditionally hard to treat numerically. These problems have been overcome by recent theoretical developments [3]. In this novel scheme, the localized valence electrons are handled in a cost-effective way, allowing the treatment of systems of sufficiently large size to study disordered materials.

3. Liquid and glassy SiO_2

We started our investigation of disordered SiO_2 materials with the liquid state performing a first-principles molecular dynamics simulation [3–5]. The study of the diffusion events revealed a jump-like motion, confirming the picture that arose from classical molecular dynamics simulations [6]. By quenching to low temperatures, we generated a model of the glass consisting of a chemically ordered network of corner-sharing tetrahedra[6, 7]. The calculated structure factor for this model structure[6] was found in excellent agreement with neutron diffraction data [8], as shown in Fig. 1.
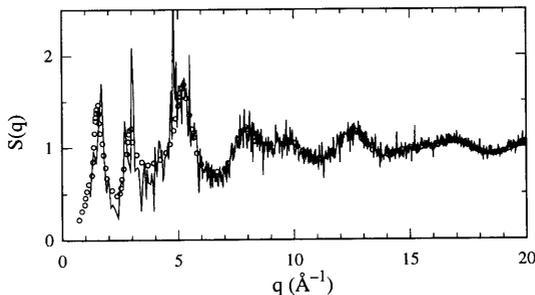

Figure 1: Static neutron structure factor $S(q)$ for vitreous SiO_2. Circles are experimental data from Ref. [8].

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4. Vibrational properties of vitreous silica

The availability of a structural model for vitreous silica proved very useful for the study of the vibrational properties of this material. The inelastic neutron [9], the infrared [10] and the Raman spectra [11] show several features which are poorly understood. In the high frequency region corresponding to the Si-O stretching motions, the neutron spectrum shows a doublet [9]. The similar magnitude of the LO-TO splitting, observed in infrared measurements [10], supported an interpretation in terms of a separation of longitudinal and transverse motions [12, 13]. Instead, our investigation has unambigously shown that the neutron doublet derives from distinct sets of normal modes, which can be characterized according to different symmetry representations of the isolated tetrahedron (Fig. 2) [14].
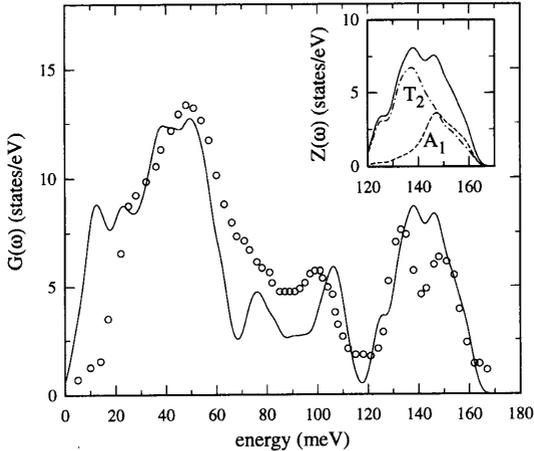
Figure 2: Calculated effective neutron density of states $G(\omega)$ (solid) compared to neutron scattering data of Ref. [9] (circles). Inset: calculated density of states $Z(\omega)$ (solid) and its projection on symmetry adapted modes of the SiO_4 tetrahedra A_1 (dashed) and T_2 (dash-dotted).

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In the infrared absorption spectrum, the intensity ratio between the two principal peaks could not be explained using classical potential models, not even including more sophisticated polarization effects [15]. By calculating the full Born charge tensors from first principles, we were able to reproduce the correct intensity ratio and to relate this effect to off-diagonal contributions in the dynamical charge tensor of the oxygen atoms (Fig. 3) [16].
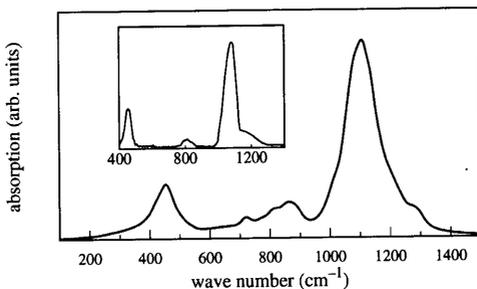

Figure 3: Infrared absorption spectrum $\alpha(\omega) \sim \omega \operatorname{Im} \epsilon_\perp(\omega)$ calculated with full charge tensors. Inset: Experiment from Ref. [10].

