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Phase transitions and short timescale sinusoidal motions

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Abstract

While the effects of phase transitions of mantle materials are considered in convection studies, models of geophysical processes that occur on shorter timescales, such as seismic normal modes and Earth tides, often ignore these effects. A common justification is that the latent heat released from the material changing phase could not conduct away from the boundary on timescales shorter than those of convection, and thus the phase transition would not proceed. In this study, we first examine the behavior of a phase boundary to a periodic pressure perturbation by solving the heat equation. If all the latent heat is released at an infinitely thin boundary, we find that the phase transitions do not proceed. However, if the latent heat is released over a region of 1–5 km thickness, which might occur due to the divariant nature of the phase boundaries, then some of the material changes phase regardless of the period of the forcing. We apply these results to predictions of seismic normal mode center frequencies and elastic Love numbers. The perturbations to the normal mode frequencies can be two orders of magnitude greater than the differences between the observed frequencies and those predicted using the Preliminary Reference Earth Model. However, we have not considered kinetics, the energetics of the mechanisms of the phase transitions, in this formulation. This work suggests a greater knowledge of the kinetics near equilibrium phase boundaries is required because the kinetics may be the limiting factor in these short period, small amplitude motions.

Keywords: phase transitions; discontinuities; thermal conductivity

1. Introduction

The seismic discontinuities at 410 and 660 km depth are widely believed to be caused by phase transitions of the $[Mg,Fe]_2SiO_4$ system. The hydrostatic pressures at these depths correspond to the pressures observed in laboratory experiments for the transitions from olivine to wadsleyite and ringwoodite to perovskite plus magnesiowüstite. These phase transitions are explicitly considered in convection studies and can significantly affect the style of convection in the mantle (e.g., [1]). At timescales shorter than a few million years, however, the effects of these phase transitions are often ignored.

Two early studies of the response of the Earth to a series of glaciation cycles (glacial isostatic adjustment or GIA) provide a context for this

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simplification. O'Connell [2] investigated the effects of phase transitions on GIA by solving a modified Stefan problem; the heat equation is solved for a first order phase transition with the two phases separated by an infinitely thin boundary (i.e., all of the latent heat is released at this boundary). He assumed (as will we) that the phase boundary moves through the background pressure and temperature gradients so that the pressure and temperature conditions at the boundary always lie on the line defined by the Clausius–Clapeyron slope. The deglaciation event was modeled as a sudden (step function) decrease in pressure. In this context, O'Connell showed that the phase transition of olivine to wadsleyite has a response time of 4.5 million years. Thus, he argued that on the 10^4–10^5 year timescale of GIA, these transitions would not be important. This argument could be extended to imply that one could ignore the effects of phase transitions for any process with a timescale shorter than that of GIA. Christensen [3] showed, however, that this result does not hold if the phase change occurs over a range of pressures due to a binary mineral system. In this case the latent heat would be released over a radial distance corresponding to the range in pressure over which the phase change occurs. Christensen assumed that the phase transition would be isentropic (thermal diffusion would not occur), and his formulation is independent of time. He found that the two-phase region acts as a reservoir for the latent heat and that some material would always change phase.

Tamisiea and Wahr [4] (hereafter referred to as TW) investigated the effect of phase transitions on GIA by using a viscoelastic earth model (e.g., [5]) while incorporating thermal conduction through the heat equation. In this formalism the thermal and mechanical equations couple only at the phase boundary. This technique allows one to include the effects of latent heat release for either of the boundary types (thin or thick) described above. TW found that when the latent heat is released over a thick region, the elastic load Love numbers (in the context of GIA–period forcings) will be different from those derived assuming that mantle material cannot change phase (i.e., chemical boundary conditions). This result suggests the intriguing possibility that material may change phase during short timescale geophysical processes, such as tidal motion or seismic normal modes.

If phase transitions can occur on short timescales, some inferences of Earth properties derived from observations of geophysical processes may be systematically biased. For example, the Earth's radial density profile is primarily obtained from analysis of seismic normal modes. If phase transitions have a significant impact on the seismic normal modes, the radial density profile found by assuming that mantle material does not change phase would be in error. In addition, phase transitions could provide a mechanism for bulk attenuation in the mantle. If the pressure perturbation corresponding to a seismic normal mode causes material to change phase, a portion of the mechanical energy could be dissipated through the generation and conduction of latent heat. While bulk attenuation is difficult to measure, its presence in the mantle is suggested by the anomalously large damping rates observed for the seismic radial modes ${}_nS_0$ [6].

