



# Understanding the atomic dynamics and thermodynamics of glasses: Status and outlook



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## ABSTRACT

The heat capacity of glasses at temperatures of about  $\sim 10$  K for a long time was considered to be anomalously higher than that of the corresponding crystals. The related excess of the low-energy vibrational states, the so-called 'boson' peak, was similarly considered to be anomaly distinguishing glasses from crystals and related to their disordered state. Recent results reveal that (i) the difference in the discussed properties occurs not because the glass is structurally disordered, but because it (usually) has lower density than that of the corresponding crystal, (ii) the heat capacity of glasses and crystals with the same densities is quite similar, and (iii) the boson peak is the glassy counterpart of the van Hove singularity of the corresponding crystal. We analyze the generality of the new results and discuss the compatibility of the suggested interpretation of the boson peak with available experimental data. Analyzing the relation of the new results to various theoretical models, we discuss a possible experimental approach to explore further the nature of the low-frequency vibrational excitations in glasses.

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## 1. Introduction

Before 1950s, the low temperature heat capacity of glasses and other amorphous solids was considered to be similar to that of the corresponding crystals, because the number and the thermal population of the long wavelength phonons were supposed to be independent of translational periodicity [1]. In particular, the specific heat of glasses was expected to follow the Debye  $T^3$  law, and "the point was so obvious that it did not encourage experimental investigations" [2].

The "non-encouraged" experiment, however, was conducted and unexpectedly revealed two anomalies: At  $\sim 10$  K, the thermal conductivity of glasses was found to be several orders of magnitude smaller [3], and the heat capacity several times bigger [4] than those of the corresponding crystals. These observations initiated detailed investigations of the role played by disorder in the atomic dynamics and thermodynamics of glasses.

The anomalously low thermal conductivity was relatively soon successfully explained by the extensive phonon scattering caused by disorder. Disorder decreases the mean free path of the phonons, and, therefore, tremendously decreases the thermal conductivity.

The understanding of the excess of the heat capacity, on the contrary, demanded somewhat longer studies. The excess of heat capacity in glasses at  $\sim 10$  K as compared to that of the corresponding crystals was found to be associated to a similar excess in the vibrational excitations in the  $\sim 1$  THz frequency range of the density of states (DOS)  $g(E)$  [5]. In the reduced DOS  $g(E)/E^2$  presentation, these states form a distinct peak (the so-called 'boson' peak) at a position where the reduced DOS of the corresponding crystals is nearly flat (more precisely, on the low-energy slope of the acoustic van Hove singularity). Similar to phonons (and contrary to the tunneling excitations located at significantly lower energies), these excess states follow the Bose statistics, explaining the name of 'boson' peak.

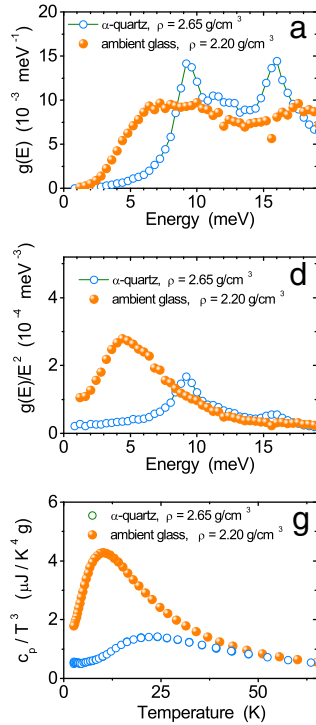
This excess of heat capacity at low temperature and the corresponding excess in the vibrational density of states are universally observed for all glasses and with all relevant experimental techniques. Nevertheless, the results of numerous experimental and theoretical studies still do not converge to a unified answer to *how disorder causes these features*.

Unexpectedly, recent experiments [6,7] have suggested that disorder possibly *does not do it*. Being entirely responsible for the anomalous thermal conductivity of glasses, disorder almost does not affect the frequency spectrum of the atomic vibrations and, correspondingly, the heat capacity of glasses. Different from the thermal conductivity case, the difference in the heat capacity of glasses and crystals is caused by

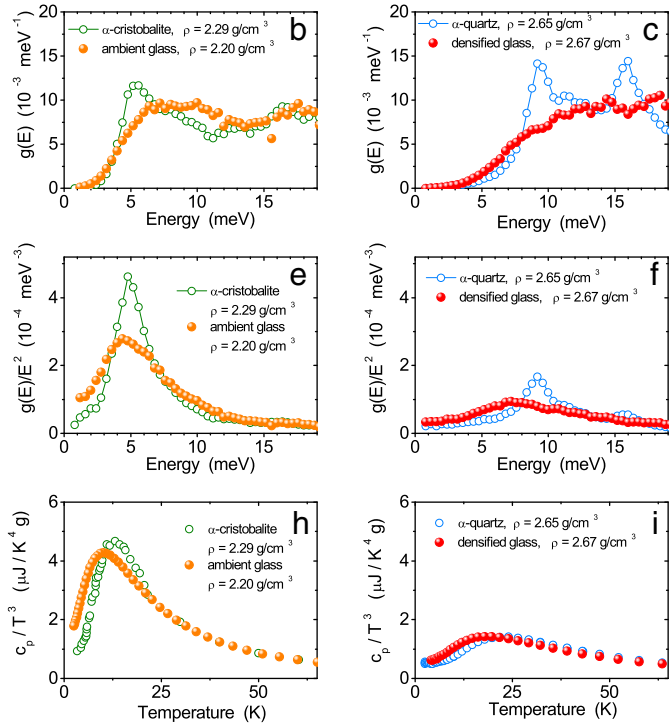
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Most common SiO<sub>2</sub> glass and crystal

