Letter to the Editor

Avoidance of a continuous-random-network in vitreous silica: Entropic and energetic consequences

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ABSTRACT

The relative entropic contributions of correlated vs. uncorrelated Si−O bond length and Si−O−Si bond angle distributions in the corner-shared tetrahedral network of vitreous silica are estimated semi-quantitatively using the concept of differential entropy. The results suggest that a positively correlated Si−O vs. Si−O−Si distribution will be entropically stabilized in a glass structure over a negatively correlated distribution, which is typical of crystalline polymorphs of silica. This hypothesis lends support to the recent experimental observation of a positively correlated joint distribution of Si−O distances and Si−O−Si angles in vitreous silica by ^{17}O nuclear magnetic resonance spectroscopy. On the other hand, an estimation of the relative effect of these distributions on the ring strain energy suggests that the glass structure avoids a random or uncorrelated joint distribution of these structural parameters as in a continuous random network, due to the high strain energy associated with such a distribution.

1. Introduction

The structure of vitreous silica (SiO_2) has been studied quite extensively in the past, using a wide variety of experimental and simulation techniques [1–10]. These studies have provided a great wealth of information on the average structure and topology of the corner-shared network of SiO_4 tetrahedra that characterizes the structure of this archetypal glass-former. However, the statistical distribution of several short-range structural parameters including that of the inter-tetrahedral Si−O−Si bond angles have remained poorly constrained. High-energy X-ray diffraction experiments have provided rather accurate estimates of the Si−O and Si−Si pair distributions in the glass structure which are typically used to estimate the probability distribution function (PDF) of the Si−O−Si angles under the assumption that the Si−O and the Si−Si distances are uncorrelated quantities [2]. However, the validity of such an assumption remains questionable [3], especially since crystalline silica polymorphs display a relatively weak but clear correlation between the Si−O distances and the Si−O−Si angles (Fig. 1). Interestingly, this correlation in crystals follows the valley in the corresponding potential energy surface of $H_6Si_2O_7$ dimer molecules, obtained by Gibbs and coworkers [11] using restricted Hartree-Fock type calculations with the B3LYP/6-311 + G(2d,p) basis set (Fig. 1).

Classical molecular dynamics (MD) simulations of vitreous silica have resulted in completely uncorrelated Si−O vs. Si−O−Si PDFs that can be ascribed to the lack of explicit inclusion of a three-body term in the potential that may incorporate such correlation effects [9].

Moreover, the cooling rates used in all MD simulations are rather high compared to the experimental cooling rates, which may have unknown effects on the distributions of structural parameters and on the correlations between such distributions. On the other hand, first principles molecular dynamics (FPMD) simulations of vitreous silica, based on the density functional theory, have not explicitly addressed this issue to date [10,12]. Unfortunately, some of these FPMD studies employ low-temperature annealing of classical-MD generated structures that do not achieve global structural equilibration characteristic of the glass transition temperature and therefore, may not provide meaningful statistics.