In this paper, we investigate the possibility of phase transitions occurring on short timescales as well as the attenuation that might result from the phase changes. In Section 2 we give a short overview of the problem in addition to defining terms and specifying assumptions used throughout the paper. In Section 3, we investigate the motion of the phase boundary to a sinusoidal pressure forcing by solving the heat equation with different models of the boundary between the phases. In Section 4 we apply the results obtained in Section 3 to predictions of seismic normal mode center frequencies and elastic load and body Love numbers using the technique developed by TW. Section 5 contains the conclusions as well as a discussion of the effects of kinetics.

2. Overview and terms

When subjected to external forcing, the boundary between two different phases has a markedly different behavior depending upon whether or not the material can change phase. If the material cannot change phase, the boundary moves with the material particle surrounding it. Thus, the boundary motion is described by the Lagrangian motion of the particles and so is mechanically indistinguishable from a chemical discontinuity. However, if the material can change phase, the discontinuity moves radially through the background pressure and temperature gradients, dP/dr and dT/dr, respectively, so that the pressure and temperature conditions remain on a line defined by the Clausius–Clapeyron slope, $(dP/dT)_c$. This condition is equivalent to requiring that the phase transition always be in equilibrium. In the limiting case that no latent heat is released, this equilibrium requirement implies that the density discontinuity primarily moves to maintain a constant pressure because $dP/dr \gg (dP/dT)_c dT/dr$.

The release of latent heat will act to inhibit the phase transition from occurring. For example, at the density discontinuity caused by the olivine to wadsleyite phase transition, which has a positive Clausius–Clapeyron slope, assume that the pressure increases due to some geophysical process. In the absence of latent heat release, the phase boundary moves radially upward (olivine changes to wadsleyite) to maintain a nearly constant pressure. However, the latent heat effects cause the temperature of the material near the boundary to increase when this phase change occurs. To maintain equilibrium, the phase transition now occurs at a higher pressure, and thus the boundary moves radial downward (back towards its initial position.) Because the latent heat and the Clausius–Clapeyron slope have the same sign, a similar argument applies to the ringwoodite to perovskite plus magnesiowüstite transition, where the Clausius–Clapeyron slope is negative. Thus, the maximum amount of mantle material that can change phase (and thus the largest change from the predictions found assuming chemical boundaries) occurs when no latent heat is released.

When solving the heat equation to find the temperature perturbation due to latent heat release, we consider two scenarios. First, we assume that the boundary between the two phases is a simple surface: i.e., all the material on either side of the boundary is either in one phase or the other. When solving the heat equation, this implies that all of the latent heat generated by material changing phase will be released at that surface. We will refer to this scenario as a thin phase boundary. Second, we assume that there is a region over which both phases coexist due to the divariant nature of the phase transition. Thus, because temperature and pressure perturbations would cause the material throughout this region to change phase, the latent heat would be released over a thick region. We refer to this scenario as a thick boundary. These two scenarios, which we will show produce significantly different effects, lead to notably different temperature perturbations caused by the latent heat release. If the same amount of material changes phase, the thick boundary will produce a smaller temperature perturbation because the latent heat produced will be distributed over the thick region as opposed to being entirely released at a surface as in the thin boundary case.

Throughout this discussion we have assumed that the phase boundary is always in equilibrium. This implies that there is enough kinetic energy in the pressure or temperature perturbation caused by the geophysical process to overcome the potential energy barrier associated with diffusion, nucleation of a new phase, or growth of an existing phase from another. These energy considerations are loosely grouped together in the term kinetics. These potential energy barriers imply that a geophysical process may need to subject material to pressure and temperature conditions far from equilibrium in order for the material to change phase. We will not consider the kinetics in the calculations below but will further discuss its implications on this problem in the conclusions.

3. Periodic forcing of the heat equation

In a manner similar to O'Connell [2] and Christensen [3], we initially examine the response of a phase boundary to an arbitrary sinusoidal pressure forcing by solving the one-dimensional heat equation. This approach allows one to discern the behavior of the boundary without the complications associated with the motion of the surrounding material. Our goal is to explore the ability of mantle material to change phase as a function of both the period of the pressure forcing and the width of the phase boundary. The general results from these calculations will be applied in Section 4 to the more complete case where the thermal and mechanical equations are coupled in a spherical Earth model.

Suppose we apply a sinusoidal pressure change, $\Delta P(t) = A\ \sin(\omega t)$, to the region surrounding a phase boundary. The assumption that the boundary is in equilibrium implies that perturbations in pressure and temperature at the displaced boundary must be related through the Clausius–Clapeyron slope, $(\mathrm{d}P/\mathrm{d}T)_{\mathrm{c}}$. Thus, the position of the phase boundary, $x_{\mathrm{p}}(t)$, satisfies:

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_c \left[\frac{\mathrm{d}T}{\mathrm{d}x}x_{\mathrm{p}}(t) + \theta(x_{\mathrm{p}}(t), t)\right] = \frac{\mathrm{d}P}{\mathrm{d}x}x_{\mathrm{p}}(t) + \Delta P(t) \quad (1)$$

The terms in the square brackets on the left hand side of Eq. 1 represent changes in temperature due to the movement of the boundary through the background temperature gradient, $\mathrm{d}T/\mathrm{d}x$, and the release of latent heat, $\theta(x_{\mathrm{p}}(t),t)$. The terms on the right hand side of Eq. 1 represent changes in pressure due to the movement of the boundary through the hydrostatic pressure gradient, $\mathrm{d}P/\mathrm{d}x$, and the applied pressure change, ΔP.