Furthermore, we also reproduced correctly the LO-TO splitting and showed that this splitting occurs in the limit of vanishing wavevector, clarifying its relation with the neutron spectrum [16].

The Raman spectrum shows the appearance of two unusually sharp lines which could not be related to the vibrations of a continuous random network [11]. Our work conclusively associates these lines to oxygen breathing motions in three- and four-membered rings (Fig. 4) [17]. The occurence of such rings in vitreous silica is therefore definitely established. This opens the way to a characterization of the structure of vitreous silica of unprecedented quality. Indeed, a quantitative measure of the concentration of such rings as deduced from the
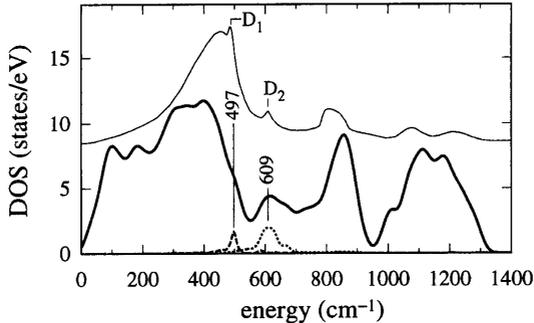
Figure 4: Calculated vibrational density of states of model silica (solid) [14] and projections on the breathing modes of the three- (dotted) and the four-membered (dashed) rings. The experimental Raman spectrum (thin) is from Ref. [11].

intensity of the sharp Raman lines would provide information concerning the ring statistics, a conceptual way of describing the structure which has remained only theoretical so far.

5. The E´1 defect]

We then used our first-principles method to investigate the E´1 defect in a-quartz and the analogous Eg' in vitreous silica [18, 19]. A major motivation for the investigation of this charged defect is its responsabi- lity in the degradation of SiO_2 -based electronic devices. Our approach is particularly suited to study defects because the possibility of relaxing atomic coordinates allows us to compare the energies of competitive configurations. In this way, a microscopic structural description of the defect has been found [20]. Our work supports the attribution of both the E1' and Eg' defects to positively charged oxygen vacancies. Using the calculated electron spin densities for our model E´1, we fully characterize the hyperfine interactions with nearby [29]Si, which are measured in electron spin resonance experiments [21]. Our results [20] explain well both the strong and the weak features that are observed in the experimental spectra (Table 1).

Table 1: Hyperfine parameters for α-quartz. Experimental data are from Ref. [21].

	Experiment			Theory		
	values (MHz)	θ	ϕ	values (MHz)	θ	ϕ
A_{strong}	1269.7	114.1°	229.7°	1434.5	113.0°	228.3°
	1095.0	128.3°	340.4°	1248.5	101.3°	318.5°
	1094.5	132.1°	115.9°	1245.5	159.0°	70.4°
A_{1weak}	27.5	140.7°	284.5°	61.9	141.6°	281.8°
	22.3	125.5°	133.9°	45.3	127.0°	157.3°
	22.1	104.6°	33.1°	45.9	119.3°	50.3°
A_{2weak}	26.0	58.9°	260.9°	67.3	59.7°	252.9°
	21.0	104.4°	179.9°	51.3	93.3°	168.6°
	20.9	35.0°	111.4°	50.3	25.3°	78.6°
A_{3weak}				11.5	131.4°	347.3°
				10.2	99.6°	186.6°
				9.6	148.7°	83.3°

