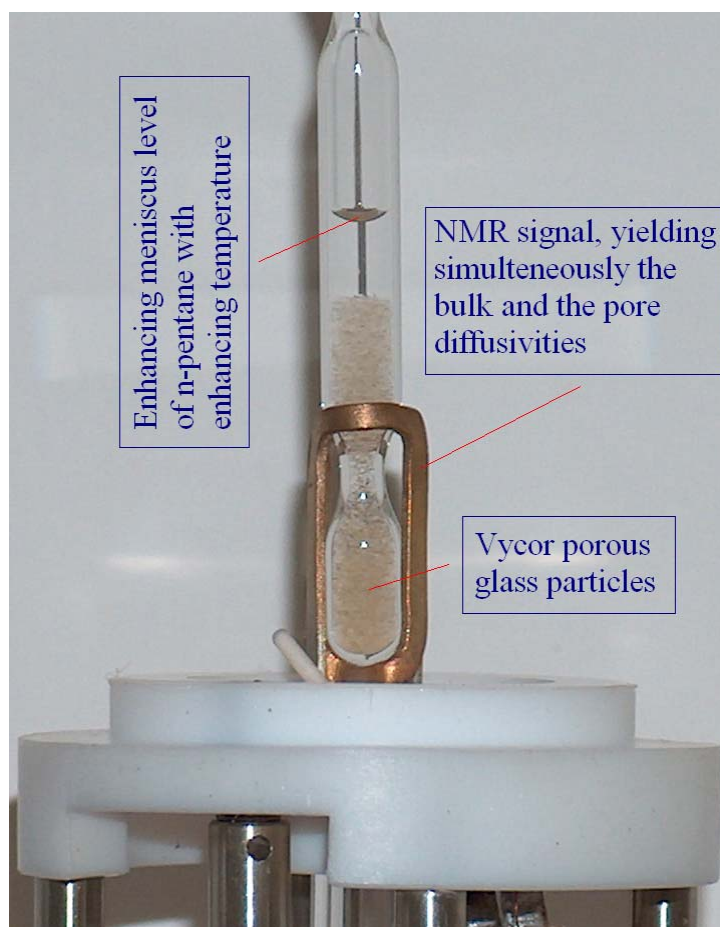


Direct Assessment of Transport Properties of Supercritical Fluids Confined to Nanopores

Muslim Dvoyashkin, Rustem Valiullin, Jörg Kärger, Wolf-Dietrich Einicke, Roger Gläser



SI Figure. High-pressure glass tube with Vycor porous glass and n-pentane in an NMR radio-frequency coil.

Diffusion model.

To calculate the effective diffusivities D_{eff} at temperatures above T_{cp} (the pore critical temperature), the fast-exchange approximation, which well holds under our experimental conditions, has been used. In this approach, D_{eff} is given by the sum of two diffusivities, D_a in the adsorbed phase at the pore walls, and D_i in the pore interior with their respective weights:

$$D_{\text{eff}} = f_a D_a + f_i D_i, \quad (1)$$

where f_a and f_i are the relative fractions ($f_a + f_i = 1$) of the molecules adsorbed at the pore walls and in the pore interior, with the densities ρ_a and ρ_i , respectively. f_a was taken to correspond to one monomolecular layer with the density as in the bulk state, ρ_i was taken to be equal to the supercritical density.

As a simple estimate, one may consider D_a to behave as the intrapore diffusivity at the full pore saturations, i.e. model it by the Arrhenius law using the data at $T < T_{cp}$. D_i is calculated using the gas-kinetic approach, i.e. is given by

$$\frac{1}{D_i} = \frac{1}{D_M} + \frac{1}{D_K}. \quad (2)$$

Here, D_M and D_K are the molecular and the Knudsen diffusivities given by $D_M = \lambda \bar{g}/3$ and $D_K = d \bar{g}/3$, respectively, \bar{g} is the mean molecular velocity, λ is the mean free path of the bulk fluid, and d is the pore diameter.