

## Experimental evidence of a liquid-liquid transition in interfacial water

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received 5 October 2004; accepted in final form 2 May 2005

published online 27 May 2005

PACS. 64.70.Ja – Liquid-liquid transitions.

PACS. 61.25.Em – Molecular liquids.

PACS. 61.12.Ex – Neutron scattering (including small-angle scattering).

**Abstract.** – At ambient pressure, bulk liquid water shows an anomalous increase of thermodynamic quantities and apparent divergences of dynamic properties on approaching a temperature  $T_s$  of 228 K. At normal pressure, supercooled water spontaneously freezes below the homogeneous nucleation temperature,  $T_H = 235$  K. Upon heating, the two forms of Amorphous Solid Water (ASW), LDA (Low Density Amorphous Ice) and HDA (High Density Amorphous Ice), crystallise above  $T_X = 150$  K. As a consequence, up to now no experiment has been able to explore the properties of liquid water in this very interesting temperature range between 150 and 235 K. We present nanosecond-time-scale measurements of local rotational and translational dynamics of interfacial, non-crystalline, water from 77 to 280 K. These experimental dynamic results are combined with calorimetric and diffraction data to show that after exhibiting a glass transition at 165 K, interfacial water experiences a first-order liquid-liquid transition at 240 K from a low-density to a high-density liquid. This is the first direct evidence of the existence of a liquid-liquid transition involving water.

Three possible scenarios (for a review see [1]) have been proposed for elucidating the peculiar properties of liquid water: 1) the “stability limit hypothesis” [2, 3] which supposes that a continuous spinodal line bounds the superheated, stretched and supercooled states of liquid water; 2) the “singularity free hypothesis” [4], based on a percolation picture, in which an increase of the number of water molecules with four hydrogen bond coordination leads to relaxation phenomena that resemble a genuine transition; 3) the existence of a low-temperature critical point ( $T_c \approx 220$  K,  $P_c \approx 100$  Mpa and  $\rho_c \approx 1 \text{ g} \cdot \text{cm}^{-3}$ ) separating two distinct forms of supercooled liquid water, LDL (Low Density Liquid) and HDL (High Density Liquid) [5].

Although the phase diagram of bulk water has been extensively studied, relatively little experimental work has been devoted to the study of the related dynamic quantities. Diffusivity measurements of amorphous solid water support continuity between ASW (Amorphous Solid Water) and liquid water [6]. Computer Molecular Dynamics (CMD) simulations of the dynamics of water in the deeply supercooled regime also support the absence of a thermodynamic

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singularity at  $T_S = 228$  K, and interpret the anomalies of liquid water as a kinetic glass transition [7]. In conflict with these results, a strong to fragile glass transition at  $T_S$  has been invoked to describe the dynamics of two layers of water molecules confined in vermiculite clays [8].

In our study, water is adsorbed as a monolayer on Vycor (Vycor brand porous glass no. 7930 is a product of Corning Glass Works), a porous hydrophilic silica glass.

*Sample preparation.* – A partially hydrated sample was prepared by absorption of water in the vapour phase, until a level of hydration corresponding to a monolayer coverage was obtained (25% hydration).

A DSC (Differential Scanning Calorimetry) experiment was performed on such a 25%  $H_2O$  hydrated Vycor sample and a strong first-order transition, showing rather large hysteresis, was detected around 240 K (fig. 1). Takamuku *et al.* [9] have performed a detailed analysis of thermal, structural and dynamic properties of water in porous silica at various hydration levels. Their thermogram at low hydration shows a doublet at 231 and 236 K and is indeed surprisingly similar to the thermogram shown in fig. 1. They measure a heat of freezing (integration of the doublet) of 1.23 kJ/mol, *i.e.* significantly lower than the heat of freezing of bulk water (6.01 kJ/mol). Such a reduced melting energy with respect to bulk is common when materials are confined [10] and by no way proves that water is adsorbed as a monolayer on the surface. Isotherm of adsorption on Vycor is characteristic of a Type-IV isotherm (IUPAC classification): it shows a rapid increase of amount of material adsorbed onto the substrate at low pressure. This is a clear signature of a high adsorbate-surface interaction. Nevertheless, in porous systems, capillary condensation leading to water “plugs” formation [11] is a real possibility. We have checked by small-angle neutron scattering (not shown) that capillary condensation affects only 10% of the total water mass involved in hydrated Vycor.

