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## Comment on “The putative liquid-liquid transition is a liquid-solid transition in atomistic models of water” [I and II: J. Chem. Phys. 135, 134503 (2011); J. Chem. Phys. 138, 214504 (2013)]

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## Comment on “The putative liquid-liquid transition is a liquid-solid transition in atomistic models of water” [I and II: *J. Chem. Phys.* 135, 134503 (2011); *J. Chem. Phys.* 138, 214504 (2013)]

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Limmer and Chandler’s (LC) calculations for the ST2 model of water<sup>1,2</sup> show evidence of only a single metastable liquid at conditions where other studies<sup>3–6</sup> report a liquid-liquid transition (LLT). Although the reversible nature of ST2’s LLT has been recently demonstrated,<sup>7,8</sup> the origin of the disagreement with LC’s calculations remains unresolved. Here, we show that the simulation code made available to us by LC implements a hybrid Monte Carlo (HMC) sampling protocol that is inappropriate for rigid polyatomic water models. The resulting sampling errors significantly distort ST2’s equation of state and hence have prevented LC<sup>1,2</sup> from accurately characterizing the model’s phase behavior.

Average potential energies computed for ST2 along an ambient pressure isobar with LC’s HMC code (Fig. 1) deviate significantly from the values obtained from our publicly available HMC code<sup>9</sup> and a molecular dynamics (MD) code for ST2 generously provided to us by the authors of Ref. 10. These systematic errors are caused by LC’s use of a velocity initialization routine that is inappropriate for rigid water models. The correct equation of state for ST2 is recovered when we simply correct LC’s velocity initialization routine (Fig. 1).

LC’s HMC sampling scheme<sup>1,2</sup> uses short microcanonical MD trajectories as trial MC moves and the standard HMC acceptance criterion:<sup>11</sup>  $P_{\text{acc}}^{\text{old} \rightarrow \text{new}} = \min(1, e^{-\beta \Delta U} e^{-\beta \Delta K})$ , where  $\beta = (k_B T)^{-1}$  and  $\Delta U = U^{\text{new}} - U^{\text{old}}$  and  $\Delta K = K^{\text{new}} - K^{\text{old}}$  are the changes in potential and kinetic energy, respectively. For  $N$  rigid water molecules,  $K \equiv \frac{1}{2} \sum_i [m_i (\mathbf{v}_i^{\text{cm}} \cdot \mathbf{v}_i^{\text{cm}}) + \omega_i^T \mathbf{I}_i \omega_i]$  for  $i \in N$ , where  $m_i$  is the molecular mass,  $\mathbf{v}_i^{\text{cm}}$  is the center of mass velocity,  $\omega_i$  is the angular velocity, and  $\mathbf{I}_i$  is the inertia tensor. Although this expression is invariant to the choice of reference frame, rigid body kinematics are conveniently formulated using the angular velocity  $\hat{\omega}_i$  in the body-centered frame where the inertia tensor is a diagonal matrix  $\hat{\mathbf{I}}_i$ . Hence we adopt this reference frame for our analysis.

The assignment of initial center-of-mass and angular velocities,  $\mathbf{v}_i^{\text{cm},0}$  and  $\hat{\omega}_i^0$ , at the start of every MD trial move is incorrect in the LC code: the generated velocity distributions deviate from Maxwell-Boltzmann (MB) statistics and violate equipartitioning of  $K$ . Consequently, LC’s velocity initialization routine generates artificially low rotational temperatures and artificially high translational temperatures that are both significantly different from the expected (nominal) temperature (Fig. 1). The underlying error, as explained in the [supplementary material](#), is a violation of the rigidity of the ST2 molecules. Although the initial distribution of  $K$  generated by LC’s velocity initialization scheme obeys canonical statistics at the expected temperature, the energy is incorrectly partitioned between the molecular degrees of freedom; accordingly, our unambiguous tests show that LC’s HMC scheme produced large sampling errors (Fig. 1) and fails numerical consistency checks (see the [supplementary material](#)).

We correct LC’s code by implementing a routine that draws initial velocities ( $\mathbf{v}_i^{\text{cm},0}, \hat{\omega}_i^0$ ) from the MB distribution at the beginning of each MD trial move (Fig. 1), as is a common practice.<sup>11,12</sup> This procedure ensures that equipartition is satisfied and that the rotational and translational degrees of freedom are initialized at the desired temperature. When these conditions are met, the sampling errors vanish and the correct equation of state for ST2 is recovered (Fig. 1).

LC’s code predicts potential energies for ST2 that are too large (Fig. 1), as if sampling is being performed at artificially high temperatures. By extrapolating the data from their original code (Fig. 1, left) and aligning the predicted potential energy to the temperature corresponding to the correct equation of state for ST2, we estimate that LC’s HMC algorithm samples at effectively ca. 285 K when the set temperature is 230 K. This discrepancy is consistent with our previous analysis, which showed that LC’s free energy (FE) calculations for ST2 underpredict the melting temperature of ice Ic by 30–45 K at 2.6 kbar.<sup>7</sup> Both analyses therefore suggest that LC’s code samples at artificially high temperatures, which has prevented observation of ST2’s LLT in their studies.<sup>1,2</sup> Indeed, when we perform FE calculations with LC’s original code, only a single liquid basin (e.g., Fig. 2, left) is observed over the range of conditions relevant to ST2’s LLT,<sup>5,6</sup> regardless of sampling

