

Supporting information to "Does supercooled water retain its universal nucleation behavior under shear at high pressure?"

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S1 Critical nuclei size (N_0^*) by seeding approach

In the seeding approach, a stable spherical ice cluster(or seed) is inserted artificially into the supercooled liquid configuration. Several seed sizes are tracked at the desired temperature and pressure according to the simulation methodology described in the main text. The approximate size of the seed that grows in about half of the set of trajectories is the critical nucleus size at that particular (T, P) . This corresponds to the peak of the free energy barrier when a specific ice cluster with N_0^* particles can either melt into the liquid phase or grow into the crystalline phase.

In this section, we show the trajectories for TIP4P/Ice water model to establish the critical cluster size for the desired pressure at $T = 240$ K. The identification of ice and

liquid molecules is done based on CHILL+ Analysis,¹ including all the hexagonal, cubic, and interfacial ice molecules. By tracking different seed sizes, we assume N_0^* from the linear fit of the largest seed that melts and the smallest seed that grows. Figures S1-(a) and S1-(b) show the trajectories depicting growth and melt of smallest and largest seeds respectively. Figures S1(c), S2 and S3 represent the analysis of critical cluster size at different pressures of 1, 100, 500, 700 and 1000 bar. Here $\Delta = (n_g - n_m)/n$ where n_g is number of trajectories that grow, n_m is number of trajectories that melt and n is total number of trajectories. The criticality is observed at $\Delta = 0$. The statistical error of N_0^* is calculated by error propagation.

Table S1 compares the critical nuclei size N_0^* obtained in this work with the reported value from the literature² for TIP4P/Ice model and Fig. S4 shows the increasing trends of critical nucleus size N_0^* with pressure in the absence of shear.

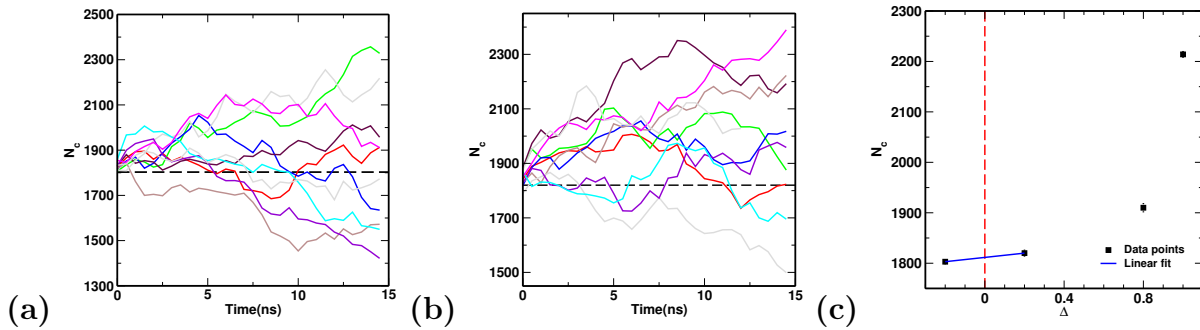


Figure S1: (a) and (b) represent 40% and 60% probable growth of the cluster at $P = 700$ bar and $T = 240$ K. (c) gives the critical cluster $N_0^* = 1811 \pm 4$ obtained from linear fit of $N_c = 1803 \pm 4$ and $N_c = 1820 \pm 6$ at $P = 700$ bar.

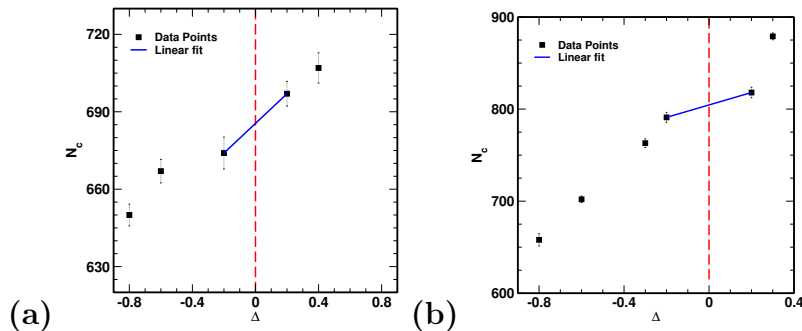


Figure S2: (a) gives the critical cluster $N_0^* = 685 \pm 4$ obtained from linear fit of $N_c = 674 \pm 6$ and $N_c = 697 \pm 5$ at $P = 1$ bar (b) gives the critical cluster $N_0^* = 804 \pm 4$ obtained from linear fit of $N_c = 791 \pm 5$ and $N_c = 818 \pm 6$ at $P = 100$ bar.