*Structure of interfacial water in 25% hydrated Vycor.* – The structure of  $D_2O$  in 25% hydrated Vycor was studied by neutron diffraction using the 7C2 spectrometer of the Orphée reactor of the Laboratoire Léon Brillouin at Saclay (France). The diffraction experiment and the analysis were performed following the scheme of ref. [12]. As already shown in other interfacial water systems [13], no Bragg peak characteristic of crystallisation is observed at this hydration, even when the temperature is decreased down to 77 K (fig. 2).

*Dynamics of water in 25% hydrated Vycor.* – In the present study interfacial water dynamics on similar 25% hydrated Vycor samples was measured as a function of temperature between 70 and 280 K on two time scales using two different inelastic neutron spectrometers. A high-energy resolution experiment, assessing dynamics up to 1 nanosecond, was performed on the IN16 spectrometer (ILL, Grenoble, France) (energy resolution  $1 \mu\text{eV}$ , dynamic range from  $+/-12 \mu\text{eV}$  and  $Q$  range  $0.1 \text{ \AA}^{-1}$  to  $1.9 \text{ \AA}^{-1}$ ). Lower-energy-resolution data, adapted for correlation times up to 15 ps, were measured over a broad dynamic range  $-2 \text{ meV}$  to  $150 \text{ meV}$  using the  $85 \mu\text{eV}$  resolution QENS spectrometer (ANL/IPNS) over the  $Q$  range  $0.5 \text{ \AA}^{-1}$  to  $2.5 \text{ \AA}^{-1}$ .

Based on incoherent neutron scattering data [14] and subsequent CMD simulations [15], a picture of the short-time (picosecond) local bulk water dynamics is available [16]. The rotational dynamic structure factor is given by

$$S_{\text{Rot}}(Q, \omega) = A_0(Q)\delta(\omega) + (1 - A_0(Q))L_{\text{Rot}}(Q, \omega) \quad \text{with} \quad L_{\text{Rot}}(Q, \omega) = \frac{1}{\pi} \frac{\tau_1^{-1}}{\tau_1^{-2} + \omega^2}. \quad (1)$$

$A_0(Q) = j_0(Qr_{\text{OH}})^2$  is the Elastic Incoherent Structure Factor of a hydrogen atom experiencing a rotation over the intramolecular OH distance,  $r_{\text{OH}}$  ( $0.98 \text{ \AA}$ ) with a correlation time  $\tau_1$ . If a molecule is not hydrogen-bonded to any other molecule, it diffuses freely with a translational



