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Response to “Comment on ‘Observations on an equation of state for water confined in narrow slit-pores’” [J. Chem. Phys. 117, 8162 (2002)]

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In their Comment on our previous paper in this journal,¹ Truskett *et al.*² address several issues in what appears to be a reasoned and balanced way. We attempted to explain some of our experimental results on the adsorption of chlorinated volatile organic compounds (CVOCs) out of water³ using existing theoretical developments, including those published by these authors.^{4,5} We found the works by Truskett *et al.*^{4,5} to be very interesting and promising in that regard. Specifically, they stated (second paragraph in the Conclusions⁴) that their model addressed the fact that “the introduction of hydrophobic confining walls reduces the average number of favorable fluid-fluid interactions per molecule, i.e., it disrupts the hydrogen-bonding pattern in the fluid.” However, we found the predictions without revising the model did not explain the effects of water we observed experimentally.³ That is, their model was not suitable for the conditions of our experimental investigations.

In our two papers,^{1,6} our interest was to explain the competitive role of water in the adsorption of CVOCs in “hydrophobic” microporous materials. To proceed we made rather minor modifications to the mean field theory models developed elsewhere.^{4,5,7,8} In conducting our analysis we developed the Helmholtz free energy and generated predictions of fluid pressure and fluid density in micropores. We did not evaluate the effects of varying temperature as pointed out by Truskett *et al.*,² nor did we evaluate the predictions of other properties of water. While we examined the predicted behavior of water in pores of varying size, we were primarily interested in pore dimensions in the angstrom range, since we were studying adsorption in molecular sieve zeolites. Consequently, we are not in a position to comment on predictions of water’s other properties, either from prior models or the modified model we used. The most we are prepared to say is that in our observations some of confined water’s properties were not predicted by the original model in the circumstances we were interested in investigating, which prompted our modifications. This Response should be read in that context.

They assumed^{4,5} that a molecule can form at most a single hydrogen bond when there is only one neighbor in its hydrogen bonding shell, and then the hydrogen bonding energy decreases as the number of neighbors in the hydrogen bonding shell increases. However, when one uses their model for water confined within hard walls, under the conditions that we investigated, one predicts that confinement

favours hydrogen bonding, as shown in our Fig. 3,¹ rather than being disruptive as one would expect. As explained in that work,¹ using the mean-field theory, we believe that this was due to the fact that molecules in the Truskett *et al.* model^{4,5} were allowed to participate in, at most, one hydrogen bond, whereas with more hydrogen bonding interactions, the expected disruption due to confinement would be manifested. Thus, we concluded that, in order to study confined liquid water, it was necessary to account for up to four favorable hydrogen bonds per molecule. Since we were interested in evaluating the effect of water on CVOC adsorption in hydrophobic microporous materials at 298 K,³ we ignored the temperature dependence of hydrogen bonding. Thus, while the term β^{-1} was lumped into the constant term ϵ^{HB} , we did not consider the additional specific temperature dependence of the magnitude and intensity of hydrogen bonding. We suggest that the accurate temperature dependence may have to be somewhat different than in their model,^{2,4,5} since in that approach the temperature dependence appears to be insignificant at normal ambient temperatures in some cases, e.g., the contribution to pressure shown in their Fig. 1.²

Regarding the orientation dependence of hydrogen bonding, we agree with Truskett *et al.*^{2,4,5} that the orientational degrees of freedom are very important for water. In order for molecules to participate in hydrogen bonding, they should be in certain positions as well as have certain favorable orientations. Because of these geometric preferences of hydrogen bonding, water forms an open structure. The model presented¹ clearly accounts for the open structure of water, accounting, therefore, (in a simple way) for the orientational dependence of hydrogen bonds. Truskett *et al.* included a geometric criterion that claims to account for the orientational character of hydrogen bonding (their criterion 3^{4,5}). However, if that was done appropriately, then this condition in itself should produce the open structure of water, without needing their criterion 4.^{4,5} So, in fact, Truskett *et al.*^{4,5} also rely mainly on the “crowding rule” to simulate the open structure of water. One can observe from our Fig. 6¹ that the hydrogen bonding term of their model that accounts for orientational dependence of hydrogen bonding made an insignificant contribution to the Helmholtz free energy, and was essentially independent of fluid density. We noted that the leading constant term, $\ln(4\pi)$, was dominant in that calculation, and thus variations with density near ambient conditions could not be expected to be important in that model.

The curve at 300 K in Fig. 1 of their Comment² is consistent with our computations with their model, as they show that hydrogen bonding is shown to play a minor role in the pressure dependence in the temperature range 250–300 K. It would be expected to decrease further in significance at higher temperatures. Their results in their Fig. 1² show that at densities near 0.6 g/cm³ the attractive forces due to hydrogen bonding are smaller than the van der Waals forces, while at densities near 1.0 g/cm³ the hydrogen bonding forces are predicted to be repulsive, rather than cohesive. There are numerous references that address these points, but three are listed to support the observations that “hydrogen bonding is the most important interaction in liquid water,”⁹ and is responsible for the relatively high boiling point of water.¹⁰ That is, hydrogen bonding is significant even at higher temperatures than considered in their Fig. 1. This feature is also illustrated clearly in Fig. 9 at temperatures up to 673 K.¹¹

Regarding the asymptotic value of the grand potential: After reviewing our previous Fig. 2¹ and the Comments by Truskett *et al.*,² we agree that the asymptotic value should be a finite positive quantity. That was demonstrated analytically by them.¹² We obtained the same value reported by Truskett *et al.*^{2,4,5} at intermediate narrow slit-pore dimensions, but

erred in the asymptotic limit. We thank the authors of the Comment² for helping to clarify this matter.

Finally, we believe that more work is needed to develop a unified model that would capture all of the interesting features of water. In that respect, we appreciated and welcomed the exchange of productive criticism, and look forward to the opportunity to continue these investigations.

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