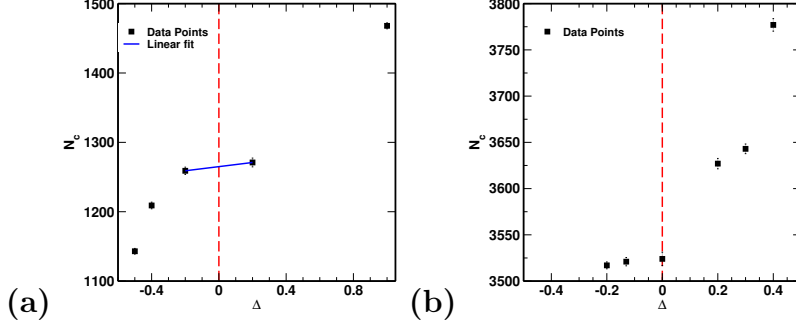


Figure S3: (a) gives the critical cluster $N_0^* = 1265 \pm 4$ obtained from linear fit of $N_c = 1260 \pm 5$ and $N_c = 1271 \pm 6$ at $P = 500$ bar (b) gives the critical cluster size of $N_0^* = 3524 \pm 7$ at $P = 1000$ bar.

Table S1: N_0^* estimated via seeding technique for TIP4P/Ice at 240 K and different pressures, compared with the literature.² Statistical Error for estimated N_0^* and the uncertainty in N_c reported in the literature are shown in parenthesis.

P (bar)	N_0^*	N_c^{*2}
1	685(4)	582(0)
100	804(4)	662(70)
500	1265(4)	1085(250)
700	1811(4)	2003(0)
1000	3524(7)	3560(0)

S1.1 Effect of pressure on nucleation rate

The effect of nucleation under varied pressure has been reported by Bianco *et al.*² where the structural identification was performed based on q_6 order parameter analysis, while the current study is based on CHILL+ analysis. Figure S5 represents the data points of current study in comparison to the literature values reported at $T=240$ K and 1 bar. At higher pressures, the nucleation rate is low, with the least reported being in the order of 10^{-109} at a pressure of 1000 bar. This is because the decreased melting temperature and increased density lead to reduced nucleating ability at high pressure.

S2 Coexistence pressure

Coexistence pressure is obtained based on direct coexistence simulations.^{2,7} At the desired temperature of 240 K, the pressure is varied according to the probable growth of ice in the

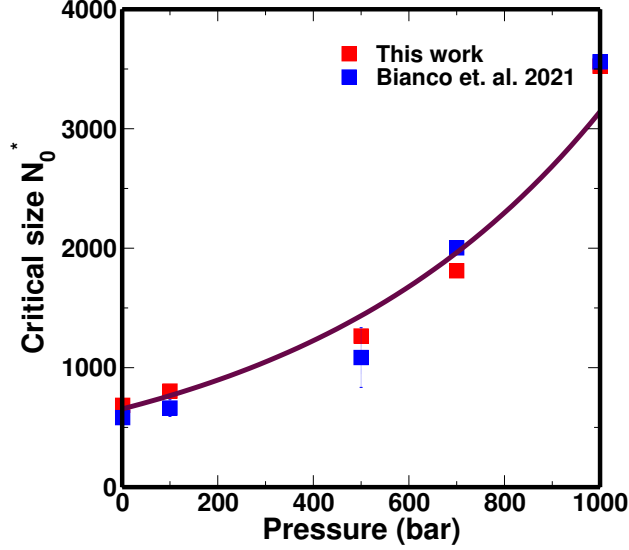


Figure S4: Critical size, N_0^* (at zero shear) at 240 K and different pressures computed based on seeding approach and compared with that of Bianco *et al.*²

system. Here $\Delta = (n_g - n_m)/n$ where n_g is number of trajectories that grow, n_m is number of trajectories that melt and n is total number of trajectories. If $\Delta > 0$, the probability of ice growth is high and hence the pressure is increased to increase the density. If $\Delta < 0$, the probability of ice to melt is high, and hence, the pressure is decreased to decrease the density. The pressure of coexistence is observed at $\Delta = 0$. Fig. S6 shows the probable ice growth around the coexistence point.