Fig. 1

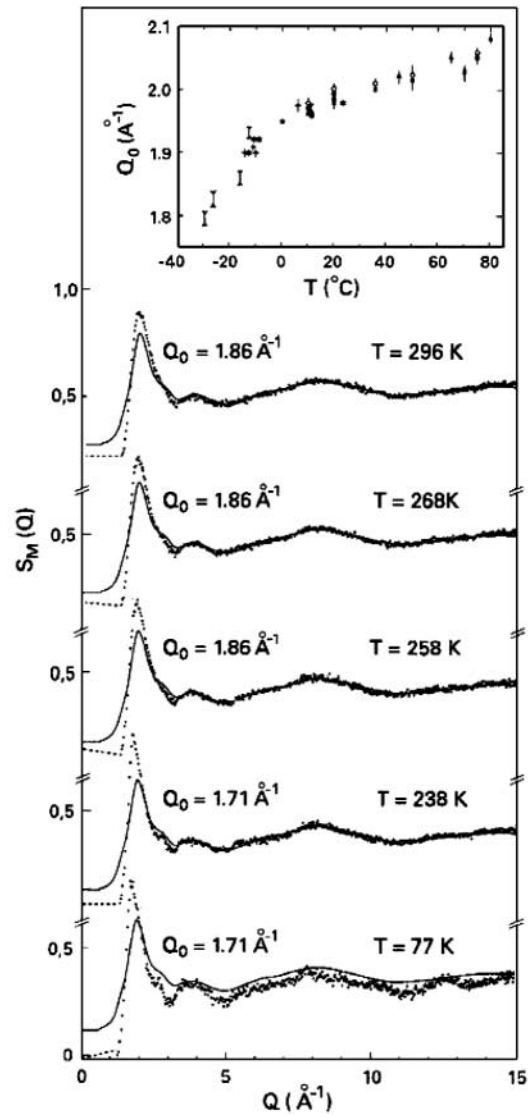


Fig. 2

Fig. 1 – Thermograms of 25% hydrated Vycor. The hydration corresponds to a monolayer of water at the Vycor surface. Cooling and heating are indicated by arrows. Scanning speed 5 K/mn. A genuine calorimetric transition, showing rather large hysteresis, is detected around 240 K. The structural and dynamic data that probe this 240 K event are given in figs. 2 and 4.

Fig. 2 – Temperature dependence of the structure factors ( $\bullet$ ) of a monolayer of water ( $D_2O$ ) on the surface of Vycor (the Vycor matrix has been subtracted). The absence of Bragg peaks over the whole temperature range shows that interfacial water inside Vycor does not nucleate to form crystals. At each temperature, the position  $Q_0$  of the First Sharp Diffraction Peak (FSDP) is given. The inset recalls the temperature dependence of the FSDP position for bulk  $D_2O$  down to the deeply supercooled regime at 242 K. The value  $Q_0 = 1.86 \text{ \AA}^{-1}$  of interfacial water at 296 K corresponds to the FSDP position of bulk supercooled water at about 260 K. For comparison, the structure factor of bulk supercooled water at 263 K (full line) is also given. In hydrogen-bonded liquids, the FSDP position can be related to the density of the system and may be considered as an index of the structure. LDA ( $Q_0^{LDA} = 1.71 \text{ \AA}^{-1}$ ) is characterized by a continuous random H-bond network in which each water molecule is locally engaged in 4 H-bonds. The sudden increase of the  $Q_0$  value between 238 K ( $Q_0 = Q_0^{LDA} = 1.71 \text{ \AA}^{-1}$ ) and 258 K, shown here, suggests a structural change from a low-density form to a higher-density form of interfacial water.

