Supporting material for "From a Liquid to a Crystal without Going through a First Order Phase Transition: Determining the Free Energy of Melting with Glassy Intermediates"

by

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1. An example calculation to determine the free energy of melting is provided below. As described in the paper, the free energy estimate is determined by summing the contributions to the thermodynamic cycle shown in Eq. 5. The cycle is comprised of seven steps. Three steps contribute to  $\Delta G_{solid}$ : tether the ice Ih molecules (S1), remove electrostatic interactions (S2), remove van der Waals interactions (S3). Four steps contribute to  $\Delta G_{ligud}$ : vitrify the liquid (L1), tether the vitrified molecules (L2),

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remove electrostatic interactions (L3), and remove van der Waals interactions (L4). Since identical force constants are used for the tethering for ice Ih and liquid configurations,  $\Delta G_{ein}$  is zero.

The free energy of each of these seven steps was estimated from twenty independent non-equilibrium switching simulations using Jarzynski's equation,

$$\Delta F = -k_B T \ln \left\langle e^{-W/k_B T} \right\rangle, \tag{S1}$$

where  $k_B$  is the Boltzmann constant, T is temperature and W is the work associated with each switching.

To avoid a float point overflow on a computer, the actual evaluation of Eq. S1 is performed with

$$\Delta F = \left\langle W \right\rangle - k_{B} T \ln \left( \left\langle \exp \left( \frac{\left\langle W \right\rangle - W}{k_{B} T} \right) \right\rangle \right), \tag{S2}$$

where > indicates an average.

Table S1 summarizes the integrated work for each repetition used to calculate the free energy difference for the TIP4P model at 240 K. The estimate calculated from Jarzynski's equation is reported in the last row. As discussed in the paper, the glassy intermediate state is different for each realization of the switching. In order to avoid attempting to determine the free energy of glass, only the sum of the liquid work values, (labeled L1-4) is used to calculate the liquid free energy. According to Table S1, the excess free energy of solid  $\Delta G_{solid} = -(1375.711+4395.712-902.612)$  kcal/mol

= -4868.811 kcal/mol and the excess free energy of liquid is  $\Delta G_{liquid}$ 

= -4880.246 kcal/mol. The free energy of melting is then -11.4356 kcal/mol or -0.0381 kcal/mol per water molecule for TIP4P at 240 K.

	Integrated work value (kcal/mol)							
Run	S1	S2	S3	L1	L2	L3	L4	L1-4
1	1388.041	4482.820	-893.337	-1450.619	1252.952	6330.702	-1254.157	4878.877
2	1406.532	4423.255	-852.618	-1450.483	1297.730	6425.145	-1328.658	4943.733
3	1402.601	4461.256	-880.873	-1446.610	1294. 522	6363.114	-1288.785	4922.242
4	1401.185	4442.640	-867.270	-1453.762	1265.747	6358.914	-1287.440	4883.459
5	1391.773	4438.317	-852.236	-1452.035	1338.930	6418.345	-1315.210	4990.030
6	1416.737	4423.012	-863.248	-1455.009	1339.188	6358.688	-1262.609	4980.258
7	1385.436	4460.415	-868.885	-1456.725	1328.264	6354.412	-1272.801	4953.150
8	1385.071	4435.208	-842.882	-1455.300	1457.621	6381.488	-1318.402	5065.407
9	1408.220	4421.723	-852.754	-1451.375	1322.311	6405.926	-1310.361	4966.500
10	1405.290	4430.515	-859.087	-1455.039	1287.197	6332.554	-1265.012	4899.700
11	1426.739	4394.284	-842.735	-1453.373	1271.090	6326.686	-1248.121	4896.283
12	1384.747	4473.069	-880.154	-1452.505	1288.596	6334.948	-1280. 420	4890.619
13	1377.663	4502.070	-904.040	-1460.067	1305.473	6377.479	-1265.759	4957.126
14	1386.320	4443.339	-849.295	-1450.231	1261.104	6301.188	-1214.062	4897.998
15	1397.938	4431.922	-851.159	-1453.891	1346.082	6372.903	-1300. 591	4964.503
16	1395.599	4443.390	-861.693	-1460.739	1230.124	6451.021	-1340.561	4879.846
17	1389.728	4469.187	-881.363	-1450.780	1315.470	6340.860	-1251.408	4954.142
18	1374.284	4476.751	-873.080	-1452.988	1338.344	6345.753	-1253.553	4977.556
19	1394.249	4441.728	-858.492	-1453.429	1289.689	6366.209	-1288.174	4914.296
20	1449.892	4434.747	-854.892	-1444.517	1261.297	6431.066	-1326.503	4921.343
Jarzynski	1375.711	4395.712	-902.612					4880.246

Table S1. The integrated work value for TIP4P model at 240 K. L1-4 is the sum of the work performed in the liquid steps L1 through L4. The free energy estimated with Jarzynksi's equation is reported in the last row.

2. Melting temperature of TIP4P water measured with a slower vitrification and faster tethering.

Ice crystallization is a very slow process, not achievable on simulation timescale. Thus, the speed of vitrification should have no effect on reliability of the glassy intermediate thermodynamic path. Nonetheless, tests are performed to test the effect of choosing different vitrification rate. In our test, the electrostatic interaction is turn on in 6 ns instead of 3 ns as described in the paper. In addition, we accelerated the rate for applying tethering. This rate also should not affect the reliability of our method as long as the liquid is sufficiently vitrified. Nonetheless, the new calculations apply the first tethering step in 3 ns instead of 5 ns as described in the paper.

Figure S1 report the free energy of melting as a function of temperature for TIP4P ice calculated with the slower vitrification and faster tethering rates. The new choices of simulation parameters resulted in a  $T_M$  of 230±1 K.



Figure S1. The Gibbs free energy of melting for TIP4P water models as a function of temperature. A positive value indicates ice Ih is more stable. The dotted line is the linear least squares fit used to interpolate the melting temperature.