Nanosecond Freezing of Water at High Pressures: Nucleation and Growth near the Metastability Limit

Philip C. Myint, Alexander A. Chernov, Babak Sadigh, Lorin X. Benedict, Burl M. Hall, Sebastien Hamel, and Jonathan L. Belof^{*} Lawrence Livermore National Laboratory, Livermore, California 94550, USA

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The fundamental study of phase transition kinetics has motivated experimental methods toward achieving the largest degree of undercooling possible, more recently culminating in the technique of rapid, quasi-isentropic compression. This approach has been demonstrated to freeze water into the high-pressure ice VII phase on nanosecond timescales, with some experiments undergoing heterogeneous nucleation while others, in apparent contradiction, suggest a homogeneous nucleation mode. In this study, we show through a combination of theory, simulation, and analysis of experiments that these seemingly contradictory results are in agreement when viewed from the perspective of classical nucleation theory. We find that, perhaps surprisingly, classical nucleation theory is capable of accurately predicting the solidification kinetics of ice VII formation under an extremely high driving force ($|\Delta \mu/k_BT| \approx 1$) but only if amended by two important considerations: (i) transient nucleation and (ii) separate liquid and solid temperatures. This is the first demonstration of a model that is able to reproduce the experimentally observed rapid freezing kinetics.

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First-order phase transitions and their kinetics remain a fascinating topic with applications to virtually every major industry and to frontier fields like astronomy and inertial confinement fusion [1]. Despite its significance, many aspects of this topic are still largely unexplored, even for a fundamentally important substance like water at ambient pressure [2–4]. At this low pressure, it is difficult to deeply undercool liquid water [5,6], and so the driving force for freezing is rather limited in magnitude. In contrast, water becomes deeply undercooled (by up to 150 degrees; see Fig. 1) and remains as a metastable liquid for less than a microsecond in dynamic compression experiments performed over the past two decades, where it is rapidly compressed along a quasi-isentrope to pressures above 1 GPa [7–14]. Some of these experiments have achieved peak pressures of above 6 GPa [10,11,13], and their conclusion is that water freezes almost instantaneouslywithin a few tens of nanoseconds-if it gets overdriven to this point along the quasi-isentrope. For this reason, the 6-7 GPa range is said to represent a metastability limit for the liquid.

The dynamic compression experiments have employed one of two techniques (see our review paper [18]): multiple-shock or ramp compression. In both techniques, a thin water sample sandwiched between two thicker solid windows is compressed from ambient conditions along the quasi-isentrope into the ice VII region of the phase diagram (Fig. 1). Ice VII is a cubic high-pressure solid phase discovered over 80 yr ago [19] that may be present in oceanic super-Earths [16,17] and even in Earth's mantle [20]. No theoretical model developed to date has been able to reproduce the rapid (submicrosecond) liquid-ice VII transition kinetics observed in any of the experiments [18].

In this study, we show how a computational framework that couples classical nucleation theory (CNT) [21–26] and growth with hydrodynamic simulations can reproduce the transition kinetics observed in experiments where water freezes to completion rapidly at the metastability limit. We first apply CNT to explain past experimental observations, which indicate that freezing at this limit occurs primarily through homogeneous nucleation. We then show that, in order for simulations to reproduce experimental data, one must account for the fact that water under extreme conditions freezes into ice VII via transient nucleation and with essentially no thermal boundary layer at the solid-liquid interface.

The dynamic compression experiments can be divided into two categories, depending on the peak pressure achieved in the setup and the window material. It has been reported that if the peak pressure is around 5 GPa or less, freezing occurs over hundreds of nanoseconds but only if the windows are made of silica and not sapphire [7-9,12,13]. Freezing does not occur at all on submicrosecond timescales with sapphire windows. This materialdependent behavior suggests that, at pressures of less than around 5 GPa, freezing occurs primarily through heterogeneous nucleation of ice VII along the window surfaces. On the other hand, if the peak pressure goes beyond the



FIG. 1. Representative experimental setup for multiple-shock compression and the phase diagram for water superimposed on an illustration of a hypothetical oceanic exoplanet. The quasiisentropic loading path before the onset of freezing to ice VII may be approximated by the liquid principal isentrope. Ice VII has a body-centered cubic (bcc) lattice of oxygen. All the curves in the phase diagram are produced from our equation of state (EOS) for the two water phases [15]. Unlike single-shock compression (where the relevant curve is the Hugoniot), quasiisentropic compression can probe deeply undercooled states, since the temperature rise along its loading path is far more attenuated. The two-phase isentropes for the oceanic super-Earths Gliese 581d (GJ 581d) and Gliese 1214b (GJ 1214b) are initiated at surface temperatures of 340 and 400 K, respectively, which are rough estimates taken from Refs. [16,17].

metastability limit of 6–7 GPa, freezing achieves completion within just a few tens of nanoseconds, and it does so regardless of the window material (i.e., even with sapphire windows) [10,11,13]. This material-independent behavior suggests that freezing at these deeply undercooled conditions is dominated by homogeneous nucleation within the bulk of the water.

