



# Earth's inner core nucleation paradox

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## ABSTRACT

The conventional view of Earth's inner core is that it began to crystallize at Earth's center when the temperature dropped below the melting point of the iron alloy and has grown steadily since that time as the core continued to cool. However, this model neglects the energy barrier to the formation of the first stable crystal nucleus, which is commonly represented in terms of the critical supercooling required to overcome the barrier. Using constraints from experiments, simulations, and theory, we show that spontaneous crystallization in a homogeneous liquid iron alloy at Earth's core pressures requires a critical supercooling of order 1000 K, which is too large to be a plausible mechanism for the origin of Earth's inner core. We consider mechanisms that can lower the nucleation barrier substantially. Each has caveats, yet the inner core exists: this is the nucleation paradox. Heterogeneous nucleation on a solid metallic substrate tends to have a low energy barrier and offers the most straightforward solution to the paradox, but solid metal would probably have to be delivered from the mantle and such events are unlikely to have been common. A delay in nucleation, whether due to a substantial nucleation energy barrier, or late introduction of a low energy substrate, would lead to an initial phase of rapid inner core growth from a supercooled state. Such rapid growth may lead to distinctive crystallization texturing that might be observable seismically. It would also generate a spike in chemical and thermal buoyancy that could affect the geomagnetic field significantly. Solid metal introduced to Earth's center before it reached saturation could also provide a nucleation substrate, if large enough to escape complete dissolution. Inner core growth, in this case, could begin earlier and start more slowly than standard thermal models predict.

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## 1. Introduction

Growth of the solid inner core is generally considered to be the primary driver of Earth's present geodynamo (Lister and Buffett, 1995), providing the major source of energy for convection in the liquid outer core. The core formed during accretion and is usually considered to have been completely molten initially. Secular cooling of the Earth ultimately brought the center of the core to the temperature at which macroscopic solid metal is thermodynamically stable (Nimmo, 2015). This is a necessary but insufficient condition for the onset of inner core crystallization. Before a liquid can begin to solidify, a stable crystalline cluster of atoms must form, and this requires that an additional thermodynamic barrier is surmounted (Christian, 2002). This energy barrier, known as the nucleation barrier, is due to the excess energy at the interface between crystal and liquid, which is a large fraction of the total energy when the crystalline cluster is small. In general, a liquid

must be cooled below the liquidus temperature, where macroscopic solid becomes stable, in order for the first stable crystal to form (e.g. Christian, 2002).

The nucleation problem has been studied intensively in regard to the precipitation of water droplets and ice in Earth's atmosphere, using laboratory experiments as well as empirical observations (Pruppacher and Klett, 1998). Water droplets in deep convective clouds have been observed to cool to  $-37.5^{\circ}\text{C}$  before freezing (Rosenfeld and Woodley, 2000). Even where dust is ubiquitous, water droplets must supercool substantially, typically to temperatures less than  $-10^{\circ}\text{C}$ , before ice nucleates. Crystal nucleation in liquid metals and alloys has also been investigated carefully and extensively, due to the industrial importance of this process (e.g. Christian, 2002). However, to our knowledge, no previous study has considered or evaluated quantitatively the thermodynamic barrier to nucleation in Earth's inner core, or its consequences for inner core formation and core evolution. In this paper, we provide a detailed assessment of the nucleation barrier for crystallization from the liquid iron alloy in Earth's core, based on experimental, computational and theoretical constraints.

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## 2. Classical nucleation theory

Our assessment of the energetic barrier to inner core nucleation is founded on classical nucleation theory, which was developed 90 yrs ago based on the works of Gibbs (see [Christian \(2002\)](#) for review). This theory, although approximate, remains the predominant tool used to evaluate and extend experimental data and is buttressed by a wealth of experimental observations (e.g. [Turnbull, 1950](#); [Christian, 2002](#)). It has also been numerically validated for simple systems such as metals by hard sphere models ([Auer and Frenkel, 2004](#)) and molecular dynamics simulations ([Shibuta et al., 2016](#)), and has been applied successfully to many other systems with more complicated liquid and crystalline structures ([Sosso et al., 2016](#)).

In the classical nucleation framework, the stability of a crystalline cluster of atoms, or nucleus, is governed by the competition between its internal free energy, which scales with the volume of the cluster, and the interfacial energy between it and the liquid, which scales with its surface area ([Turnbull, 1950](#); [Christian, 2002](#)). The Gibbs free energy change can be written as

$$\Delta G = \left\{ \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma_{ls} \right\} S(\theta), \quad (1)$$

where  $\gamma_{ls}$  is the interfacial energy,  $\Delta G_v$  denotes the volume free energy change and  $r$  is the nucleus radius. The parameter  $S(\theta) = (2 - 3\cos\theta + \cos^3\theta)/4$  applies to heterogeneous nucleation on a pre-existing surface within the liquid ([Christian, 2002](#)), where  $\theta$  is the wetting angle between the nucleus and the surface. For nucleation in a homogeneous liquid (which is one without a pre-existing surface at the location where the melting temperature will be reached), or on a surface with  $\theta = 180^\circ$ ,  $S(\theta) = 1$ . If, on the other hand, a surface exists that the nucleus wets strongly ( $\theta \ll 180^\circ$ ),  $S(\theta)$  becomes small.