6. The Si(001)-SiO$_2$ interface

In the last part of our study we investigated the microscopic structure at the Si(001)-SiO$_2$ interface. The traditional interpretation of photo-emission spectra [22] had been challenged by a recent experiment in which spherosiloxane clusters were deposited on Si(001) [23]. Since the correct interpretation of photoemission results directly bears on the adopted interface models, we started our investigation by addressing this issue. We first generated several interface models by attaching various crystalline oxides to Si(001) and allowing for full relaxation within our first-principles approach (Fig. 5) [24–26]. Then, we calculated Si 2r core-levels for silicon atoms in different bonding con-figurations at the interface and found that the traditional interpretation was confirmed [26–29]. Our study showed that the role of core-hole relaxation is important contributing to about 50% of the shifts. In order to understand the experiment which challenged the traditional interpretation of Si 2r shifts, we adressed the system composed of spherosiloxane clusters on Si(001) [30]. The conclusion of this investigation is that the apparent inconsistency of these experimental
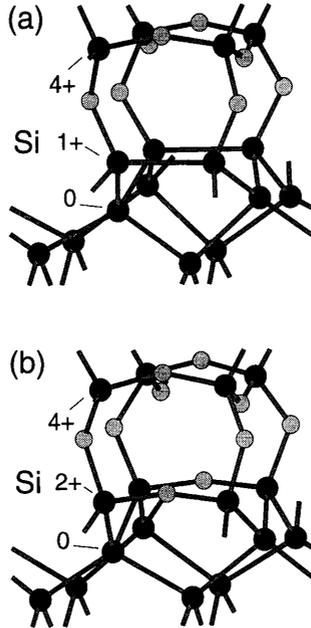
Figure 5: Ball and stick models showing the relaxed positions of two interface structures generated in this work: (a) dimer model, (b) oxygen bridge model. The formal Si partial oxidation states are indicated.

results with the traditional interpretation are likely due to a too simplistic assumption in the experimental work of the cluster-on-surface structure.

The incorporation of a low concentration of nitrogen atoms at the $Si(001)$-SiO_2 currently appears as the most promising way to meet industrial requirements for the near future. Further improvement of the quality of electronic devices therefore critically relies on information regarding the situation of the incorporated nitrogen atoms. We established a correspondence between the bonding properties of these incorporated nitrogen atoms and the N 1s core-level shifts as measured in photoemission experiments [31, 32]. Our study leads to an interpretation of N 1s photoemission spectra, in which the N atom

always forms three bonds to silicon atoms, both in the neighborhood of the interface and further in the oxide [31, 32].

More recently, with the scope of characterizing the atomic processes occuring during oxidation, we simulated the oxidation of several layers of the silicon substrate by using first-principles molecular dynamics in high-temperature conditions [33]. A shortliving bonding configuration could be identified in which an oxygen atom is bonded to three silicon atoms. This appears to be the dominant mechanism through which topological modifications of the structure occur in the neighborhood of the interface. The structure resulting from the final quench represents the first example of a computer-generated model of the interface.

7. Conclusion

In conclusion, the use of first-principles methods in the context of disordered SiO_2 systems has provided a valuable tool to investigate properties which had remained inaccessible so far. These methods provide total energies and forces that act on the ions, and are therefore particularly convenient to generate microscopic models even when the detailed atomic structures are unknown.

The real wealth of the present study resides however in the use of various techniques of analysis which allow a continuous comparison with experimental data. A special effort has been devoted in the present research study to relate the microscopic model to the most appropriate piece of experimental information. By establishing these links consistently within first-principles schemes, the intrinsic accuracy of these approaches could be maintained up to the comparison with experiment. This lead to the explanation of several poorly understood features in the experimental spectra, providing a deeper insight in the underlying physical properties. The application to disordered SiO_2 systems in this work demonstrates that the appropriate use of numerical simulation provides an extremely powerful tool to investigate the disordered state of matter.

8. Acknowledgements

References

[1] "The physics and technology of amorphous SiO2", edited by R.A.B. Devine (Plenum Press, New York, 1988).

[2] The Physics and Chemistry of SiO2 and the Si-SiO2 Interface 2, edited by C.R. Helms and B.E. Deal, (Plenum Press, New York, 1993).