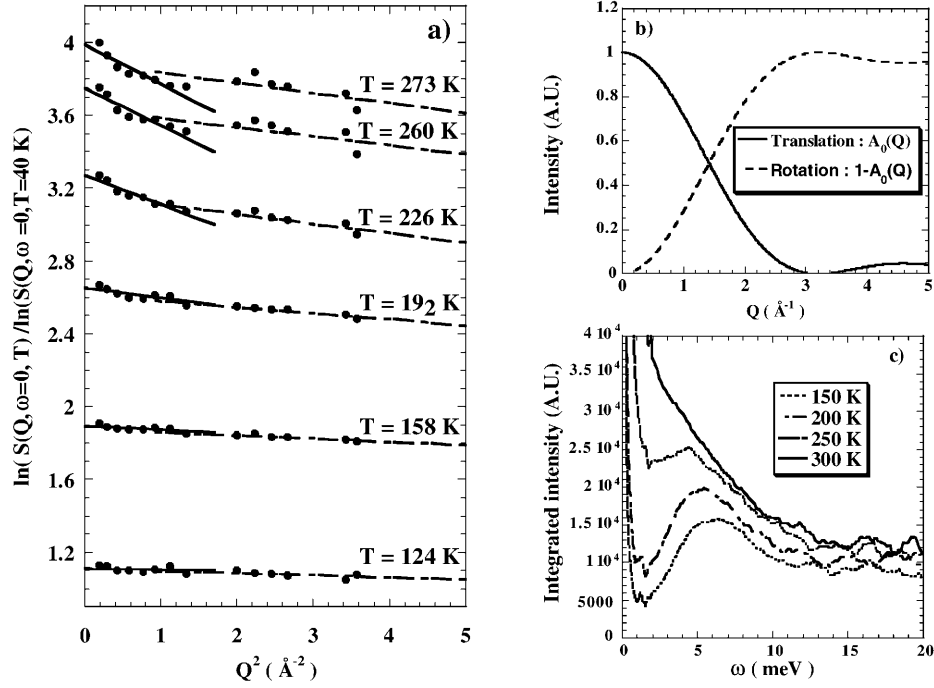


Fig. 3 – a) Normalized  $\ln S(Q, \omega = 0)$  vs.  $Q^2$  at selected temperatures in the range 77 K, 280 K. At high temperature, two distinct linear regions may clearly be defined. b) As shown in eq. (3), the translational and rotational contributions to the scattered intensity are strongly  $Q$ -dependent, making it possible to discriminate between them. From the data in the low- $Q$  range [ $0.1 \text{\AA}^{-1}$ - $1.0 \text{\AA}^{-1}$ ] of a), we extract a first characteristic mean-square displacement,  $\langle u^2 \rangle_{\text{Trans}}$ , related to the water molecule long-range diffusion. From the data in the higher- $Q$  range [ $1.1 \text{\AA}^{-1}$ - $1.9 \text{\AA}^{-1}$ ] we define  $\langle u^2 \rangle_{\text{Rot}}$ , a mean-square displacement related to the local molecular reorientations [16]. At  $1 \mu\text{eV}$  resolution (fig. 3a), both mean-square displacements are related to correlation times shorter than 1 nanosecond. c) The quasi-elastic signal,  $S(Q, \omega)$  vs.  $\omega$  due to the liquid-like diffusive motions responsible for the  $\langle u^2 \rangle_{\text{Rot}}$  temperature dependence, is shown as a function of temperature (QENS spectrometer, ANL/IPNS, 15 ps timescale).

diffusion coefficient  $D_t$  and the dynamic structure factor is

$$S_{\text{Trans}}(Q, \omega) = \frac{1}{\pi} \frac{f(Q)}{f(Q)^2 + \omega^2}, \quad \text{where} \quad f(Q) = \frac{D_t Q^2}{1 + D_t Q^2 \tau_0}. \quad (2)$$

This is obeyed until one or more H-bonds are formed again. The molecule will remain on this “site” for a residence time  $\tau_0$  (of the order of 1 ps at room temperature), before experiencing this cycle again. If these rotational and translational dynamics are uncorrelated, the global dynamics of a single water molecule is described by the convolution of eqs. (1) and (2):

$$S_{\text{inc}}(Q, \omega) = A_0(Q) \cdot S_{\text{Trans}}(Q, \omega) + (1 - A_0(Q)) S_{\text{Trans}}(Q, \omega) \otimes L_{\text{Rot}}(Q, \omega). \quad (3)$$

For each temperature, the scattered intensity was normalized to the scattered intensity measured at the lowest temperature (70 K).

While a detailed line-shape analysis makes it possible to extract all the parameters of eq. (3), due to the limited neutron flux on such a high-resolution instrument as IN16, such