To find $x_{\mathrm{p}}(t)$ from Eq. 1 for a given $\Delta P(t)$, one needs to find the associated $\theta(x_{\mathrm{p}}(t),t)$. This temperature perturbation will depend upon whether the latent heat is released over a mixed phase region (thick boundary) or at a thin boundary between two phases. For simplicity, we treat the thin boundary case as the limit of the thick boundary where the width of the boundary goes to zero. To describe the mixed phased region, we follow the approach used in TW. We define $n(x,t)$ as the fraction of the material at x that is in the same phase as the material above the boundary region at time t. The function $n(x,t)$ is centered at $x_{\mathrm{p}}(t)$ [i.e., $n(x_{\mathrm{p}}(t),t) = 1/2$] and varies between 0 below the boundary and 1 above the boundary. Because we are only modeling the fact that the latent heat is released over a thick region and not the mechanisms causing it, we choose $n(x,t)$ to be a mathematical function that makes the evaluation of θ simple (see below):

$$n(x,t) = \mathrm{Erfc}[(x_{\mathrm{p}}(t) - x)/W]/2 \quad (2)$$

where W is the half-width of the boundary. Note that if the boundary is 5 km wide ($W = 2.5$ km), $n(x,t)$ varies by 0.84 in a 5 km region centered about $x_{\mathrm{p}}(t)$. If $W \to 0$, $n(x,t)$ effectively becomes a step function, and the thick boundary reduces to the thin boundary. Because the position of this distribution will change with time (as the center of the phase boundary, $x_{\mathrm{p}}(t)$, moves), the latent heat release will be proportional to the time derivative of $n(x,t)$.

Boundary conditions are also required to solve the heat equation:

$$\dot{\theta} = \kappa \nabla^2 \theta \quad (3)$$

where κ is the thermal diffusivity and the overdot is a partial time derivative. Because the latent heat should not conduct far away from the phase boundary on short timescales, there will be no significant interaction between boundaries. Thus, we consider an infinite medium where the temperature perturbation goes to zero at $\pm\infty$. We assume that the boundary between the two phases of the material is initially at $x_{\mathrm{p}}(t=0) = 0$. At the phase boundary, the general conditions of a Stefan problem apply (e.g., [7]): the temperature across the boundary is continuous and the discontinuity in the temperature gradient is equal to the rate of latent heat release per unit area divided by the thermal conductivity.

We use a Green's function approach to solve the problem. We break the two-phase region into thin layers and add the contributions from each layer to find the total temperature perturbation. The rate of latent heat release for a thin layer of thickness $\mathrm{d}x'$ at x' and time t' is $-\rho L\dot{n}(x',t')\mathrm{d}x'$, where ρ is the density and L is the latent heat release per unit mass. Note that in this section the density is assumed to be the same above and below the boundary so that no mechanical motion occurs in the material. Thus, the temperature perturbation due the latent heat release is:

$$\theta(x,t) = \frac{\rho L}{k}\int_0^t \int_{-\infty}^{\infty} \dot{n}(x',t') \frac{\sqrt{\kappa}}{\sqrt{4\pi(t-t')}}$$

$$\exp\left[-\frac{(x-x')^2}{4\kappa(t-t')}\right] \mathrm{d}x' \, \mathrm{d}t' \quad (4)$$

where k is the thermal conductivity [7,8]. Using our choice, Eq. 2, for $n(x,t)$, we find that the temperature perturbation is:

$$\theta(x,t) = \frac{\rho L}{k}\int_0^t \frac{\kappa \dot{x}_p(t')}{\sqrt{\pi}} \frac{1}{\sqrt{W^2 + 4\kappa(t-t')}}$$

$$\exp\left[-\frac{(x-x_p(t'))^2}{W^2 + 4\kappa(t-t')}\right] dt' \quad (5)$$

Note that this equation reduces to that obtained by Carslaw and Jaeger [7] for the Stefan problem for a thin boundary ($W = 0$):

$$\theta(x,t) = \frac{\rho L}{k}\int_0^t \frac{\sqrt{\kappa}\dot{x}_p(t')}{\sqrt{4\pi(t-t')}} \exp\left[-\frac{(x-x_p(t'))^2}{4\kappa(t-t')}\right] \mathrm{d}t' \quad (6)$$

Using Eqs. 1 and either 5 or 6, a solution for $x_p(t)$ can be found by iteration (see [9]).

