

Strongly enhanced elastic modulus of solid nitrogen in nanopores

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In this paper we show that solid nitrogen has considerably enhanced elastic properties in the nanopores of a porous glass. Particularly, the first adsorbed molecular layer near the pore wall possesses a shear modulus more than twice as high as the bulk modulus. The interaction between pore surface and pore filling provides a mean for the enhancement of elastic properties. Our discovery shows that nanoconfinement in porous samples can be used to influence the mechanical properties of substances.

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The possibility of building nanostructures has resulted in continuing research of the physical properties on the nanoscale. Many factors influence the electronic and the mechanical properties of such objects. For the characterization and development of new devices it is of great importance to know and understand the fundamental elastic behavior of objects with dimensions of some nanometers. There is no general rule that nano-objects are elastically stronger or weaker than the corresponding bulk counterparts, but nanoeffects can lead to interestingly different properties.

The yield strengths of nanowires, nanoporous structures, and nanocrystalline samples are usually found to be increased.^{1–3} A reduction of the grain size in nanocrystalline copper below a critical value of several nanometers, however, leads again to a smaller strength due to a change of the microscopic deformation mechanism.⁴ The elastic moduli of nanostructures can show values in the range of the corresponding bulk material or also higher or lower moduli and even for the same type of structure, e.g., nanowires or thin films.^{1,3,5} A decrease of the elastic modulus of thin films in comparison to bulk was often observed^{6,7} and could be explained by surface energy considerations.⁸ In contrast, molecular statics and *ab initio* calculations showed the possibility of both a decrease and an increase of the elastic modulus with decreasing thickness depending on atomic coordination and electron redistribution.⁹ Additional factors influencing the elastic behavior on the nanoscale are stress¹⁰ and surface tension.¹¹

Silk is a natural example of a macroscopic material that possesses its good mechanical properties as a result of nanoconfinement (β -sheet nanocrystals).¹² Confinement on the nanoscale can also be achieved with other objects of macroscopic dimensions such as filled porous samples. Nanoporous samples usually possess a high specific surface in the range of 100 m² per 1 g of the sample. Consequently, great amounts of nanoconfined substances can be easily produced and also in such macroscopic samples nanoeffects can be used. The effective elastic properties of such empty porous samples are considerably influenced by the ligament size and the properties of the surface of pore walls.^{2,13–15} Recently, also the electrical tuning of the strength of nanoporous gold has been achieved.¹⁶

For the determination of the elastic properties of nitrogen on the nanoscale we fill with nitrogen a nanoporous sample (Vycor[®] glass) that consists of a nearly pure network of silicon dioxide. Like a sponge, the sample has randomly orientated

and interconnected pores, however, with substantially smaller pores with an average pore diameter of 8 nm (porosity $\phi \approx 25\text{--}26\%$). The melting and freezing temperatures in nanopores are usually shifted to lower temperatures.¹⁷ In many cases the structure of the pore surface prevents a freezing of the first few surface layers of adsorbate near the pore wall.^{18–20} As a result, e.g., the simple argon undergoes a continuous freezing and melting transition over a very broad temperature range of about 40 K.^{20,21} The phenomenon is related to the so-called premelting and interfacial melting that is best known for ice.²³ A fine possibility to study elastic properties and liquid-solid phase transition are measurements with ultrasonic shear waves. Together with the effective density of the sample ρ , the effective shear modulus G of the porous sample can be determined in that way ($G = c^2\rho$, with the ultrasonic velocity c). As liquids cannot sustain shear stress an increase of the effective shear modulus will only be observed when the adsorbate is solid. The carrier frequency of the ultrasonic pulses was ≈ 7 MHz. The wavelength was in the range of a few hundred micrometers, thus being much larger than the pore diameter (8 nm). To ensure an equilibrium condition of the adsorbate at each temperature, several hours were waited between individual temperature steps. For the measurement of a complete temperature cycle, we thus needed almost 2 months. (More details of the method can be found in Refs. 24 and 21.) With this method we could show that argon in porous glass exhibits a shear modulus that corresponds to the modulus of bulk argon.^{20,21} As we shall show, this behavior cannot necessarily be generalized to substances other than argon.

