Comment on "Single-File Diffusion of Confined Water Inside SWNTs: An NMR Study"

In their paper, Das *et al.*[1] report on the observation of single-file diffusion (SFD) of water in SWNTs with a diameter of 1.4 nm—a regime of molecular propagation when molecules confined to narrow channels cannot overpass each other. This results in the mean square displacements $\langle z^2(t)\rangle$ growing as $\sqrt{t}$, rather than linearly with time t typical of normal diffusion. This pattern was found by fitting the nonexponential diffusion spin−echo attenuations, recorded using pulsed field gradient NMR, to an analytical expression for diffusion in long straight channels, isotropically oriented in space. Satisfactory fits obtained have been taken as a proof of the applicability of this model and the consequently obtained dependency $\langle z^2(t)\rangle \propto \sqrt{t}$ as a sign of SFD. We are wondering, however, how it is possible that molecules moving in a strongly correlated manner could be displaced over such long distances comparable to those in bulk water, as revealed by Figure 7. Moreover, to justify SFD the authors are forced to provide sophisticated arguments, such as a frozen-shell model, to explain SFD in a pore accommodating a few water molecules in the cross-section. Finally, the mean square displacement in single-file systems is confined by the limiting value $(1 - \theta)^2L^2/(6N)$ for $t \rightarrow \infty$ (relative loading θ, tube length L),[2] which is by at least the particle number N smaller than for normal diffusion. With displacements of about 10 μm as reported in ref 1 this would require astonishingly large file lengths. In our opinion, the experimental findings might be more consistently explained by normal diffusion in a curvilinear space.[3] Indeed, SWNTs of such high aspect ratios cannot sustain straight shape and, therefore, bend. Diffusive motion within such channels as well leads (i) to nonexponential diffusion attenuations, similar to those in Figure 5a and (ii) to $\langle z^2(t)\rangle \propto \sqrt{t}$ for random coils. Our estimates show that, using the model of ref 3, one may self-consistently describe all experimental data presented by Das *et al.*, assuming water diffusivities in SWNTs comparable to bulk diffusivities ($\sim 10^{-9}$ m^2 s^{-1}) and a reasonable persistence length λ for SWNTs of a few micrometers.

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Reply to Comment by Valiullin and Kärger on Our Paper "Single-File Diffusion of Confined Water Inside SWNTs: An NMR Study"

The comment by Valiullin amd Kärger (VK)[1] suggests an alternative explanation to our observation[2] of $\langle z^2(t)\rangle \propto \sqrt{t}$ for confined water in single-walled carbon nanotubes (SWNT) of average diameter 1.4 nm. VK suggest that normal diffusion of water confined inside nanotubes in curvilinear space[3] can be an alternative explanation to our inference of single-file diffusion of water confined inside the nanotubes. The former mechanism requires a persistence length of the SWNT to be a few micrometers (as also stated by VK). We can fit our data shown in Figures 5 and 6 of ref 2 with the eq 9 of ref 3 with a value of persistence length $\lambda \approx 5$ μm. This value is not at all realistic for nanotubes used in our experiments. As estimated and discussed extensively in ref 4, the persistence length of an isolated SWNT of diameter 1.4 nm at room temperature is much larger, ~100 μm, which increases to ~1 mm for a smallest close-packed bundle of seven (see eqs 3 and 4 of ref 4). With these large persistence lengths of nanotubes as compared to the root-mean-square distance (~10 μm) seen in our measurements, we are **not** convinced that normal diffusion in curvilinear space is an appropriate mechanism for our observations of $\sqrt{t}$ dependence of the mean square displacement. We may add that the mean square displacement $\langle z^2\rangle$ can be consistent with a limiting value $\sim(1 - \theta)^2L^2/6N$ for some choices of the parameters. However, in the absence of reliable estimates of the parameters, it would not be prudent to overemphasize this aspect.

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LETTERS TO THE EDITOR

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