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Is ambient water inhomogeneous on the nanometre length scale?

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According to a recent article [1] the structure of water should be regarded as inhomogeneous on the 1nm length scale. Near a critical point the large number fluctuations which arise from stochastic processes, and which, for a single component fluid, are represented by the $Q = 0$ value of the structure factor

$$S(Q \to 0) = \frac{\langle (N - \langle N \rangle)^2 \rangle}{\langle N \rangle} \qquad \textbf{[1]}$$

where N is the number of molecules in any given volume of the fluid and the angle brackets indicate ensemble averages, cause $S(Q)$ to rise at low Q with a diverging correlation length given by the Ornstein-Zernike relation, equation (2) of [1]. Well away from a critical point, $S(Q)$ can also rise at small Q depending on the density and the interplay between attractive and repulsive forces [2]. Does a rise in $S(Q)$ at small Q justify the claim made in [1] that the non-critical fluid is heterogeneous on some (much shorter) length scale? We think not.

To understand why, general considerations from small angle scattering theory for a two-component system [3] suggest the anomalous $Q = 0$ rise has an amplitude given by

$$S_A(0) = \phi(1 - \phi)\frac{(\Delta\rho)^2}{\langle \rho \rangle} v_c \qquad \textbf{[2]}$$

where ϕ is the volume fraction of one component, $\Delta\rho$ is the density difference between the two components, and v_c is a ``correlation volume''. While we would contest the idea that either $S_A(0)$ or v_c can be determined with any degree of reliability for a fluid far away from its critical point, even if these values were known this would still leave the assignment of ϕ and $\Delta\rho$ from (2) indeterminate. Moreover it is not difficult to show that the density differences allowed by (2), for a given v_c and using the data of Fig. 3 of [1], have similar magnitude to the stochastic fluctuations in density which arise from applying (1) to the same volume. Hence it is not possible to conclude from the rise of $S(Q)$ at small Q that ambient water density fluctuations are qualitatively different from the highly dynamic number fluctuations which characterize all liquids.

Spectroscopic (Raman, IR, XAS, XES, etc.) and diffraction data from water also cannot be used to imply two-state behaviour. Isosbestic points, in which intensity shifts from one part of a response function to another about a stationary point, can wholly be explained as a consequence of a continuous distribution of local environments [4, 5]. Further, there is so far still no consensus on what XAS and XES data imply for the local geometry of water molecules.

With these observations, the currently accepted picture of water, in which each molecule is typically hydrogen-bonded to 4 others in a roughly tetrahedral arrangement, and with rarely more than 1 additional non-bonded molecule in the first coordination shell, is retained.

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3. **Glatter O, Kratky O (eds.) (1982) Small angle x-ray scattering, chap. 2, p. 45 (Academic Press, London).**
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