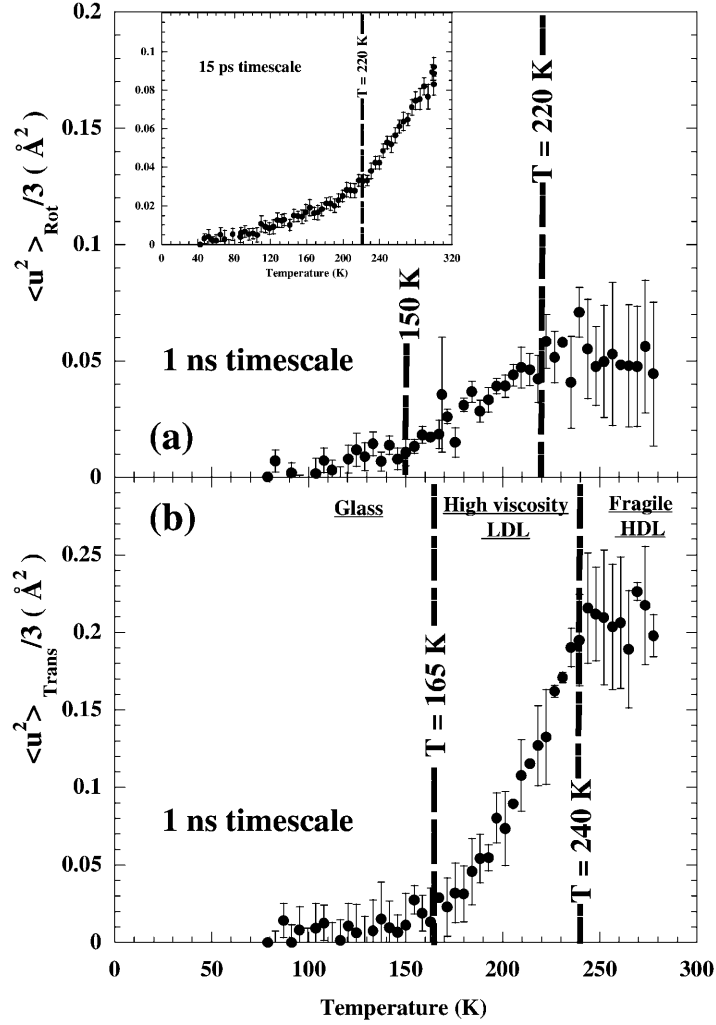


Fig. 4 – Temperature dependence of rotational and translational mean-square displacements of interfacial water  $\langle u^2 \rangle_{\text{Rot}}$  (a) and  $\langle u^2 \rangle_{\text{Trans}}$  (b) have been extracted from the two  $Q$  ranges defined in fig. 3. The measurements were performed at  $1 \mu\text{eV}$  energy resolution, *i.e.* the dynamics is determined up to 1 ns. Inset: temperature dependence of  $\langle u^2 \rangle_{\text{Rot}}$  measured at  $80 \mu\text{eV}$  resolution (QENS, ANL/IPNS), *i.e.* the dynamics is measured up to 15 ps.

a detailed analysis can only be made at a few temperatures. A wider temperature range can be explored using an “elastic scan” [17]. Figure 3 shows selected normalised curves  $\ln(S(Q, \omega = 0))$  *vs.*  $Q^2$  at various temperatures. The mean-square displacements deduced from the low [ $0.1 \text{\AA}^{-1}$ - $1.0 \text{\AA}^{-1}$ ] and high  $Q$  ranges [ $1.1 \text{\AA}^{-1}$ - $1.9 \text{\AA}^{-1}$ ], denoted  $\langle u^2 \rangle_{\text{Trans}}$  and  $\langle u^2 \rangle_{\text{Rot}}$ , are associated with the long-range translational diffusion and local rotational dynamics, respectively (fig. 4).

The mean-square displacements for interfacial water show three dynamic regimes with two crossover temperatures at 150 and 220 K (fig. 4a) for  $\langle u^2 \rangle_{\text{Rot}}$ , and at about 165 and 240 K for  $\langle u^2 \rangle_{\text{Trans}}$  (fig. 4b). Such an upward shift for translations compared to rotations is in line

with the mechanism of ref. [16], since the ability for a given molecule to experience translation follows a previous simultaneous break of all its H-bonds (*i.e.* molecule reorientation).

The absence of rotational dynamics below 150 K ( $\langle u^2 \rangle_{\text{Rot}} \approx 0$ ) but significant dynamics above (strong increase of  $\langle u^2 \rangle_{\text{Rot}}$ ) this temperature, while no structural change is detected, is a clear signature of a rotational glass transition at 150 K. The same arguments apply to  $\langle u^2 \rangle_{\text{Trans}}$  to conclude that interfacial water experiences a translational glass transition at 165 K.

The two known forms of bulk ASW (HDA or LDA) crystallize at  $T_X = 150$  K. This first-order nucleation process is thought to be due to a slightly increased reorientational mobility which allows the system to locally reorganize and find the minimum energy configuration, *i.e.* the crystal form. The 150 K interfacial water “rotational glass transition” observed here could be relevant to this physics, although, in the present system, it does not lead to crystallization. Interestingly also, this interfacial water (translational) glass transition is found to occur at the same temperature as the calorimetric glass transition of bulk water ( $T_g = 165$  K) reported by Velikov, Borick and Angell [18].

Above 165 K, the molecular reorientations become more probable and/or their amplitude increases, as shown by the increasing values of both  $\langle u^2 \rangle_{\text{Trans}}$  and  $\langle u^2 \rangle_{\text{Rot}}$ . As shown in fig. 3c, on a 15 ps timescale, quasi-elastic scattering due to diffusive liquid-like motions is clearly seen at 200 K and above. When the QENS  $85 \mu\text{eV}$  data are treated as in fig. 3, the corresponding  $\langle u^2 \rangle_{\text{Rot}}$  shows a clear transition (inset of fig. 4a) at 220 K. The corresponding sharp transition and levelling off observed on the high resolution  $\langle u^2 \rangle_{\text{Rot}}$  (fig. 4a) results from an instrumental saturation effect. This transition in the local dynamics at 220 K (fig. 4a) is followed around 240 K by a transition in the long-range translational behaviour of the water molecules (fig. 4b). Again due to the sudden fast dynamics at 240 K some saturation also occurs.