The largest amplitude of the motion of the phase boundary that would result from the pressure forcing in Eq. 1 is the case where the temperature perturbation from the latent heat release, θ, is zero. This corresponds to a situation where either no latent heat is released by the phase transition or the period of the forcing is sufficiently slow that the latent heat can effectively conduct away from the boundary. For this end case scenario the motion of the boundary, $x_p(t)$, is given by $A_o \sin(\omega t)$ where $A_o = A/[(\mathrm{d}P/\mathrm{d}T)_c(\mathrm{d}T/\mathrm{d}x) - (\mathrm{d}P/\mathrm{d}x)]$. When analyzing the motion of the boundary that includes the effect of the release of latent heat, we fit the results of Eqs. 1 and either 5 or 6 to the function $A' \sin(\omega t - \delta) + c_1 t + c_0$ where δ corresponds to the phase lag between the application of the pressure forcing and the motion of the phase boundary. While the coefficients c_1 and c_0 are included because the resulting motion of the phase boundary is not purely sinusoidal, these coefficients are small and will not be considered further. In the following discussion, we report both the phase lag and the amplitude ratio of the boundary response, defined as A'/A_o. Thus, the degree that the amplitude ratio is less than 1 indicates the extent that the release of latent heat inhibits the phase transition.

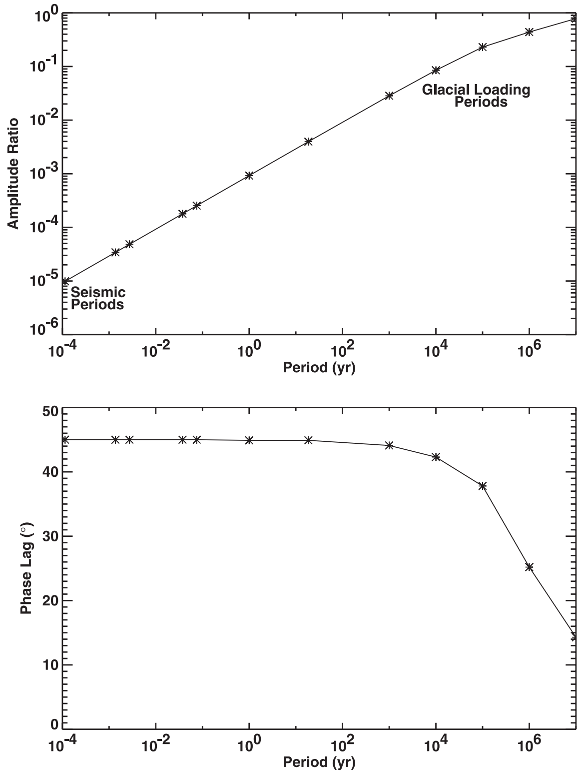

Fig. 1. Response and phase shift of a thin boundary to a sinusoidal pressure forcing. The amplitude ratio is the amplitude of the boundary motion when latent heat is released divided by the amplitude of the boundary motion when no latent heat is released. The angle is the phase lag between the pressure forcing and the resulting boundary motion.

In Fig. 1, we show the amplitude ratio and phase lag for a thin boundary versus the period of forcing, given the general values of the parameters listed in Table 1. The periods in this figure range from 1 h (the timescale of the longest seismic normal mode, ${}_0S_2$) to 10^7 years. In between are periods for a variety of geophysical processes, such as the 18.6 year tide and glacial loading (10^4–10^5 years). The top panel of Fig. 1 shows that for short timescale processes the amplitude

Table 1
Parameters used in Section 3

Parameter	Value	Units
$(\rho L)/k$	-1.1×10^{8}	s K m^{-2}
κ	1×10^{-6}	m^2 s^{-1}
$\mathrm{d}P/\mathrm{d}x$	-4×10^{4}	Pa m^{-1}
$\mathrm{d}T/\mathrm{d}x$	-8.9×10^{-4}	K m^{-1}
$(\mathrm{d}P/\mathrm{d}T)_c$	-2.5×10^{6}	Pa K^{-1}

ratio is very small. For example the amplitude ratio is less than 10^{-5} for the period of $_0S_2$. Thus, nearly none of the material would change phase when subjected to pressure perturbations at these timescales. The amplitude ratio is approximately proportional to the square root of the forcing period for periods less than 10^4 years, at which point the amplitude response is approximately 10%. The bottom panel of Fig. 1 shows that the phase lag of the boundary movement to the applied pressure perturbation is 45° for period up to 10^4 years and then decreases. Thus, if a significant amount of the material changed phase, the phase transitions could provide a source of bulk attenuation. However, the results in the top panel indicate that for a thin boundary, a phase boundary would behave as a chemical discontinuity for period much less than 10^4 years because an insignificant amount of the material would change phase. These results confirm, in the case of a thin boundary, previous beliefs that one could ignore the complication of phase boundaries in short period geophysical processes.