These results can be understood from the perspective of CNT. According to CNT [21–26], the steady-state homogeneous nucleation rate $J_{\text{homo}}^{\text{st}}$ is given by

$$J_{\text{homo}}^{\text{st}} = \mathcal{B}_{\text{homo}} \exp\left(\frac{-\Delta G_{\text{homo}}^*}{k_B T}\right),\tag{1}$$

where $\mathcal{B}_{\text{homo}}$ is a preexponential factor that reflects the number of available nucleation sites, ΔG^*_{homo} is the nucleation energy barrier, k_B is the Boltzmann constant, and T is the temperature [18]. Details regarding quantities like $\mathcal{B}_{\text{homo}}$ and ΔG^*_{homo} are summarized in Supplemental



FIG. 2. (a) Ratio of exponential and preexponential factors for heterogeneous vs homogeneous nucleation as a function of contact angle θ for three different pressures along the isentrope in Fig. 1. (b) Comparison of the time evolution of the ice VII phase fraction ϕ for these pressures, with the inset showing the behavior at early times. Freezing occurs primarily via homogeneous (heterogeneous) nucleation at higher (lower) pressures. Table 1 of Supplemental Material [27] shows the values of the quantities used to produce these plots.

Material [27]. The heterogeneous nucleation rate J_{hetero}^{st} may be analogously defined as $J_{hetero}^{st} = \mathcal{B}_{hetero} \exp(-\Delta G_{hetero}^*/k_BT)$, in which ΔG_{hetero}^* is related to ΔG_{homo}^* through the effective contact angle θ that ice clusters form on the water-window surface. While the detailed molecular basis for heterogeneous nucleation in this system is currently unknown, the concept of a contact angle provides an effective barrier-reduction mechanism that enables the analysis of the experimental results without the need to postulate specific atomistic processes.

Figure 2(a) shows that the exponential term overwhelmingly favors J_{hetero}^{st} , especially at smaller values of θ which are indicative of better "wetting" of the window surfaces by ice than by water, but this bias towards J_{hetero}^{st} decreases significantly at higher pressures. In contrast, the ratio $\mathcal{B}_{hetero}/\mathcal{B}_{homo}$ is relatively insensitive to the pressure and greatly favors J_{homo}^{st} , since there are far more nucleation sites (i.e., water molecules) in the three-dimensional bulk of the water than along the two-dimensional window surfaces. Thus, at some sufficiently high pressure, perhaps near the metastability limit, there is a crossover where J_{homo}^{st} becomes larger than J_{hetero}^{st} . These arguments can be further understood by examining the time evolution of the ice



FIG. 3. Our simulation results for the ramp-compression experiment of Dolan *et al.* [10]. All of the results correspond to those from our dual-temperature model unless otherwise indicated. (a) compares the pressure wave profile for four cases, three of which are from our simulations run with different models and the fourth from Dolan *et al.* To aid in understanding, (a) also shows how the driving force $\Delta \mu/k_B T$, the ice VII phase fraction ϕ , and the transient nucleation factor I(t) evolve with time. (b) portrays the temperature in the two phases, (c) illustrates the induction time τ and number of ice molecules n^* in critical size clusters, and (d) depicts the nucleation rate J and growth rate γ , including insets that focus on the behavior near the onset of the transition.

VII phase fraction ϕ [Fig. 2(b)]. The time derivative $\partial \phi / \partial t$ due to homogeneous nucleation is given by the Kolmogorov-Johnson-Mehl-Avrami (KJMA) equation [59–63] presented in Eq. (6) below. At 7 GPa, the homogeneous nucleation rate is so overwhelming that the distance between the neighboring crystals is small and complete solidification is achieved after roughly 10 ns. In contrast, the solidification front in heterogeneous nucleation has to, regardless of the pressure, travel the thickness of the entire water sample, which is a much longer distance. Thus, even if we assume instantaneous saturation of the two water-window surfaces of the setup by ice nucleation, the upper-bound limit on ϕ_{hetero} is $\phi_{hetero} = 2\gamma t/\ell$, where γ is the cluster growth rate [see Eq. (2) below] and $\ell = 0.01$ cm is a representative thickness.