On a timescale of 1 nanosecond, below 165 K, interfacial water is a low-density amorphous material ( $Q_0 = Q_0^{\text{LDA}} = 1.71 \text{ \AA}^{-1}$ , see fig. 2) showing no long-range translational dynamics ( $\langle u^2 \rangle_{\text{Trans}} \approx 0$ ). Above 165 K, no change is observed in water density ( $Q_0 = Q_0^{\text{LDA}} = 1.71 \text{ \AA}^{-1}$ , fig. 2) but translational dynamics becomes possible on a 1 nanosecond timescale, as shown by the  $\langle u^2 \rangle_{\text{Trans}}$  non-null value. This is a clear signature of a glass transition at 165 K. At 240 K, this Low Density Liquid (LDL) experiences a first-order transition (see thermograms in fig. 1) to transform in a High Density Liquid, HDL ( $Q_0 = 1.86 \text{ \AA}^{-1}$ , fig. 2). At a temperature  $T$  above 240 K, the structure and the dynamics of this liquid are similar to that of bulk water at a temperature  $T + 30$  K (see fig. 2). This temperature shift can be interpreted within the percolation model of water, assuming that only three hydrogen bonds can be formed between interfacial water molecules instead of four in bulk [19].

*Discussion.* – Most of the recent studies devoted to the physics of water have focused on the possible coexistence of two structures of liquid water between  $T_g$  and the postulated critical point at  $T_s = 228$  K. The idea of such a coexistence line was first supported by the existence of a hypothetical first-order phase transition between LDA and HDA. Despite the recent detection of possible HDL water at the silica/ice interface [20], up to date, the study of liquid water above  $T_X = 150$  K being impossible, the understanding of the nature of the coexistence of LDA and HDA has appeared to be the only way to understand the properties of the hypothetical liquid above  $T_X$ . The nature of this LDA/HDA transition is nevertheless still under intense debate as shown by the conflicting results recently published [21, 22].

From diffraction data, it appears that water at the hydrophilic surface of Vycor does not crystallise. Moreover, the DSC, diffraction and dynamic data, taken together, show that after experiencing a glass transition at 165 K, interfacial water experiences a genuine first-order transition from low-density liquid to a higher-density liquid at 240 K.

The H-bond interaction of the interfacial water molecule with the numerous dangling OH groups (16 silanols/nm<sup>2</sup>) at the Vycor surface supports the similarity (the value of  $T_g = 165$  K in particular) between a water monolayer absorbed on Vycor and bulk water. Since it is a liquid in the temperature range of most interest around 228 K, “Vycor interfacial water” should be a promising model system for improving our knowledge of the physics of water below the bulk water homogeneous nucleation temperature. The investigation of the effects of pressure on the liquid-liquid transition in Vycor interfacial water could be the route to a deeper understanding of the peculiar properties of low-temperature water.

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The authors would like to thank Dr. M. JOHNSON (ILL) for his assistance during the experimentation on IN16 spectrometer, Dr. A. I. KOLESNIKOV (IPNS) for very fruitful discussions and Prof. R. THOMAS (Oxford University) for a critical reading of the manuscript.

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- [16] A water molecule is hydrogen-bonded on average to three or less neighbouring molecules [1]. If due to thermal energy, one hydrogen bond O—H—O moves apart from linearity, by more than 25° [15] the bond breaks. When three of the four H-bonds possibly engaged by a molecule are simultaneously broken, the molecule follows a rotational diffusive movement, characterised by a correlation time  $\tau_1$ , associated by Teixeira *et al.* [14] to the H-bond lifetime.
- [17] This means recording for few minutes the  $Q$ -dependence of the elastic intensity. In a way similar to the X-Ray Debye-Waller effect, the  $Q$ -dependent Gaussian intensity loss  $\exp[-Q^2 \cdot \langle u^2 \rangle]$  can be related to the spatial extension ( $\langle u^2 \rangle$ ) of atoms around their equilibrium position.
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