Fig. 2 shows the amplitude ratio and phase lag for a thick boundary versus the period of forcing, which in this case ranges only from 10^2 to 10^7 years. The thick boundary has a behavior very different from that of the thin boundary. First, note that the ordinate scale of the top panel is linear and not logarithmic as it is in Fig. 1. As the period of the pressure forcing decreases, the amplitude ratio for a given boundary thickness converges to a constant. This constant is larger for larger values of boundary thickness. The phase lag has a similar behavior for long period as that of a thin boundary, but the amplitude of the phase lag starts to decrease for periods between 10^4–10^6 years depending upon the boundary thickness. When the amplitude ratio has converged to a constant value, the phase lag has decreased to zero. Thus, for a thick boundary, some material will always change phase independent of the period of the forcing, but there will be no attenuation.

These non-intuitive results for the thick boundary can be explained by considering the ability of the latent heat to conduct out of the mixed phase region. Say, for example, that a pressure perturbation causes material to change phase throughout the thick boundary centered at x_p. Let us define d as the distance that the heat released at x_p could conduct away from x_p in the absence of any other heat sources. If d is less than the distance around x_p that material is changing phase,

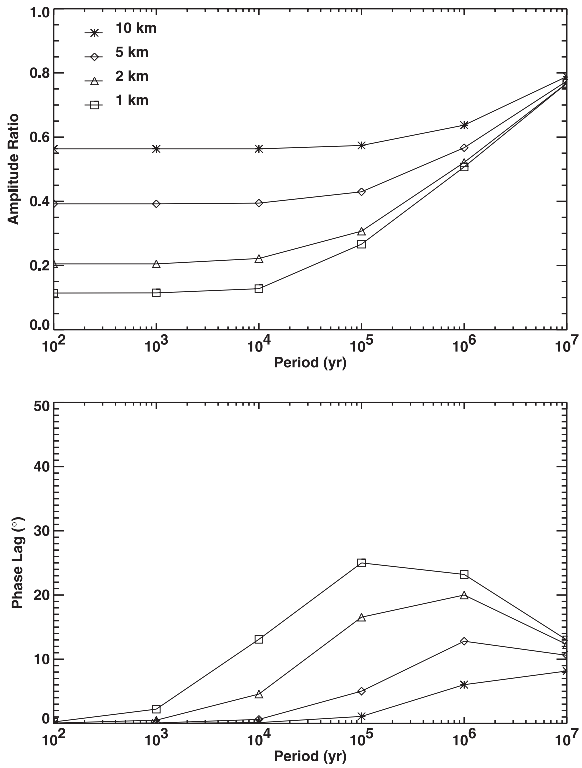

Fig. 2. Response and phase shift of boundaries with varying thickness to a sinusoidal pressure forcing. While the same quantities are plotted as in Fig. 1, note that the ordinate scale is now linear in the top panel. The lines connecting the symbols do not necessarily represent the behavior of these quantities between the abscissa values; rather they are included to facilitate identification of the different boundary thicknesses.

W, then the heat cannot conduct away. Instead, the temperature will simply rise. Because the total amount of heat released is more widely distributed, the temperature increase is less for thicker boundaries than for thinner boundaries. Thus, the amplitude response is greater for the thicker boundaries.

The same argument explains the behavior of the phase lag between the applied pressure forcing and the boundary motion. Because the phase lag is a result of the heat conducting away from the region, the phase lag is small if $d < W$. As an example, we examine the results for a period, τ, of 10^5 years. A rough measure of d is given by $\sqrt{\kappa\tau}$, which in this case is ~ 1.8 km. There is a significant phase lag for 1 and 2 km thick boundaries ($W = 0.5$ and 1 km respectively) while the 5 and 10 km thick boundaries experience a much smaller phase lag (Fig. 2). When no heat conducts away from the boundary (i.e., the amplitude ratio becomes a constant), there is no phase lag. This result agrees with Christensen's [3] when he assumed an isentropic phase change.

One can draw two important conclusions from this method of exploring the behavior of a phase boundary. First, if the phase boundaries in the mantle are best modeled as infinitely thin discontinuities, one would not need to consider the possibility of phase changes for periodic processes with periods much shorter than 10^4 years. Second, some material will change phase for thick boundaries regardless of the forcing period. Because the amplitude ratio becomes a constant and the phase lag goes to zero for short period processes, $x_p(t)$ is proportional to $\Delta P(t)$. Inverting this result (expressing $\Delta P(t)$ in terms of $x_p(t)$) and using Eq. 1, one finds that the temperature perturbation can be represented as a constant times the radial extent of the material that changes phase, which in this section is $x_p(t)$. This result will be used below.