## Glasses and crystals with the same densities



**Fig. 1.** The density of states  $g(E)$  (a–c), the reduced density of states  $g(E)/E^2$  (d–f), and the heat capacity  $c_p/T^3$  (g–i) for various glassy and crystalline polymorphs of SiO<sub>2</sub>. The left panels (a, d, g) compare the *most common* glassy and crystalline polymorphs and reveal a noticeable difference in the displayed properties. The middle and the right panels compare the glassy and crystalline polymorphs with *matched densities*, namely, the low-density (b, e, h) and high-density (c, f, i) polymorphs. They demonstrate that the atomic dynamics and thermodynamics of the glassy and crystalline polymorphs with matched densities do not differ much from each other. Adapted from Ref. [7]. The heat capacity data for  $\alpha$ -cristobalite (h) are from Refs. [13,14].

another inherent feature of glasses, namely, by their (usually) lower density.

## 2. Results of the new experiments

Fig. 1 summarizes the results of the recent experimental studies of SiO<sub>2</sub> glasses and crystals by inelastic X-ray scattering [7]. SiO<sub>2</sub> is not only *the* archetypal and most studied system. More importantly, SiO<sub>2</sub> exists in various glassy and crystalline polymorphs with different structures and densities.

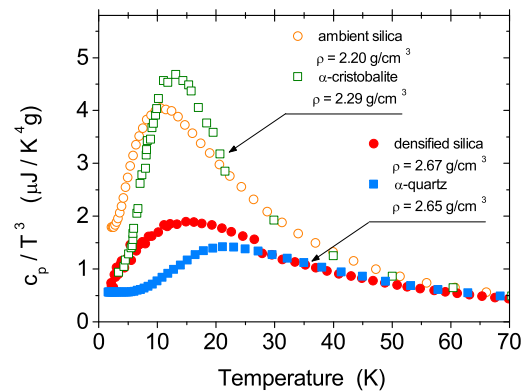
Disordered materials are normally characterized by a specific volume larger than that of the corresponding ordered ones. This trend is well documented in the literature (often discussed as the excess volume of glasses). Therefore, the density of a glass is normally smaller than the density of the corresponding crystal. In this respect, the SiO<sub>2</sub> system is extremely interesting: The density ( $\rho$ ) of the most common SiO<sub>2</sub> glass (ambient vitreous silica,  $\rho = 2.20 \text{ g/cm}^3$ ) is, similar to other systems, smaller than the density of the crystal stable at ambient conditions ( $\alpha$ -quartz,  $\rho = 2.65 \text{ g/cm}^3$ ). However, SiO<sub>2</sub> also exists in another, lower-density crystalline form ( $\alpha$ -cristobalite,  $\rho = 2.29 \text{ g/cm}^3$ ). The density of this crystal is nearly the same as the density of the ambient glass. Furthermore, SiO<sub>2</sub> exists also in another, higher-density glassy form (densified vitreous silica,  $\rho = 2.67 \text{ g/cm}^3$ ) [8]. The density of this glass is nearly the same as the density of  $\alpha$ -quartz.

Thus, SiO<sub>2</sub> offers a fantastic  $2 \times 2$  matrix of (dis)order versus density, which allows for an empirical, i.e., model-independent evaluation of the relative role played by structural disorder and density. In a graphical form, this evaluation is presented in Fig. 1.

The left column of Fig. 1 compares the DOS, reduced DOS and specific heat for the most common SiO<sub>2</sub> glass and crystal polymorphs: ambient vitreous silica and  $\alpha$ -quartz. It perfectly illustrates the concept of the “anomalous” atomic dynamics and thermodynamics of glasses

discussed in the Introduction. However, this couple of glass and crystalline polymorphs corresponds to the “diagonal” of the matrix previously referred to: they differ both in (dis)order and in density. Since we want to understand the effect of disorder and to exclude the effect of density, such a “diagonal” comparison is clearly not sufficient.

The comparison of SiO<sub>2</sub> glasses and crystals with matched densities is presented in the middle and right columns of Fig. 1. Leaving on a side for the moment of any interpretation, we simply summarize the objective experimental observations: (i) the boson peak of glasses appears as a smooth counterpart of the van Hove acoustic singularity of the corresponding crystals (Fig. 1e, f); (ii) the DOS of glasses appears as a smooth



**Fig. 2.** The data available in literature for the specific heat  $c_p/T^3$  of various glassy and crystalline polymorphs of SiO<sub>2</sub> [4,13–15]. The specific heat shows a clear correlation with density and nearly no dependence on the presence or absence of disorder. Note that the recent measurements (Fig. 1i) do not confirm the sudden increase of the specific heat for the densified silica glass on cooling below 27 K reported in Ref. [15].

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