S2.1 Effect of pressure on the chemical potential difference

In order to determine the chemical potential difference between the supercooled water and ice I_h at a constant temperature of 240 K, we compute the coexistence pressure at the desired temperature based on the direct coexistence simulations described in the main text and perform thermodynamic integration with respect to the point of coexistence (since $\Delta\mu=0$ at coexistence).²

The coexistence pressure of the TIP4P/Ice water model at 240 K computed based on direct coexistence simulations is close to 2500 bar, as shown in the section S2. Thus, chemical potential difference computed at different pressures with regard to the coexistence pressure

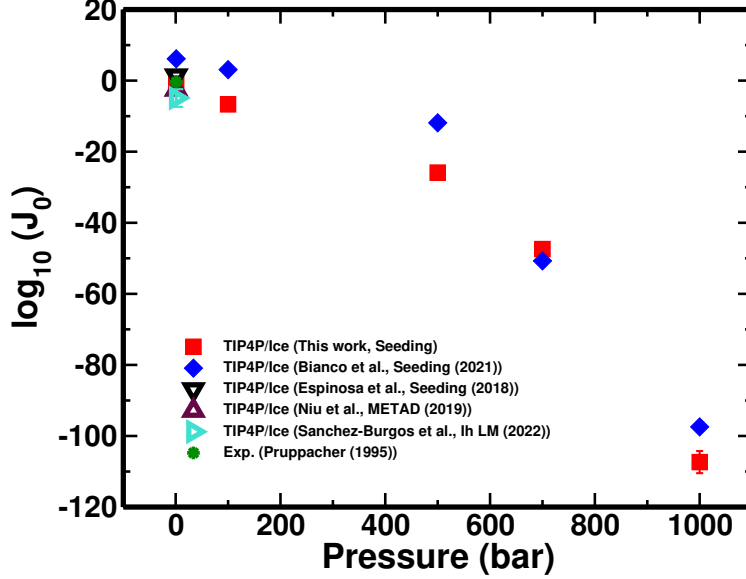


Figure S5: Nucleation rate at $T = 240$ K as a function of Pressure. The data points of the current study are represented in squares and the literature results of TIP4P/Ice are represented as diamonds,² triangle down,³ triangle up⁴ and triangle right.⁵ The experimental result of water drops at 1 bar is represented as a circle.⁶

showed that, with an increase in pressure, the difference of chemical potential between supercooled water and ice I_h crystal decreases as shown in Fig. S7. This implies that the tendency of liquid molecules to crystallize decreases with an increase in pressure.

S3 Molar volume

The table S2 represents the 9th order polynomial fit coefficients of the molar volume of ice and liquid with pressure at $T = 240$ K.

Table S2: Coefficients of the polynomial fit for v_{mol}^{ice} and v_{mol}^{liq} at 240 K. The polynomial equation is given as $A_0P^9 + A_1P^8 + A_2P^7 + A_3P^6 + A_4P^5 + A_5P^4 + A_6P^3 + A_7P^2 + A_8P + A_9$

v	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9
(nm^3)	$(\times 10^{-31})$	$(\times 10^{-27})$	$(\times 10^{-23})$	$(\times 10^{-20})$	$(\times 10^{-17})$	$(\times 10^{-14})$	$(\times 10^{-11})$	$(\times 10^{-9})$	$(\times 10^{-6})$	$(\times 10^{-2})$
v_{mol}^{ice}	0.33478	-0.38755	0.1852	-0.47166	0.68919	-0.57757	0.25904	-0.51074	-0.24375	3.24733
v_{mol}^{liq}	-2.41422	2.84505	-1.41267	3.84175	-6.21574	6.04727	-3.34629	9.1351	-3.1743	3.14742

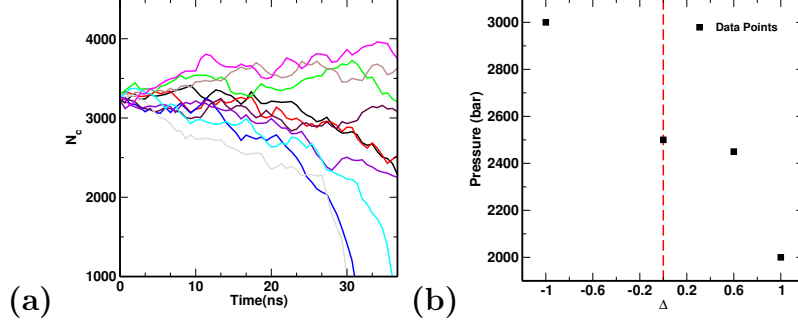


Figure S6: (a) represents 50% probable growth of the ice block at $P = 2500$ bar and $T = 240$ K. (b) represents probable growth of ice in a system of 4096 ice and 4132 liquid molecules analysed at different pressures and $T=240$ K. At $\Delta = 0$, the coexistence is observed at 2500 bar.