4. Application to geophysical processes

We now include the qualitative results based on a simplified model obtained in Section 3 into the calculations of predictions of various geophysical observations, such as seismic normal mode center frequencies. Section 3 only considered the motion of the phase boundary through the material. However, if phase transitions are caused by geophysical processes, then the movement of the material itself is also important. In the case of GIA, for example, the displacement of the density discontinuities causes a restoring buoyancy force that drives flow in the mantle. Thus, useful predictions can only be obtained by solving both the mechanical and thermal equations. In this section we will limit our consideration to seismic normal modes and elastic Love numbers for forcing periods less than 100 years, such as tidal forcings. Therefore, we need only to consider a thick boundary because the effects from a thin phase boundary would be negligible.

In the context of GIA, TW introduced a method for coupling the thermal and mechanical equations at the phase boundary. This method allows one to include the effects of phase transitions and latent heat conduction by modifying the continuity condition on the radial displacements at the boundary. Because the Lagrangian displacements no longer describe the displacement of the density discontinuity, as described in Section 2, the Lagrangian radial displacements of material on either side of the boundary are no longer equal [4,10]. The only difficulty in applying the TW formalism directly to the seismic normal mode problem is that the method of TW solves the equations in the Laplace transform domain whereas the equations in the seismic normal mode problem are solved in the Fourier transform domain. However, the fact that for a thick boundary the temperature perturbation is proportional to the radial extent of the material changing phase, independent of the frequency of the pressure perturbation, allows one to apply this formalism.

TW described the temperature perturbation due to latent heat release, using a spherical harmonic expansion, as $\theta_l(s) = \theta_{lo}(s)[U_{l-}(s) - \delta R_l(s)]$, where l is the spherical harmonic degree, s is the Laplace transform variable, $U_{l-}(s)$ and $\delta R_l(s)$ are the Lagrangian displacements of the material initially below the boundary and of the density discontinuity respectively, and θ_{lo} is an integral factor that accounts for the distribution and conduction

Table 2
Thermal parameters used in Section 4

Parameter	Value		Units
	400 km	670 km	
T^a	1753	1873	K
k^b	2.93	7.39	W m^{-1} K^{-1}
α^c	2.76×10^{-5}	2.96×10^{-5}	K^{-1}
c_P ^{d}	1.315×10^3	1.34×10^3	J kg^{-1} K^{-1}
$(dP/dT)_c^e$	2.5×10^6	-2.5×10^6	Pa K^{-1}

[a] Value at 670 km obtained from Ito and Katsura [13] and extrapolated to 400 km using an adiabatic temperature gradient.
[b] Derived from Hofmeister [14] and includes both lattice and radiative contributions. Corrected for temperature and pressure.
[c] Obtained from Saxena [15] and corrected for both temperature and pressure.
[d] Obtained from Saxena [15] and corrected for pressure.
[e] Chosen to be within a range found by experiment [16].

of the latent heat release (see TW eq. 27). The factor $[U_{l-}(s) - \delta R_l(s)]$ represents the radial extent of the material that changes phase. TW found that for large values of the Laplace variable (around $s > 10^{-10}$ s^{-1}) $\theta_{lo}(s)$ becomes a constant, θ_{lo}^s, independent of s for thick boundaries. This follows for the same reasons, detailed in Section 3, that the temperature perturbation is a constant times the radial extent of the material changing phase. This conclusion from Section 3 can be written in the Fourier transform domain as $\theta_l(\omega) = \theta_{lo}^{\omega}[U_{l-}(\omega) - \delta R_l(\omega)]$, where ω is the Fourier transform variable and θ_{lo}^{ω} is a constant. Transforming both $\theta_l(\omega)$ and $\theta_l(s)$ back to the time domain and comparing the results, one finds that $\theta_{lo}^{\omega} = \theta_{lo}^{s}$. Thus, we obtain θ_{lo}^{s} using the method described in TW (eq. 27) with $s = 10^{-6}$ s^{-1} and apply the boundary condition on $U_l(\omega)$ (TW Eq. 19 without the assumption of incompressibility and replacing all of the Laplace transformed variables with Fourier transformed variables.)

We apply the new boundary conditions in a code developed by Smith [11], which calculates the seismic normal modes on a rotating earth. The most widely observed and interpreted characteristics of the Earth's normal mode spectrum are the center frequencies, and so it is these that we consider. To avoid complications caused by multiplet splitting, we have reduced the rotation rate of the Earth used in the code by four orders of magnitude. We use the Preliminary Reference Earth Model (PREM) [12] as the elastic Earth model and use the thermal parameters given in Table 2. The thermal diffusivity, κ, and the latent heat per unit mass, L, are calculated from $\kappa = k/(\rho_- c_P)$ and $L = \Delta\rho T (dP/dT)_c/(\rho_- \rho_+)$ where the values of density are taken from PREM and the subscripts − and + indicate values taken below and above the boundary, respectively.