[3] A. Pasquarello, K. Laasonen, R. Car, C. Lee and D. Vanderbilt, Physcal Review Letters 69, 1982 (1992).

[4] R. Car and M. Parrinello, Physcal Review Letters 55, 2471 (1985).

[5] For a review see G. Galli and A. Pasquarello, in "Computer Simulation in Chemical Physics", edited by M.P. Allen and D.J. Tildesley (Kluwer, 1993) p. 261.

[6] J. Sarnthein, A. Pasquarello, and R. Car, Physical Review Letters 74, 4682 (1995).

[7] J. Sarnthein, A. Pasquarello, and R. Car, Physical Review B 52, 12690 (1995).

[8] S. Susman, K.J. Volin, D.L. Price, M. Grimsditch, J.P. Rino, R.K. Kalia, P. Vashishta, G. Gwanmesia, Y. Wang, and R.C. Liebermann, Physical Review 43, 1194 (1991).

[9] J.M. Carpenter and D.L. Price, Physcal Review Letters 54, 441 (1985).

[10] C.T. Kirk, Physical Review B 38, 1255 (1988).

[11] Galeener, F.L., Solid State Communications 44, 1037 (1982).

[12] R.M. Pick and M. Yvinec, in Lattice Dynamics, edited by M. Balkanski, (Paris, Flammarion, 1977), p.\ 459.

[13] A. Lehmann, L. Schumann, K. Hübner, Physica Status Solidi (b) 117, 689 (1983).

[14] J. Sarnthein, A. Pasquarello and R. Car, Science 275, 1925 (1997).

[15] M. Wilson, P.A. Madden, M. Hemmati, and C.A. Angell, Physcal Review Letters 77, 4023 (1996).

[16] A. Pasquarello and R. Car, Physical Review Letters 79, 1766 (1997).

[17] A. Pasquarello and R. Car, Physical Review Letters 80, 5145 (1998).

[18] R.H. Silsbee, Journal of Applied Physics 32, 1459 (1961).

[19] R.A. Weeks, Physical Review 103, 570 (1963).

[20] M. Boero, A. Pasquarello, J. Sarnthein and R. Car, Physical Review Letters 78, 887 (1997).

[21] M.G. Jani, R.B. Bossoli, and L.E. Halliburton, Physcal Review B 27, 2285 (1983).

[22] F.J. Himpsel, F.R. McFeely, A. Taleb-Ibrahimi, J.A. Yarmoff, and G. Hollinger, Physical Review 38, 6084 (1988).

[23] M.M. Banaszak Holl and F.R. McFeely, Physics Review Letters 71, 2441 (1993).

[24] A. Pasquarello, M.S. Hybertsen and R. Car, Applied Surface Science 104/105, 317 (1996).

[25] A. Pasquarello, M.S. Hybertsen and R. Car, Applied Physics Letters 68, 625 (1996).

[26] A. Pasquarello, M. S. Hybertsen and R. Car, Physical Review Letters 74, 1024 (1995).

[27] A. Pasquarello, M.S. Hybertsen and R. Car, Physical Review B 53, 10942 (1996).

[28] A. Pasquarello, M.S. Hybertsen and R. Car, Journal of Vacuum Science and Technology B 14, 2809 (1996).

[29] A. Pasquarello, M.S. Hybertsen and R. Car, Physica Scripta T66, 118 (1996).

[30] A. Pasquarello, M.S. Hybertsen and R. Car, Physical Review B 54, R2339 (1996).

[31] G.-M. Rignanese, A. Pasquarello, J.-C. Charlier, X. Gonze, and R. Car, Physical Review Letters 79, 5174 (1997).

[32] A. Pasquarello, M.S. Hybertsen, G.-M. Rignanese, and R. Car, in Fundamental Aspects of Ultrathin Dielectrics on Si-based Devices, edited by E. Garfunkel, E. Gusev and A. Vul, (Kluwer, Dordrecht, 1997) p. 89.

[33] A. Pasquarello, M.S. Hybertsen, and R. Car, Nature, in press (1998).