S4 Viscosity simulations

The viscosity of liquid water at thermodynamic equilibrium is constant over multiple orders of $\dot{\gamma}$. However, supercooled water shows dynamic behavior at higher shear rates.⁸ Supercooled water is Newtonian at lower shear rate till a crossover shear rate beyond which it behaves as a non-Newtonian fluid. Ribeiro *et al.* reported the behavior of supercooled water with change in $\dot{\gamma}$ at different temperatures by fitting the viscosity data of TIP4P/Ice model with Carreau model, since the viscosity is well within 1 Pa-sec.⁸ In fact, for simple liquids with relatively low viscosity, Carreau model was found to be a good fit for the simulation viscosities.⁹ The Carreau model is defined as,⁸

$$\frac{\eta_{\infty}}{\eta_N} = \left[1 + \left(\frac{\dot{\gamma}}{\dot{\gamma}_0} \right)^2 \right]^{\frac{n-1}{2}} \quad (\text{S1})$$

Where η_N is the Newtonian viscosity, $\dot{\gamma}_0$ is the crossover shear rate and n is the shear-thinning exponent which ranges between 0 and 1.⁸

Table S3 shows the Carreau fit parameters obtained for different pressures.

From the above data, the crossover shear rate, $\dot{\gamma}_0$ was found to be increasing with increase in pressure. This is analogous to the increase in crossover shear rate with temperature of TIP4P/Ice model by Ribeiro *et al.*⁸ The Newtonian viscosities of TIP4P/Ice model are

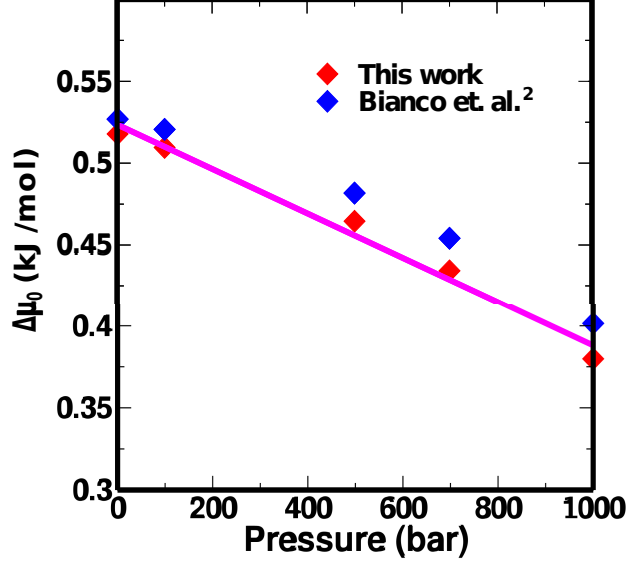


Figure S7: Difference of chemical potential, $\Delta\mu_0$ (at zero shear) between liquid and ice crystal of TIP4P/Ice water model at 240 K at different pressures compared with results from Bianco *et al.*²

Table S3: Carreau fit parameters for computing viscosity, η at 240 K. The error associated with the Newtonian viscosity is shown in paranthesis.

P(bar)	η_N (Pa-sec)	$\dot{\gamma}_0(\times 0.001 ps^{-1})$	n
1	0.0744071 (0.0005)	0.81858	0.24437
100	0.0569114 (0.0016)	0.82185	0.34515
500	0.0279539 (0.0011)	1.27466	0.50466
700	0.0236262 (0.0013)	2.04373	0.43427
1000	0.0157405 (0.0008)	3.26407	0.47009

one-order higher than the experimental viscosity. Similar trend for TIP4P/Ice model was observed by Goswami *et al.*¹⁰ where various transport properties of different water models were computed to study the sheared nucleation behavior. In our study, since we assume the liquid to be Newtonian, we consider the shear rate range within $0.001 ps^{-1}$ below the crossover shear rate for the pressure range of 1 to 1000 bar.