Table 3
Perturbations to seismic modal center frequencies

Mode	$\delta\omega^a$ (μHz)					$\delta\omega_{obs}$ ^{b}
	1 km[c]	2 km[c]	5 km[c]	10 km[c]	NLH[d]	(μHz)
$_0S_2$	−0.36	−0.61	−1.04	−1.37	−2.02	0.15
$_1S_2$	0.60	1.03	1.82	2.45	3.73	0.30
$_0S_5$	−3.69	−6.27	−10.81	−14.26	−20.94	0.10
$_1S_5$	1.34	2.46	4.98	7.56	16.30	0.20
$_2S_5$	−11.22	−19.49	−34.99	−47.73	−76.71	0.30
$_0S_{12}$	−42.89	−70.03	−112.71	−141.29	−188.93	0.20
$_2S_{12}$	15.78	26.62	45.75	60.71	92.72	0.50
$_0S_{22}$	−62.55	−98.19	−149.00	−179.92	−226	.80
0.15						
$_1S_{22}$	18.57	29.97	47.78	59.91	81.15	3.50

[a] $\delta\omega = \omega - \omega_{chem}$ where ω_{chem} is the solution obtained using the normal (chemical) boundary conditions which do not allow material to cross the boundary.
[b] Observation errors taken from Masters and Widmer [17] included for comparison.
[c] Thickness of phase boundary over which the latent heat is released.
[d] Assumes that no latent heat (NLH) is released.

Table 4
Elastic load Love numbers h_l^L and k_l^L for PREM

Boundary type/boundary thickness	$-h_l^L$			$-k_l^L$		
	$l=2$	$l=10$	$l=30$	$l=2$	$l=10$	$l=30$
Chemical	0.9917	1.4233	2.2888	0.3054	0.06914	0.04065
Phase/1 km	1.0498	1.5209	2.3203	0.3085	0.07285	0.04133
Phase/2 km	1.0898	1.5838	2.3380	0.3106	0.07524	0.04164
Phase/5 km	1.1589	1.6853	2.3626	0.3143	0.07912	0.04209
Phase/10 km	1.2104	1.7555	2.3774	0.3171	0.08180	0.04241
Phase, NLH[a]	1.3085	1.8771	2.3996	0.3225	0.08646	0.04283

[a] Assumes that no latent heat (NLH) is released.

The perturbations of the center frequencies from the chemical boundary solutions for a range of seismic normal modes are shown in Table 3. Each of these modes is sensitive to the material properties and to the boundaries in the transition zone. The largest effect on the frequencies occurs for the unrealistic model of a phase boundary that releases no latent heat because the release of latent heat will act to inhibit the phase transition of material, as described in Section 2. As one would expect given the results in Section 3, the size of the perturbation is reduced as the thickness of the phase boundary decreases. However, even for the narrowest boundary, 1 km thick, the effects can be significantly larger than the observational errors of the center frequencies, which are presented in the last column of the table. For another point of comparison, we computed the effect of moving the 670 km discontinuity in PREM to 660 km using the standard boundary conditions (i.e., chemical boundaries). This causes a perturbation of 3 μHz for the case of ${}_0S_{22}$, which is approximately 20 times smaller than the perturbation caused by a 1 km thick phase boundary. The size of these perturbations suggests the seismic normal modes could offer a probe into the effective behavior of the mantle phase transitions. These results also suggest that the radial density profile in the transition zone, which is primarily determined from seismic normal mode data, may need to be re-examined due to the possible systematic mismodeling of phase boundaries as chemical boundaries. However, while these perturbations are quite large, the kinetics of the phase transitions will likely reduce the effect, as will be discussed in the conclusions.

Finally, we also examine the effects of phase transitions on the elastic Love numbers which represent the response of the solid Earth to either an instantaneously applied surface mass load (load Love number represented by the superscript L) or potential load (body Love number represented by the superscript B). The Love numbers h_l and k_l represent the radial displacement and the potential perturbation, respectively, caused by the component of the load described by spher-

Table 5
Elastic body Love numbers h_l^B and k_l^B for PREM

Boundary type/boundary thickness	h_l^B			k_l^B	
	$l=2$	$l=10$	$l=30$	$l=2$	$l=10$
Chemical	0.6036	0.07618	0.04193	0.2982	0.007042
Phase/1 km	0.6139	0.07695	0.04211	0.2987	0.007072
Phase/2 km	0.6210	0.07743	0.04221	0.2991	0.007097
Phase/5 km	0.6334	0.07822	0.04235	0.2998	0.007120
Phase/10 km	0.6427	0.07876	0.04244	0.3003	0.007144
Phase, NLH[a]	0.6606	0.07969	0.04256	0.3013	0.007174