During cooling of a sample filled with approximately one surface layer of nitrogen [virtually constant volume filling fraction $f \approx 0.12$;²⁵ see Fig. 1(b)] or completely filled pores [see Fig. 1(c)], the effective shear modulus of the (partially) filled sample starts to increase below a temperature of $T \approx 55$ K (see Fig. 2); bulk nitrogen freezes at 65 K.²⁶ This is a clear sign that the adsorbed nitrogen starts to freeze (and crystallize) on cooling. As expected, the increase is considerably higher for the completely filled sample as more nitrogen can crystallize. A close look reveals, however, a peculiarity: One surface layer of nitrogen, i.e., only $\approx 12\%$ of the amount necessary for complete filling, causes an increase of the effective shear modulus that corresponds to about 20% of the increase observed for complete filling. This contrasts with our observance for argon, where surface layers contributed proportionally to their filling fraction with the shear modulus of bulk argon.^{20,21}

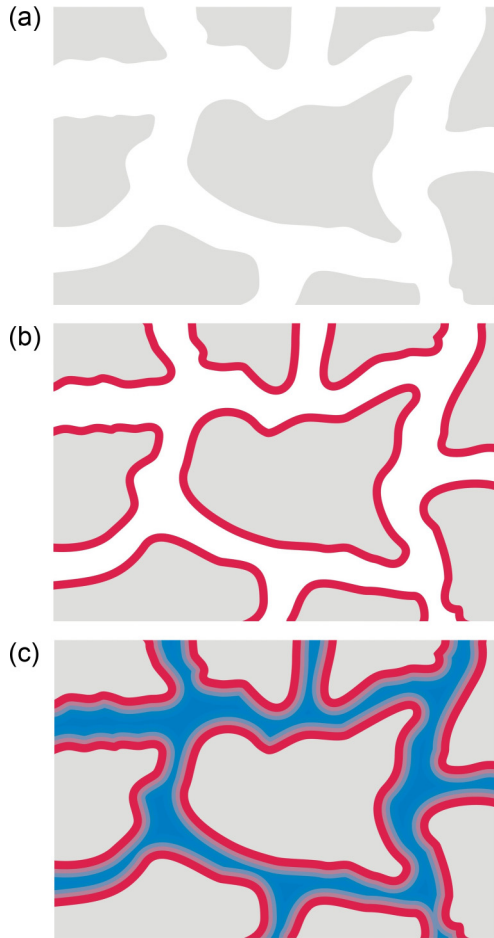


FIG. 1. (Color online) Schematic sketch of nanoporous Vycor glass for different fillings. (a) Structure of the empty sample. (b) At low fillings with nitrogen the adsorbate forms a surface layer (red) with enhanced elastic properties on the pore walls. (c) The completely filled sample. The influence of the pore wall on the filling decreases gradually with increasing distance from the wall. Our analysis shows that in the pore center bulk properties (marked in blue) are reached.

The unusual behavior of the effective shear modulus at different fillings of nitrogen shown in Fig. 2 signifies already different elastic properties of the pore filling. Obviously, the first adsorbed surface layer near the pore wall possesses a higher shear modulus than the rest of the adsorbate or the whole pore filling in the case of complete filling.

We have developed an effective medium analysis for the determination of the intrinsic shear modulus of pore fillings and could experimentally confirm its validity.^{20–22} Thus it is possible to quantify the differences between the shear moduli of different fillings. The effective modulus G is a function of the shear modulus of the empty sample G_0 , the material of the framework (quartz glass) G_Q , the pore filling G_{filling} , and its volume fraction $f = V_{\text{ads}}/V_{\text{pore}}$.^{20–22}

$$G = G_0 + \left(1 - \frac{G_0}{G_Q}\right) f G_{\text{filling}}. \quad (1)$$

Here G , G_0 , and G_Q are measured values and f is determined via the measured number of adsorbed molecules (see Ref. 27).

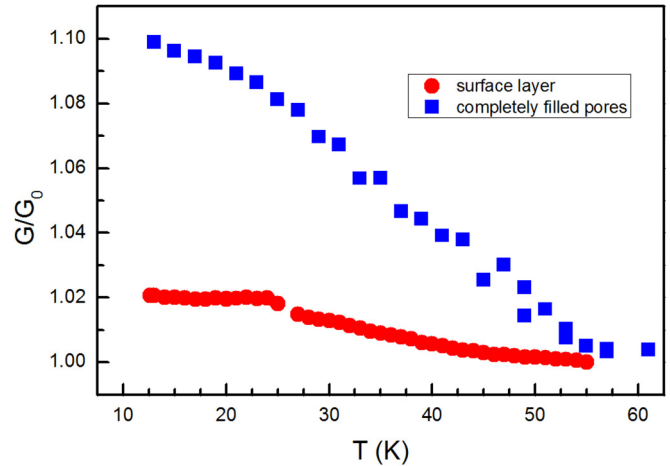


FIG. 2. (Color online) Effective shear modulus of the sample scaled with the modulus of the empty sample at two different fillings: During cooling the effective modulus starts to increase below a temperature of about 55 K. The increase is considerably higher for complete filling ($f = 1$) than for one surface layer ($f \approx 0.12$). At the lowest temperature, however, the increase for the surface layer corresponds to about 20% of the increase for the completely filled sample.