The first and only experimental indication to date, in favor of a correlation between the Si−O distances and the corresponding Si−O−Si angles in the vitreous silica network, comes from a two-dimensional (2D) ^{17}O dynamic-angle-spinning (DAS) nuclear magnetic resonance (NMR) spectroscopic study [3]. The results of this study provided intriguing evidence in favor of the existence of a rather strong positive correlation between these structural parameters (Fig. 1). As noted above, a positive correlation is quite the opposite of what is observed in crystalline silica polymorphs. More recently, similar 2D ^{17}O DAS NMR studies of vitreous silica quenched from high pressures (up to ~14 GPa) have shown that such a positive correlation remains intact upon densification of the structure, however, the mean of the joint PDF moves in the direction of smaller Si−O−Si angles and longer Si−O distances [6]. The pressure-dependent trajectory of this mean also appears to follow the enthalpy minimum in Fig. 1, occupied by the corresponding quantities in crystalline silica polymorphs [6]. Nevertheless, previous
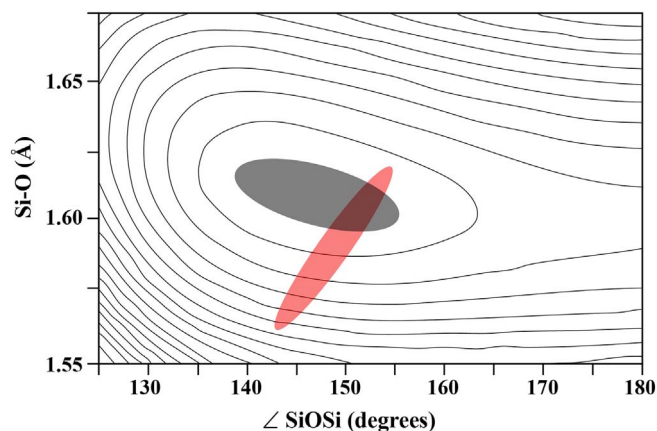
Fig. 1. Energy contours representing potential energy surface for Si—O—Si angle vs. Si—O distance calculated by Gibbs et al. [11] for the $H_6Si_2O_7$ molecule using a restricted Hartree-Fock analysis with B3LYP/6-31IG(2d,p) basis set. Contour spacing is 2 kJ/mol with the minimum energy configuration at 0 kJ/mol. The gray-shaded ellipse represents the region occupied by Si—O vs. Si—O—Si values for practically all crystalline silica polymorphs with Si in tetrahedral environment. The narrow orange-shaded ellipse represents the joint PDF of positively correlated Si—O distances and Si—O—Si angles in vitreous silica as determined by ^{17}O DAS NMR [3].
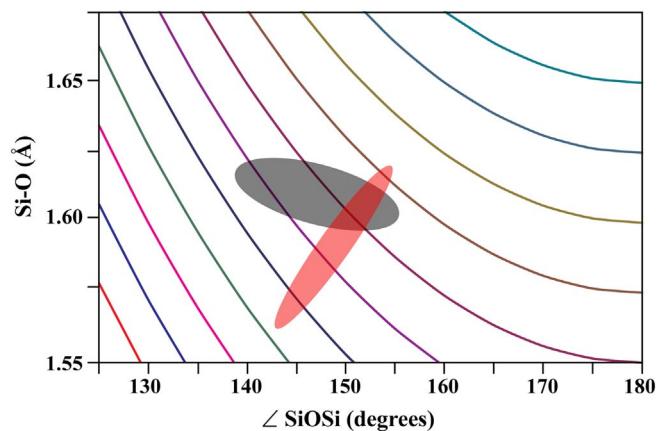

Fig. 2. Contours representing iso Si—Si distances are overlain on the gray- and orange-shaded ellipses from Fig. 1. Contour lines increase from Si—Si = 2.8 Å at the bottom left corner to 3.3 Å at the top right corner, in steps of 0.05 Å.

calorimetric measurements [13] have demonstrated that the energetic difference between vitreous silica and the majority of its crystalline polymorphs is rather small ($\leq \pm 5$ kJ/mol). Therefore, the configurational entropic contributions of structural disorder must be considered in order to understand the distribution of the short-range structural parameters and any correlations between them that are stabilized in the glassy/supercooled liquid state. One interesting observation that lends support to this conjecture is that the experimentally determined positively correlated Si—O vs. Si—O—Si joint PDF in vitreous silica extends in the direction that is nearly perpendicular to the iso Si—Si distance contours (Fig. 2) i.e. the joint distribution maximizes the variation in inter-tetrahedral Si—Si distances between the neighboring $SiO_{4/2}$ tetrahedra in the glass structure. This structural characteristic of the glass is in clear contrast with the case for the crystalline polymorphs where the Si—O vs. Si—O—Si correlation extends in the direction nearly parallel to the Si—Si contour (Fig. 2), thereby minimizing the variation in the inter-tetrahedral distance as to be expected in structures constrained by strict geometric order at all length scales. It must be noted here that entropic contributions from structural disorder at the short-range is significantly larger than that from disorder at the intermediate and longer range. Here we consider the problem of estimating the entropy contribution from nearest neighbor bond length and bond angle

distributions in vitreous silica. We provide evidence in favor of the hypothesis of entropy maximization being an important controlling factor that gives rise to a positive correlation between Si—O and Si—O—Si PDFs. Furthermore, the effect of ring strain energetics on structural correlations is also discussed.