Beyond a critical radius the nucleus can survive and grow, but to reach this critical size requires cooling below the melting temperature. The critical supercooling that corresponds to this critical radius, is given by the classical theory of nucleation as

$$\frac{\Delta T_c}{T_m} = \left[ \left( \frac{16\pi}{3} \frac{\gamma_{ls}^3}{(\Delta H_f)^2 \Delta G^*} \right) S(\theta) \right]^{\frac{1}{2}}, \quad (2)$$

where  $\Delta G^*$  denotes the activation energy for nucleus formation,  $\Delta H_f$  is the latent heat of fusion per unit of volume, and  $\Delta T_c = T_m - T_c$  represents the critical supercooling below the melting temperature  $T_m$ .

Alternatively, it is sometimes convenient to express the critical conditions for nucleation in terms of the degree of supersaturation, rather than supercooling. The critical supersaturation ratio  $c/c_{eq}$  is written as

$$\frac{c}{c_{eq}} = \exp \left( \sqrt{\frac{16\pi}{3} \frac{\gamma_{ls}^3 V_m^2}{(RT)^2 \Delta G^*}} \right) \quad (3)$$

where  $V_m$  is the molar volume of the precipitating solid and  $R$  is the gas constant.  $c/c_{eq}$  is the supersaturation ratio with  $c$  the concentration of supersaturated solute and  $c_{eq}$  the equilibrium concentration.

The formation rate of nuclei with the critical radius is described by an exponential law. For steady state homogeneous nucleation, the nucleation rate per unit volume is given by

$$I_{hom} = I_0 \exp \left( -\frac{\Delta G_a}{kT} \right) \exp \left( -\frac{\Delta G^*}{kT} \right), \quad (4)$$

where  $k$  is the Boltzmann constant,  $\Delta G_a$  is the activation energy for diffusion, and the prefactor  $I_0$  depends on temperature and the material properties. The prefactor  $I_0$  is poorly known but has a typical value  $10^{42}$  ([Christian, 2002](#)) and is not sensitive to temperature. Its exact value is not important because the second exponential term is very large and is the primary control on the nucleation rate. The temperature dependence of the first exponential, which denotes the atomic jump frequency, is much smaller than the temperature dependence of the second exponential term, which corresponds to the probability of growth of a nucleus. At temperatures well above the glass transition, the first exponential can be approximated as  $\exp(-\Delta G_a/kT) = 10^{-2}$  ([Christian, 2002](#)), and we can rewrite equation (4) simply as

$$I_{hom} = 10^{40} \exp \left( -\frac{16\pi}{3} \frac{\gamma_{ls}^3}{(\Delta H_f)^2} \frac{T_m^2}{\Delta T^2 kT} \right). \quad (5)$$

The nucleation rate (Eq. (5)) increases rapidly with an increase of the supercooling ( $\Delta T = T_m - T$ ) and decreases abruptly when a very low temperature ( $T$ ) is reached, where diffusion in the liquid becomes negligible ([Fig. 1a](#)). The exponential form of the nucleation rate implies that nucleation is extremely unlikely occur when the supercooling is substantially smaller than the critical value. During cooling, the nucleation rate remains negligible until the critical supercooling temperature is closely approached ([Fig. 1c](#)).

## 3. Homogeneous nucleation

When no pre-existing surfaces exist within the liquid, the supercooling required for nucleation in liquid metals is large. Before reliable experiments on homogeneous nucleation in liquid metals and alloys had been conducted, it had been assumed that the interfacial energy between solid and liquid metallic phases was small, based on their similarity in density and other properties. It was therefore surprising when early experiments found that liquid metals had to be supercooled about 20% below their melting temperature ( $\Delta T_c/T_m \sim 0.2$ ) before nucleation began ([Turnbull, 1950](#); [Gomersall et al., 1965](#); [Christian, 2002](#)). In more recent experiments, performed without containers using levitation methods, on samples that had been purged more rigorously of solid impurities that could provide heterogeneous nucleation sites, even larger values have been measured, as high as  $\Delta T_c/T_m = 0.3$  for pure liquid iron ([Schade et al., 1987](#)). The large supercooling required to crystallize liquid metals through homogeneous nucleation has been demonstrated to be due to the presence of local icosahedral order in the liquid, which is incompatible with the extended structural order of the crystal and leads to a large interfacial energy between liquid and solid metal ([Kelton et al., 2003](#)). In liquid iron specifically, the icosahedral order has been suspected to persist and perhaps become stronger at high pressures, but there has not yet been experimental observations to support or refute this idea ([Boehler and Ross, 2015](#)).

Molecular dynamics simulations on pure iron ([Zhang et al., 2015](#)) at pressures up to 350 GPa find that  $\Delta T_c/T_m \sim 0.32$  over a wide range of pressures, similar to the experimental measurements at ambient pressure. Inferences based on superheating systematics in high-pressure shock wave experiments yield a similar estimate,  $\Delta T_c/T_m \sim 0.31$ , for the critical supercooling of iron at 270 GPa ([Luo and Ahrens, 2004](#)).

There is some dependence of the critical supercooling on composition. In systems where the liquid and solid compositions are significantly different, as they are in Earth's core, the interfacial energy is typically larger ([Eustathopoulos, 1983](#); [Christian, 2002](#)). This tends to increase the magnitude of the critical supercooling. Although the critical supercooling can decrease somewhat in solid-solution systems, it remains large in the iron alloy systems that

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