Thus we obtain the average of the modulus of the pore filling for both measurements [see Fig. 3(a)]. The average shear modulus increases for both fillings over a broad range with decreasing temperature. This confirms that the adsorbed nitrogen in the nanopores freezes continuously; a reduction of temperature increases the fraction of solid nitrogen. Below $T \approx 25$ K the shear modulus of one surface layer remains almost constant and the nitrogen layer seems to be completely frozen.

The conclusions drawn from the increase of the effective shear modulus (see above and Fig. 2) are further confirmed by the moduli of one surface layer and the complete pore filling [see Fig. 3(a)]: Whereas the modulus of the complete filling is in the range of 1.0 GPa at low temperatures, the first layer exhibits an unusual high modulus around 1.7 GPa. We can compare these elastic properties with the behavior of bulk nitrogen [see Fig. 3(b)].²⁸ Solid bulk nitrogen is known to change its crystalline structure from hexagonally closed packed (β phase) to face centered cubic (α phase) during cooling ($T \approx 35$ K). This structural transformation is accompanied by an increase of the shear modulus [see Fig. 3(b)]. At low temperatures the shear modulus of bulk nitrogen is only 0.8 GPa.

We do not observe a step in the average shear modulus that would hint at a structural transformation of the crystal structure of the adsorbate, so we can assume that the α phase is suppressed in the nanopores. This is in accordance with x-ray measurements of two similar types of completely filled porous glass samples: The confinement in nanopores prevents the transition of the crystalline structure from the β phase to the α phase. At low temperature a quasi-hcp structure (with lattice defects) is maintained in the pore center.²⁹ This absence of a reorientation during cooling shows an influence of nanoconfinement on nitrogen. The impact of confinement in pores on the structure of the pore filling

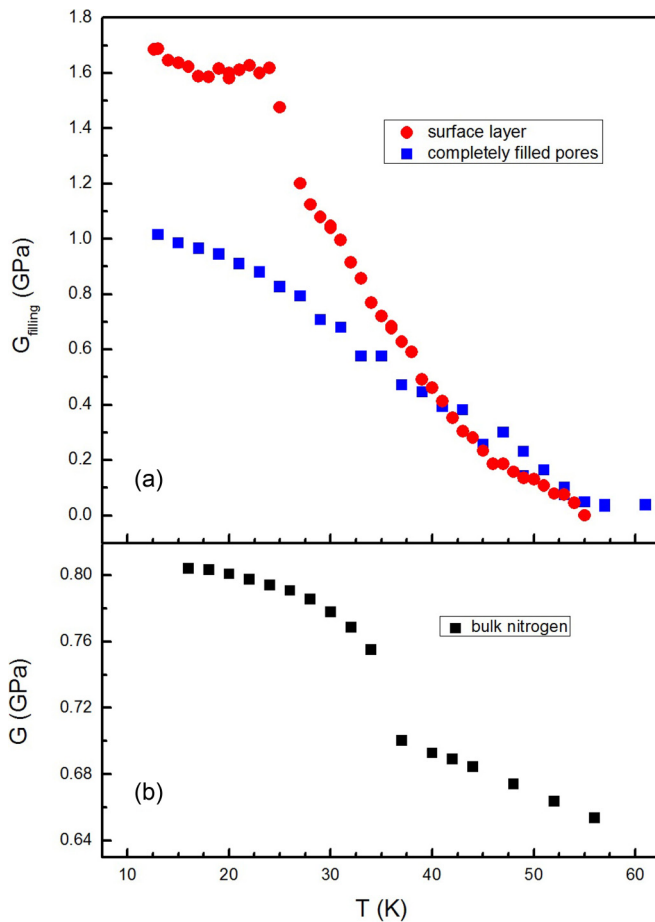


FIG. 3. (Color online) Shear modulus of one surface layer, of the adsorbate for completely filled pores, and of bulk nitrogen as a function of temperature. (a) Below ≈ 40 K the modulus of the surface layer deviates considerably from the modulus of the complete pore filling, reaching a value of ≈ 1.7 GPa at low temperatures. In comparison, the complete pore filling has a modulus of only ≈ 1.0 GPa. (b) At low temperatures the shear modulus of bulk nitrogen [calculated from ultrasonic measurements (Ref. 28)] corresponds to less than 50% of the value for one surface layer.

is known for different porous systems and can result in strains and different crystalline structure or induce disorder in the first few surface layers near the pore wall.^{29–32} The structure of a thin nitrogen layer adsorbed on pore walls of porous glasses has sometimes been described as amorphous or liquidlike.^{29,32} However, the x-ray-diffraction patterns can also be interpreted as resulting from a two-dimensional triangular lattice.³²

The observance that the average shear modulus of the completely filled pore ($G_{\text{filling}} \approx 1.0$ GPa at 12 K) is only ≈ 25 – 30 % higher than the bulk modulus reveals that the greatest part of the filling possesses the elastic modulus of bulk nitrogen. Indeed, the deviation can be explained by a simple superposition of approximately two surface layers ($f_{2SL} \approx 0.25$) with an enhanced modulus and the remaining pore filling with bulk properties: $G_{\text{filling}} \approx f_{2SL} G_{\text{surface}} + (1 - f_{2SL}) G_{\text{bulk}}^{\beta}$, where $G_{\text{surface}} \approx 1.7$ GPa and $G_{\text{bulk}}^{\beta} \approx 0.76$ GPa (taken from a linear extrapolation of the shear

modulus of the β phase of bulk nitrogen at 12 K [see Fig. 3(b)]. Of course, also a continuous transition from the high surface values to bulk properties in the pore center is possible.