S5 Uncertainty in Nucleation rate

In seeding simulations, a significant error bar in critical nucleus size arises due to misrepresentation of interfacial ice molecules. An increase in seed size results in a decrease in

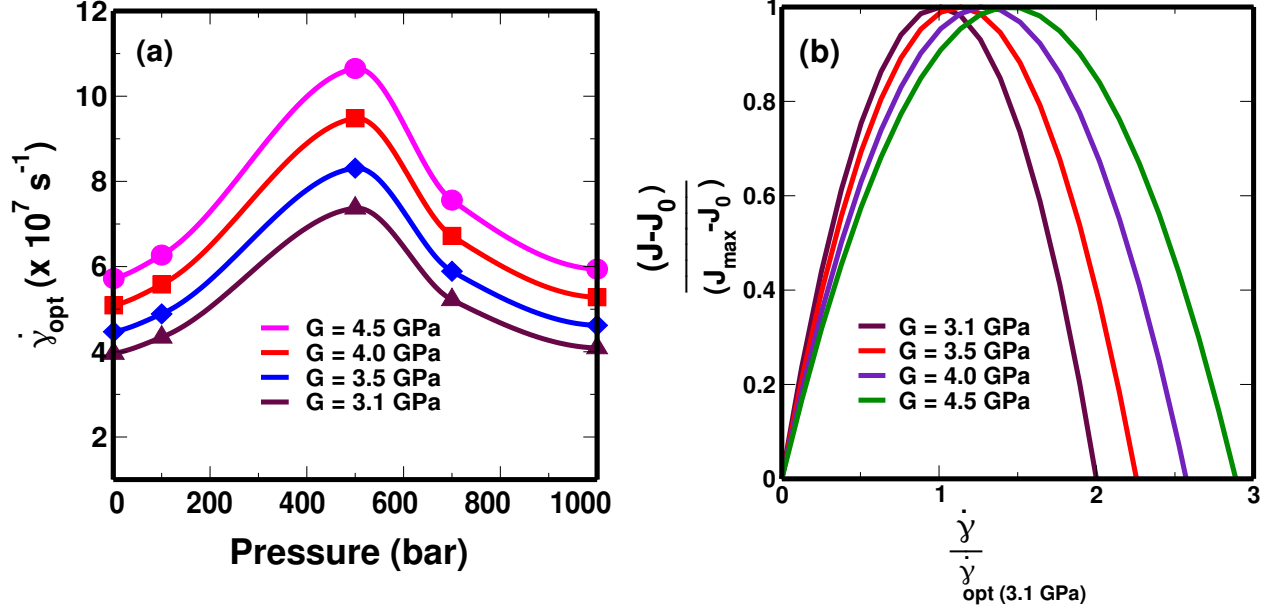


Figure S8: a) Effect of shear modulus on optimal shear rate at different pressures and (b) Effect of shear modulus on normalized nucleation rate at a pressure of 1 bar.

the number of interfacial molecules, and subsequently, the relative error associated with N_c also decreases. The error in determining the number of water molecules in critical seed also depend on the choice of order parameter used to distinguish between liquid, solid, and interfacial water molecules. Recent studies have demonstrated that the CHILL+ algorithm gives relatively lower error in misinterpreting ice molecules as liquid and vice versa.¹¹ Hence, we have implemented CHILL+ algorithm to distinguish liquid, solid, and interfacial water molecules in this work.

The exponential dependence of nucleation rate on seed size (equation 6 and 7 in the manuscript) leads to the propagation of error during nucleation rate prediction. Yet, we find that the qualitative behavior of the non-monotonicity with shear rate remains the same at different pressures.

S6 Effect of G on Optimal Shear Rate

The polyamorphous nature of ice leads to a change in shear modulus (G) with its crystallinity. For distinct cluster structures and crystal orientations of ice, the shear modulus can vary in the range of 3 GPa to 4.5 GPa.^{12,13} In this work, we assume a constant shear modulus of 3.1 GPa and predict the nucleation behaviour of water with shear. We observed that the optimal shear rate increases with an increase in G , while qualitatively maintaining similar behavior. Fig. S8 shows the variation of nucleation rate and optimal shear rates for different shear modulus. At higher G , the nucleation rates under constant low shear are relatively lower and the optimal shear rates are slightly higher. Considering the uncertainty of rheological behavior at higher shear rates and the assumption of Newtonian behavior made in the extended CNT formalism, we opted for a shear modulus of 3.1 GPa.

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