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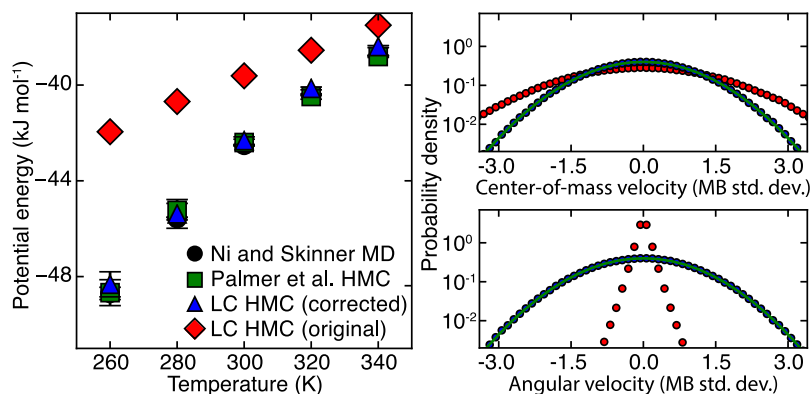


FIG. 1. (Left) Potential energies for ST2 with vacuum Ewald boundary conditions (ST2b<sup>2</sup>) at 1 bar computed using LC's HMC code (red diamonds) deviate significantly from the values generated from our HMC code (green squares) and the MD code provided by Ni and Skinner (black circles). Excellent agreement is achieved when we correct LC's velocity initialization scheme (blue triangles). (Right) Distributions of the  $x$ -components of the initial center-of-mass translational velocity  $v_i^{cm,0}$  (top) and initial body-frame angular velocity  $\omega_i^0$  (bottom) at 300 K from LC's code (red circles) deviate significantly from the Maxwell-Boltzmann (MB) distribution (green line) and violate equipartition (the translational and rotational temperatures are ca. 597 K and 3 K, respectively). Velocities from the corrected code (blue circles, indistinguishable from the green line) obey MB statistics. This violation of equipartition is repeated at the start of every MD trial move in the LC code. Velocities are in units of MB std. deviation at 300 K.

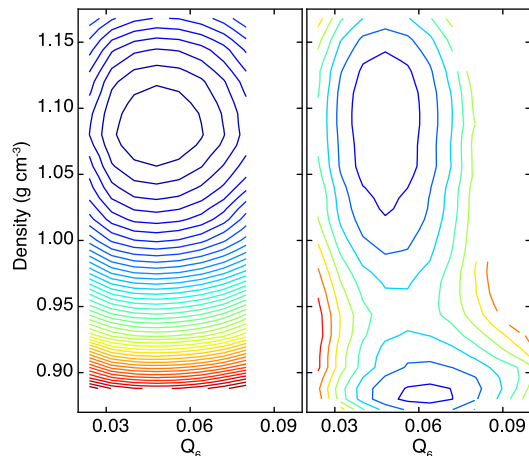


FIG. 2. Free energy surfaces for ST2 with conducting Ewald boundary conditions (ST2a<sup>2</sup>) computed at 230 K and 2.8 kbar for 216 molecules using LC's original code (left) and the version that we corrected (right). Contours are  $1 k_B T$  apart and uncertainties are  $1 k_B T$ .

duration. Hence FE surfaces consistent with LC's published results<sup>1,2</sup> are obtained using the code supplied by them to us, a code that does not correctly predict ST2's equation of state (Fig. 1). When sampling is performed with the version of LC's code that we corrected, however, the system quickly relaxes to a state with two liquid basins (Fig. 2, right). This observation is consistent with FE studies<sup>7,8</sup> which have shown, using advanced techniques to sample for orders of magnitude longer than we have done here,<sup>7</sup> that ST2's LLT is invariant to

sampling duration and distinct from the normal freezing transition. Further, it shows that LC's contrary assertions arise from a conceptual mistake in their code that leads to sampling errors.

See [supplementary material](#) for the error in LC's velocity initialization routine and additional consistency checks that have been performed.

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- <sup>1</sup>D. T. Limmer and D. Chandler, *J. Chem. Phys.* **135**, 134503 (2011).
- <sup>2</sup>D. T. Limmer and D. Chandler, *J. Chem. Phys.* **138**, 214504 (2013).
- <sup>3</sup>Y. Liu, A. Z. Panagiotopoulos, and P. G. Debenedetti, *J. Chem. Phys.* **131**, 104508 (2009).
- <sup>4</sup>F. Sciortino, I. Saika-Voivod, and P. H. Poole, *Phys. Chem. Chem. Phys.* **13**, 19759–19764 (2011).
- <sup>5</sup>Y. Liu, J. C. Palmer, A. Z. Panagiotopoulos, and P. G. Debenedetti, *J. Chem. Phys.* **137**, 214505 (2012).
- <sup>6</sup>P. H. Poole, R. K. Bowles, I. Saika-Voivod, and F. Sciortino, *J. Chem. Phys.* **138**, 034505 (2013).
- <sup>7</sup>J. C. Palmer, F. Martelli, Y. Liu, R. Car, A. Z. Panagiotopoulos, and P. G. Debenedetti, *Nature* **510**, 385–388 (2014).
- <sup>8</sup>F. Smallenburg and F. Sciortino, *Phys. Rev. Lett.* **115**, 015701 (2015).
- <sup>9</sup>Our code has been publicly available since September 2014, <http://pablonet.princeton.edu/pgd/html/links.html>.
- <sup>10</sup>Y. Ni and J. L. Skinner, *J. Chem. Phys.* **145**, 124509 (2016).
- <sup>11</sup>M. Allen and D. Quigley, *Mol. Phys.* **111**, 3442–3447 (2013).
- <sup>12</sup>G. Menzl and C. Dellago, *J. Chem. Phys.* **145**, 211918 (2016).