The high shear modulus of the surface layer must be related to the pore wall, i.e., to the structure of the surface, its chemical properties, and possibly also the high curvature. The influence of the pore wall is reduced with increasing distance to the wall and the pore center may exhibit typical bulk properties [cf. Fig. 1(c)]. The interaction between the pore surface and the nitrogen molecules thus provides a mean for considerably enhanced elastic properties of the adsorbed surface layer. However, the observance of bulk elastic properties for argon^{20,21} confined in the same porous sample poses a question: Why does nitrogen show enhanced elastic properties and argon does not?

Both substances have bulk shear moduli of the same order. Argon has a spherical structure, whereas nitrogen is a diatomic molecule with a quadrupole moment. It appears important to consider how the electrical and chemical properties influence or even determine the elastic properties of the surface layer. Previously, an infrared spectroscopy study had shown that the pore wall influences the nitrogen molecules in the first two surface layers, whereas pore condensate in the pore center remains bulklike, i.e., infrared inactive.²⁶ The porous glass has a polar pore surface with silanol OH groups.²⁶ It is known that the interaction of hydroxyl groups with nitrogen is much stronger than for argon.³³ This stronger hydrogen bonding is certainly the crucial factor that gives rise to the high elastic modulus of the adsorbed nitrogen layer. It is also well known that the interaction of the quadrupole moment of nitrogen with hydroxyl groups results in an orientation of the adsorbed nitrogen molecules and a higher density of molecules per surface area.³⁴ Taking such a higher density into account would result in even higher values for the shear modulus of the surface layer compared to those displayed in Fig. 3(a) (see Ref. 27). Thus, in any case, the surface layer exhibits a considerably enhanced modulus compared to that of bulk nitrogen.

The above interaction and possibly also the influence of the amorphous (and heterogeneous) pore wall of our porous glass sample can impose a certain structure and a different crystalline structure on the first few nitrogen layers. Therewith, the basis is formed for the observed enhanced elastic properties of nitrogen near the wall. In addition, the diatomic structure of nitrogen possibly causes more difficulties for the pore filling to accommodate to the pore surface and higher strains are induced.

Our discovery of considerably enhanced elastic properties of nitrogen confined in nanopores shows that nanoporosity can be used to change elastic properties of substances. The surface of pore walls is of particular importance and determines the degree of influence on the elastic behavior of adsorbed substances. Besides the amorphous or crystalline structure of the pore walls, also the polarizability and existing electrical moments of the pore surface and adsorbed substances can have an effect on the elastic properties of adsorbed layers. The differences between the strength of the binding of argon and nitrogen to OH groups can explain the observed differences in the elastic properties of both adsorbates. Thus the increase of the shear modulus of adsorbed layers in

comparison to the bulk shear modulus should be particularly high for systems with a strong binding between the adsorbed molecules and the pore surface. Further investigation of the fundamental correlations between the mechanical and

electrical properties of nanoporous systems and adsorbed substances and their influence on the elastic properties in nanopores will help provide tools for the tuning of mechanical properties.

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²⁵The filling fraction f can be regarded as constant over the whole temperature range. The amount of nitrogen vapor in the sample cell is negligible due to the low vapor pressure of nitrogen below 60 K and the small volume of the sample cell. A similar statement holds for argon (see Fig. 5 in Ref. 21).

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²⁷The number of adsorbed molecules n_{ads} scaled to the number necessary for complete filling n_{max} was determined experimentally. The density of the adsorbed nitrogen was regarded as independent of the filling, i.e., $f = V_{\text{ads}}/V_{\text{pore}} = n_{\text{ads}}/n_{\text{max}}$. If the density of the first surface layer ρ_{SL} differed from the average density of the pore filling ρ_{avg} , the filling fraction $f = 0.12$ would have to be replaced by $f' = \rho_{\text{avg}}/\rho_{\text{SL}} f$. According to Eq. (1), a possibly higher density of the first nitrogen layer (Ref. 34) would thus correspond to a value of the shear modulus of this layer that is even higher than the one we calculated. For completely filled pores $f = f' = 1$ always holds so that G_{filling} is determined correctly (even without knowing the exact density).

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