On the behaviour of liquids and polymers in nano-confinement

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Abstract

Materials confined in nano-scale geometries exhibit very rich physics [1] and are interesting not only from the fundamental point of view, but they are of increasing importance for nanotechnology applications. Size effects play an important role at structural phase transitions, melting transitions, in martensitic materials [1], glass transitions, etc. Very often the question arises, whether a measured size effect originates from the confinement itself, or if it appears due to the interaction with the limiting surface. Using Dynamic Mechanical Analysis (DMA) technique we have studied various molecular glass forming liquids [2] as well as supercooled water [3] confined in nanoporous silica and phase segregated polymers [4]. We show on various examples that DMA measurements can help to disentangle bulk and surface effects in many important systems, including even freezing of water in biological materials.

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References

[3] V. Soprunyuk, M. Reinecker and W. Schranz, Dynamics of liquids and polymers in nanococonfinement, Special Issue of Phase Transitions in honour of Prof. B. Hildebrand, submitted

Low-frequency elastic measurements

The sample geometry for parallel plate method is shown in Fig.1 and the Young’s modulus are presented by next equation:

\[ k = \frac{Y(q)}{S/h} \]

where the geometrical parameters of the sample h and S are given in Fig.1. The Y(q) is Young’s modulus in the q direction. The sizes of the samples were around 1-1.2 mm.

Parallel plate geometry represent purely the complex Young's modulus \( Y' = Y'' + iY'' \), where \( Y' \) and \( Y'' \) are the storage and loss modulus respectively.

Thermal expansion measurements

The changes in the linear dimensions of the sample were estimated according to the equation

\[ \text{thermal} = (L\text{final} - L\text{original}) / L\text{original} \]

where \( \text{thermal} \) – material strain, \( L\text{final} \) - the length of the sample after the change of temperature, \( L\text{original} \) - the length of the sample before the change of temperature.

Elastic properties of polymers

Fig.11, Fig12 Temperature dependence of storage modulus \( E' \) and tan of polyurea JD-2000 at different frequencies.

Fig.13 Measured temperature dependence of tan of polyurea JD-4000 (grey disks) The red full line shows fitted data. Orange and blue lines are generated by considering only either the \( \alpha \) or \( \alpha' \) relaxation. The inset sketches the spatial regions of \( \alpha \) and \( \alpha' \) relaxations.