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Anirban Mudi and Charusita Chakravarty*: Multiple Time-Scale Behavior of the Hydrogen-Bond Network in Water

Two errors made in the computation of tagged particle potential energies in ref 1 require correction. For an N -particle system with a pair-additive potential energy function, the ensemble averages of the tagged particle potential energy, $\langle u \rangle$, should be related to the total configurational energy, $\langle U \rangle$, as $\langle u \rangle = 2\langle U \rangle/N$. In ref 1, $\langle u \rangle$ was divided by an additional factor of N , where $N = 256$, when computing the data for Figures 4 and 8. The second error appears in the addition of different contributions to the tagged potential energy, u . The different contributions to the tagged particle potential energy, u , are

$$u = u_{\text{rec}} + u_{\text{screen}} + u_{\text{self}} + u_{\text{intra}} + u_{\text{vdW}} + u_{\text{lr}} \quad (1)$$

The Ewald sum contribution to the tagged potential energy has been decomposed into u_{rec} , u_{screen} , u_{self} , and u_{intra} contributions corresponding to reciprocal space, screened charge, atomic self-correction, and intramolecular self-correction terms, respectively. The contribution of short-range repulsion–dispersion interactions is decomposed into a pair-summed term, u_{vdW} , and a long-range correction term, u_{lr} . In our previous paper, the total potential energy, U , was computed correctly. When computing u , u_{lr} was set to zero. More importantly, the contribution of the u_{screen} , u_{intra} , and u_{vdW} was reduced by a constant factor of $1/2$. Details of the decomposition are discussed in refs 2 and 3.

The effect of the above errors on the power spectra associated with fluctuations in the tagged particle potential energies, $S_u(f)$, is small. The corrected tagged particle potential energy results in fluctuations of twice the magnitude and $S_u(f)$ spectra of 4 times the intensity seen in the earlier results. On the scale of Figures 1, 5, 6, and 7 of the original paper, this is a very small effect. The effect on the $\ln S_u(f)$ profile in the multiple time-scale regime is negligible, and changes in the α_u values are comparable to the statistical error. The $\ln S_u(f)$ profile shows small changes in the high-frequency region above 200 cm^{-1} . Since the changes in the $S_u(f)$ spectra are small, we do not reproduce corrected versions of the power spectra here. Reference 4 shows the $S_u(f)$ spectrum at the state point (0.9 g cm^{-3} , 230 K) as well as the recomputed α_u values for the entire set of state points.

The net effect of the above errors on the $P(u)$ distributions can be understood as follows. The u_{intra} contribution is constant for all molecules and did not affect the overall shape. The structure and width of the distribution are essentially determined by u_{screen} and u_{vdW} . The u_{rec} term gives rise to a Gaussian-type distribution which is narrow in comparison to the spread of values seen for u_{screen} and u_{vdW} . Therefore, it serves to shift the center of the $P(u)$ distribution but does not affect its shape significantly. Since the relative weights of the u_{screen} and u_{vdW} contributions were correct, the overall shape and relative heights of peaks of the $P(u)$ distribution were not affected. The scales and the mean value, $\langle u \rangle$, are, however, appreciably modified on correction. The modified Figures 4 and 8 are shown here as Figures 1 and 2, respectively.

The net effect of correcting the errors in the previous work is to rescale the power spectra and static distributions associated

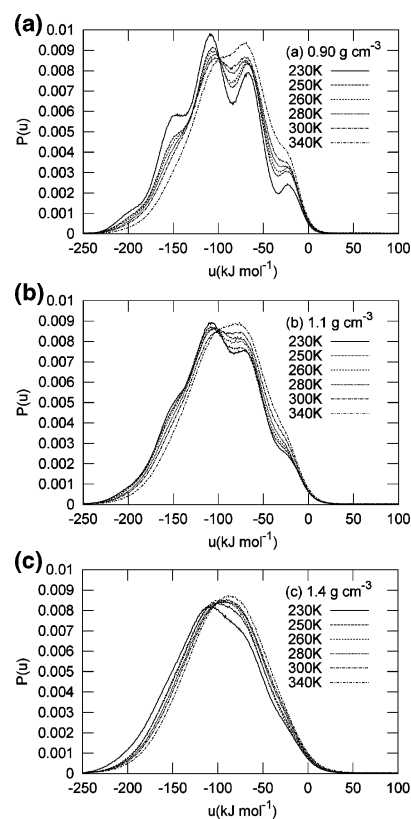


Figure 1. Static distribution of tagged particle potential energies (in kJ mol^{-1}) at different temperatures for isochores corresponding to (a) 0.9 g cm^{-3} , (b) 1.1 g cm^{-3} , and (c) 1.4 g cm^{-3} .

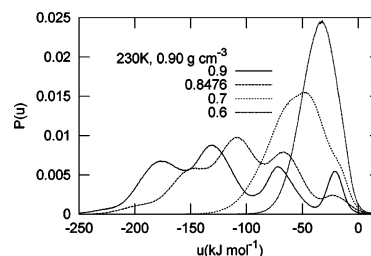


Figure 2. Static distributions of tagged particle potential energies (in kJ mol^{-1}) for different scalings of SPC/E partial charge distributions at 230 K and 0.9 g cm^{-3} . The partial charge on the oxygen atom, in units of electronic charge, is shown in the graphical key.

with the tagged particle potential energies. The overall discussion of the results and the conclusions of the original paper are not affected.

References and Notes

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