[a] Assumes that no latent heat (NLH) is released.

ical harmonic degree l. While TW previously presented results for the variation in elastic Love numbers caused by various phase boundaries models using an incompressible, five layer Earth model, the results in Tables 4 and 5 are calculated using PREM as the reference Earth model, and code modified from Dahlen [18]. The perturbation from the chemical boundary solutions can be significant even for a 1 km thick boundary (5% for h_2^L) in the case of the load Love numbers (see Table 4). As noted in TW, this size of this perturbation suggests the possibility of looking for discrepancies between the observed displacement caused by ocean tidal loading and that predicted from tide models based upon predictions of the load Love numbers calculated assuming chemical boundaries (e.g., [19]). In Table 5, we show the body tide Love numbers including k_2^B which is used in predictions of the Chandler Wobble period and the luni–solar body tide, both of which are precisely measured processes. Unfortunately, the predictions for phase boundary conditions for k_2^B vary by at most 1% from the predictions for chemical boundary conditions. If kinetics were to reduce this discrepancy further, it is unlikely that these observations could be examined to gain further insight into the nature of the seismic discontinuities.

5. Conclusions

Phase transitions generally have been ignored for geophysical processes with timescales shorter than those of mantle convection due to the long timescale of latent heat conduction in the mantle. In order to examine the validity of this assumptions, we solved a generalized Stefan problem with a sinusoidally varying pressure perturbation at the boundary. If the phase boundary is modeled as a simple surface separating the two phases of the mantle material, we find that the inability of latent heat to conduct away from the boundary does prevent any significant amount of material from changing phase for processes with periods less than 10^3 years. However, if the latent heat is released over a thick region (as one would expect from the divariant nature of the phase transition), then some material will always change phase, regardless of how short the period of forcing is. In fact, for a given boundary thickness the ratio of the material that will change phase to the amount that would change phase if no latent heat is released becomes independent of the forcing period for periods less than about 10^3 years. The thicker the boundary, the larger the ratio. There is no phase lag associated with the phase transition in this limit, though, because the latent heat does not conduct away from the boundary.

These qualitative results allow us to apply a method of coupling the thermal and mechanical equation developed for predictions of GIA by TW to predictions of seismic normal modes and elastic Love numbers. We find that thick phase boundaries can change the center frequency predictions of seismic normal modes by several orders of magnitude more than the observational errors of these measurements. Thus, it is possible that the center frequencies could provide a probe into the behavior of the seismic discontinuities. Elastic Love numbers are also affected by the introduction of phase boundaries. However, the discrepancies between the predictions generated using chemical or phase boundaries may be reduced by the kinetics of the phase transition.

Throughout this paper, we have assumed that the phase transitions remain in equilibrium, as explained in Section 2. However, to cause phase transitions, a geophysical process must not only change the pressure and temperature conditions but must also supply enough kinetic energy to overcome the potential energy barriers associated with the phase change. The mechanisms (kinetics) of interface-controlled growth and nucleation have been studied for the olivine to wadsleyite transitions but often in the context of large perturbations of pressure and temperature from equilibrium (e.g., [20]). These results are useful for models of phase transitions in subducting slabs (e.g., [21–23]). Diffusion, which is generally slower than growth or nucleation, is more likely to govern the ringwoodite to perovskite plus magnesiowüstite transition [20]. In either case, these processes are not well studied for small temperature and pressure perturbations near equilibrium.

To obtain a naive estimate of the impact of kinetics on these calculations, one could compare the interface-controlled growth rate (growth is more likely to occur near equilibrium boundary conditions than nucleation [20]) with the velocity of the density discontinuity caused by the geophysical process. If the boundary velocity was much greater than the growth rate of the new phase, then the boundary would behave as chemical boundary. Using the growth rate equation (see [22] Eq. 1) with pressure changes typical of seismic normal modes and with kinetic parameters from Rubie and Ross [24] for the olivine to wadsleyite phase transition, we find that the growth rate is several orders of magnitude smaller than the velocity of the density discontinuity caused by the seismic normal mode. However, this phase change mechanism is not appropriate for processes occurring very close to equilibrium (D. Rubie, personal communication, 2001). Thus, while impact of kinetics may be significant, we were unable to determine if they annul these results because the mechanisms responsible for near equilibrium phase transitions are not well studied. Therefore, considering that the effect of phase transitions on the seismic normal modes is large when ignoring kinetics, our results suggest a more careful investigation of the kinetics on short timescales and for small pressure and temperature perturbations is warranted.

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