The CNT-based analysis underlying the results in Fig. 2 seems promising in that it explains the major experimental finding that homogeneous (heterogeneous) nucleation is dominant at higher (lower) pressures. But, in order to pursue a quantitative comparison with data from the experiments, a computational framework that includes coupling between CNT and hydrodynamics is required. In what follows, we describe how such a framework yields a quantitative agreement with the observed pressure wave profiles from all experiments conducted to date where the peak pressure exceeds the 6–7 GPa metastability limit so that homogeneous nucleation dominates. Two self-consistent features must be included to account for the deeply undercooled states present in the experiments: (i) a dualtemperature model for the liquid and ice VII phases and (ii) relaxing the assumption of steady-state nucleation.

To clarify why the liquid and solid phases exist at two distinct temperatures, we note that at 7 GPa the undercooling of the liquid $\Delta T_U \approx 150$ K (Fig. 1) and the latent heating by solidification is $\Delta T_Q = \Delta H/C_p \approx 100$ K [see Fig. 3(b)], where ΔH is the enthalpy of fusion and C_p is the liquid isobaric heat capacity. Since $\Delta T_U > \Delta T_Q$, we have the unique scenario that the vast majority of the heat released by the solidification process is absorbed by the growing crystal. As a result, the liquid must remain at a lower temperature than the newly formed ice, close to what it would be if there were no transition, thus enhancing the nucleation rate by maintaining the initial level of under-cooling. We refer to this tracking of separate liquid and ice temperatures as the dual-temperature model. Furthermore, the growth rate γ of the clusters may be approximated as [64,65]

$$\gamma = \left(\frac{k_B T}{m}\right)^{1/2} \frac{\Delta \mu}{k_B T},\tag{2}$$

where *m* is the molecular mass and $\Delta \mu = \mu_{\text{solid}} - \mu_{\text{liquid}}$ is the bulk chemical potential difference. An analysis of the transport properties near the interface reveals that the growth mode is dominated by attachment kinetics (see Supplemental Material [27]) and supports (2) as a physical description of the interface velocity.

Even at ambient pressure where metastable phases may last for a relatively long time with rapid cooling, there may not be sufficient time for steady-state nucleation to be established [66]. As a result, a transient nucleation factor [67] must be included so that the total homogeneous nucleation rate J is

$$J(t) = (1 - \phi)I(t)J_{\text{homo}}^{\text{st}}.$$
(3)

The time dependence of I(t) suppresses nucleation at early times ($I \ll 1$), a phenomenon commonly known as transient nucleation [21–26]. It is therefore not surprising that in rapid freezing under dynamic compression—where the effective cooling rate along the isentrope can exceed an extremely high value of 10⁹ K/s—one must account for I(t) as well. Following Kashchiev [68], we take

$$I(t) = 1 + 2\sum_{k=1}^{\infty} (-1)^k \exp\left(\frac{-k^2 t}{\tau}\right),$$
 (4)

where the induction time τ describes the mean first passage time for crossing the region of critical cluster size within k_BT of the nucleation energy barrier:

$$\tau = \zeta \frac{8k_B T}{\pi^2 \lambda D^*}.$$
(5)

Here, ζ is an adjustable parameter, λ is the curvature at the top of the nucleation barrier, and D^* is an attachment rate (see Supplemental Material [27]). If we set ζ , which is the only free parameter in our model, equal to unity, Eq. (5) reduces to the classical expression obtained by Kashchiev. Simulations with our model, applying the transient nucleation theory just described, are able to quantitatively match the freezing kinetics observed in all of the dynamic compression experiments we present in both the main text and in Supplemental Material [27] by the assignment of $\zeta = 55$. The instantaneous value of $\partial \phi / \partial t$ is given by the KJMA equation [59–63] mentioned earlier:

$$\frac{\partial \phi}{\partial t} = 4\pi (1 - \phi) \gamma(t) \int_0^t J(t') \left(\int_{t'}^t \gamma(t'') dt'' \right)^2 dt'.$$
 (6)



FIG. 4. Comparison between our simulation results and three multiple-shock experiments from Dolan *et al.* [10]. The peak pressure is high enough for the transition to occur in the 8 and 12 GPa experiments but not in the 5 GPa one. With the exception of the no transition curves (dashed), all of our results are produced with the dual-temperature model. The simulations include a plasticity model for the strength of ice VII that is active after solidification (solid blue and red curves) and results in a damping of the shock wave ringing after 400 ns (8 GPa) and 180 ns (12 GPa), in closer agreement with the experimental data than without strength (dotted curves).