2. Configurational entropy of multivariate Gaussian PDFs

The configurational entropy contribution from the joint PDF of the short range structural parameters, namely the Si—O distance, the Si—O—Si angle and the Si—Si distance, is estimated by approximating their individual PDFs to be Gaussian. Such an approximation is consistent with the expectation from the central limit theorem as well as with recent experimental observations [3]. For structural variables with continuous PDFs, it is more appropriate to consider the differential entropy instead of the more familiar discrete entropy. The discrete entropy S is represented by the familiar Gibbs expression: $S = -k_B \sum_i P_i \ln P_i$, where P_i is the discrete probability of the occurrence of the i-th microstate [14]. For continuous variables, one can extend the idea of discrete entropy into differential entropy S^* by simply replacing the sum in the Gibbs' expression above with an integral such that:

$$S^* = -k_B \int P(x) \ln P(x) dx \tag{1}$$

where the integral runs over all values of a structural variable x with a PDF $P(x)$.

For a multivariate Gaussian distribution of n structural variables (x_1, ...x_n), with a mean vector $\mathbf{\mu}$ and a covariance matrix $\mathbf{K}$, the differential entropy is given by [14]:

$$S^* = \frac{1}{2}nk_B + \frac{1}{2}k_B \ln[(2\pi)^n |\mathbf{K}|] \tag{2}$$

where $|\mathbf{K}|$ is the determinant of the covariance matrix with elements K_{IJ}, which for a pair of random variables I and J that can take m pairs of values (v_i, v_j) is given by the familiar expression: $K_{IJ} = \frac{1}{m} \sum_{i=1}^{m} (v_i - \langle v_i \rangle) * (v_j - \langle v_j \rangle)$ with angular brackets denoting the mean values of I and J. Therefore, it is clear from Eq. (2) that the differential entropy S^* is proportional to $\ln|\mathbf{K}|$. We also note that for any specific variance, the differential entropy of a PDF is maximum when it is a Gaussian. Although differential entropy does not lead to an exact analogue of discrete entropy for a continuous variable, it serves well for semi-quantitative purposes, the relative trends in differential entropy being consistent with those in discrete entropy.

3. Estimation of configurational entropy: methodology

It is clear from the discussion above that for bond lengths and bond angles with PDFs characterized by specific variances, the structure will have the highest configurational entropy if the structural parameters are completely uncorrelated, as is implicit in the celebrated Continuous Random Network (CRN) model of Zachariasen [15]. This is because, for a CRN the off-diagonal elements of the covariance matrix $\mathbf{K}$ will be zero and therefore, its determinant will reach the maximum value and so will the configurational entropy. However, as noted earlier, the results of previous ^{17}O DAS NMR experiments suggest the existence of a strong positive correlation between the Si—O distance and the Si—O—Si angle in vitreous silica while crystalline SiO_2 polymorphs appear to follow a weak negative correlation [3,11]. In the following, we estimate the effect of such correlations on the configurational entropy of the vitreous silica network. As detailed below, four different scenarios are considered; each of them being characterized by the same Si—O—Si distribution but different Si—O vs. Si—O—Si correlations. Besides random correlation, two negative and one positive correlation are considered, which are designated with the prefixes n and p corresponding to negative and positive, respectively.

The ^{17}O NMR-derived positively correlated PDFs for the Si—O distance d_{Si-O} and the Si—O—Si angle θ, as reported in [3], are