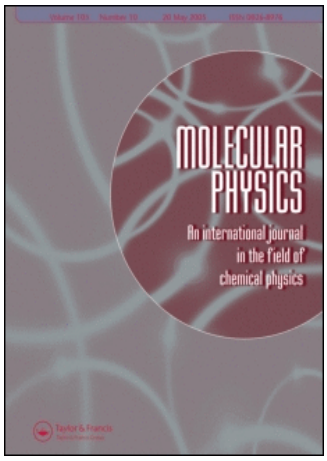

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Grand-canonical ensemble Monte Carlo study of dense liquid Lennard-Jones, soft spheres and water

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The correction to the calculated excess free energy of the SPC water [1, 2] prompted a search for the source of the large error in the calculated excess free energy of the SPC and ST2 water models in this paper. The algorithm for generating the random orientation for insertion was found to be incorrect. It was replaced by an orientation generator using the Euler angles ϕ, θ and ψ [3]: ϕ and ψ were generated randomly on the $[0, 2\pi]$ interval and $\cos\theta$ randomly in the $[-1, 1]$ interval [4].

The table describes the results of new simulations, at a density of 0.997 g cm^{-3} with 91 water molecules and with a 0·08 Å grid interval. The pressure of the SPC model was also calculated in the grand-canonical ensemble. Interpolation between the two runs for each water model gave $B = -5{\cdot}83 \pm 0{\cdot}2$ and $B = -4{\cdot}83 \pm 0{\cdot}2$ for the SPC and ST2 waters, respectively. The SPC pressure is interpolated as -150 atm. This gives the excess free energy as $-22{\cdot}9 \pm 0.4$ kJ mol^{-1} and $-21{\cdot}7 \pm 0{\cdot}4$ kJ mol^{-1} for the SPC and ST2 waters, respectively. The SPC results differ from the canonical ensemble results [2] by 0·7–0·9 kJ mol^{-1} and from those of Hermans *et al.* [5] (who use a shorter cut-off) by 0·5 kJ mol^{-1}. The deviation from the ST2 canonical ensemble excess free energy ($-22{\cdot}9$ using the MCY value [2] or $-22{\cdot}6$ from [1]) is 0·9–1·2 kJ mol^{-1}.

Results of the grand-canonical ensemble simulations.

	SPC		ST2	
B	−6·0	−5·7	−5·0	−4·8
$\langle N\rangle$(1000 K)	89·55	92·97	90·14	91·68
$\langle N\rangle$(2000 K)	89·59	91·21	88·03	91·60
$\langle N\rangle$(3000 K)	90.31	91·84	89·48	91·59
$\langle N\rangle$(4000 K)	90·62	91·88	89·39	91·77
$\langle N\rangle$(5000 K)	90·57	91·68	89·22	92·01
$\langle N\rangle$(6000 K)	90·30 ± 0·9	91·55 ± 0·9	89·49 ± 1·6	92·06 ± 1·5
$\langle N^2\rangle - \langle N\rangle^2$	6.1	4.6	11·3	10·0
P:	−170	−134		

B is the chemical potential parameter. $\langle N\rangle$ is the average number of waters at various stages of the calculation (1000 K corresponds to 1 million Monte Carlo step consisting of a displacement and an insertion or deletion attempt). The error estimates on $\langle N\rangle$ represent two standard deviations. P is the pressure in atm.

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