We solve Eq. (6) together with the governing conservation equations by running the multiphysics hydrodynamics code ARES [69] coupled with our phase transition kinetics code SAMSA. These codes and the various material models employed by them are detailed in Supplemental Material [27].

Before the ramp-compression path in the experimental study of Dolan et al. [10] has crossed the melt curve, the liquid is stable, since $\Delta \mu = \mu_{\text{solid}} - \mu_{\text{liquid}} > 0$ [Fig. 3(a)]. This is followed by a period of about 50 ns during which the water remains as a metastable liquid so that $\Delta \mu / k_B T$, τ , and the critical cluster size n^* continue to decrease. Finally, when the magnitude of the driving force reaches a sufficiently large value of $|\Delta \mu / k_B T| \approx 1$, freezing rapidly goes to completion (ϕ rises from 0 to 1) in about 10 ns, which is reflected in the sharp rise and fall of J. Optical transmission and imaging data from Dolan et al. also indicate that freezing is completed within about 10 ns. During the transition, the pressure decreases (from about 7 to 6.7 GPa), which is consistent with freezing to the more dense ice VII phase. It is apparent from Fig. 3 that both transient nucleation and the dual-temperature model are necessary to properly describe freezing at these extreme conditions. Our value of $\zeta = 55$ in Eq. (5) results in a τ such that I(t) suppresses the nucleation rate J to yield good agreement with Dolan et al. The figure also shows that, if we neglect the fact that the growth rate is faster than the rate of latent heat transport so that both phases are described by a single temperature in which the liquid is hotter than it would be in reality (and, hence, nucleation would be suppressed), then the resulting pressure profile does not match Dolan *et al.*, and freezing does not achieve completion.

Our CNT-based solidification kinetics framework also quantitatively reproduces the results of a different class of experiments that utilize multiple-shock compression (Fig. 4). The wave profile retains an idealized ringing structure in the absence of a transition, but, if freezing does occur, there is again a rapid drop in pressure. Like in ramp compression, freezing achieves completion in multipleshock compression, but it does so over 20-30 ns rather than ≈ 10 ns like in ramp compression. This is because the quasi-isentrope in multiple-shock compression attains higher temperatures (lower driving force) and so is less favorable for freezing. It is worth noting that, in the multiple-shock data illustrated in Fig. 4, there is a significant damping on the ringing immediately following the onset of freezing. This unknown source of dissipation is not accounted for by the phase transition kinetics alone, and, although not the focus of our study, we have attempted to model the damping through a strength model for ice VII that we describe further in Supplemental Material [27].

Figure 4 also depicts results for an experiment with sapphire windows where the peak pressure is only around 5 GPa. Our models correctly predict that freezing does not occur under these conditions. In contrast, previously published simulations of these "null result" experiments have artificially disallowed freezing by removing the ice VII phase from their EOS (i.e., running liquid-only models) rather than allowing a model of the kinetics to determine the final state [9,11–13,18]. The ability to reproduce this null result is an important test of our CNT-based framework, and we show in Supplemental Material [27] that it successfully reproduces similar experiments from Dolan and Gupta *et al.* [9] and Stafford *et al.* [13].

We have explained how a theoretical framework built on CNT and growth, when combined with hydrodynamics simulations, provides a quantitative agreement with experimental pressure wave profiles associated with nanosecond freezing kinetics of liquid water to ice VII via homogeneous nucleation. This is the first such demonstration of a single, unified framework that can match the phase transition kinetics observed in multiple different dynamic compression experiments. Our results suggest new experiments regarding the nature of the metastability limit: If one were to increase the ramp-compression loading rate, could liquid water remain beyond 7 GPa? In opposition to this limit is the fact that faster loading rates also generate more entropy and thus reduce the driving force; therefore, there may be an optimal loading rate which can truly achieve the metastability limit. Such future studies, informed by the results presented here, will shed light on the details of nucleation far from equilibrium and experimentally determine the limit where the classical theory breaks down.

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belof1@llnl.gov

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