Thank you very much for your insightful review. We have included your comments below in **black**, and our responses are written in **blue**.

- The first issue that I see is clarity in the meaning of key words. The manuscript deals with phase-change --- where one mineral undergoes a change in atomic structure to form another mineral (or pair of minerals). But the manuscript repeatedly refers to "components" in a way that is confusing. Thermochemical components are chemical building blocks of phases that behave as inseparable units. They can recombine in reactions and the comprise the phases. The phases are the minerals, which may undergo phase change without changes in composition (i.e., the mole fractions of components). So sentences in the manuscript like "multiple compositionally-distinct components" (line 80) are confusing and suggest that these words aren't used in the standard way. Since accepted definitions are what makes words useful, the usage of "phase" and "component" should be clarified. Because the theory assumes no chemical reaction, the distinction is somewhat blurred here --- phase change doesn't fractionate chemistry. But the words should be used correctly anyway.

We agree with the reviewer that the way we use the term ‘component’ can be confusing since it is different from the usual definition of chemical components in thermodynamics.

To avoid this ambiguity, we have replaced the term ‘component’ by ‘bulk composition’. We now define this term when it is first used, to clarify that the bulk composition is internally reactive but cannot exchange chemical components with other compositions. Each bulk composition has its own lookup table.

- The manuscript invokes an entropy equation and cites a previous work where it was derived, but doesn't emphasise that it represents conservation of energy. And yet that's the real underlying physics here. Neither temperature nor entropy are conserved quantities. Although the derivation of the entropy equation need not be repeated here, it is essential that its physical basis be discussed. Furthermore, the conservation of energy should probably play a larger role in the manuscript elsewhere. For example, in re-equilibrating the phase temperatures after a phase-change has occurred, the approach is to conserve the total entropy. To do this, heat is added (or removed) from the phases until they are all at the same temperature but the bulk entropy is constant. This leaves open the possibility that the sum of the heat increments is not zero --- and hence that energy is not conserved. Of course there are other violations of energy conservation that we ignore (work associated with density changes during equilibration, surface energy differences of mineral phases, etc) and this is reasonable. But I think that the equilibration step should use energy conservation as a constraint rather than entropy. The sum of heat increments should equilibrate the temperature and sum to zero -- even if this changes the total entropy.

We thank the reviewer for prompting us to better describe our method. We agree that the conservation of energy should play a larger role in the manuscript, and have now added a significant amount of text to Appendix B on the thermal equilibration step. In particular, we now

describe in our Appendix B why we conserve entropy rather than energy. We note that thermal equilibration at fixed pressure is actually isenthalpic, and not, in fact, a constant energy or constant entropy process. This isenthalpic process includes "*work associated with density changes"* on the scale of the finite element mesh. We explain that if thermal equilibration is rapid with respect to changes in pressure, we should consider the effect of many thermal equilibrations over very small pressure steps, rather than a single equilibration for each simulation timestep. In the limit of infinitesimally small pressure steps, isenthalpic equilibrations become isentropic. In order to approximate these small equilibration steps over the numerical timestep of the simulation, we must therefore treat the equilibration process as isentropic, rather than isenthalpic.

We have also changed the wording to use "energy conservation equation" everywhere where we refer to the full equation, and "energy balance equations" where we refer to the energy equations for the individual bulk compositions (instead of using the term "advection equation"). In the revised manuscript section 2.1, we also mention that the conservation equation for entropy (Eq. 6) is equivalent to the energy conservation equation for temperature (Eq. 3). They are simply different forms of the same equation, and the transformation between them follows from standard thermodynamic identities.

- The entropy approach that is used here is very similar in motivation and in implementation to the enthalpy method that has been used in geodynamic models of melting. It would seem appropriate to make and discuss that link in the introduction.

Thank you for reminding us of this work. We have added a reference to Katz (2008) in the discussion of the challenges associated with solving phase transitions in Section 2.

- Advection of heterogeneity in numerical models would seem to be fundamental to the success of this theory, and yet there is almost no discussion of the numerical implementation of the advective terms in the equations. Do any of the verifications test whether the advection is working properly, and whether it can handle sharp(ish) gradients? Is energy still conserved when transport is two-dimensional and velocities are non-constant?

Thank you for this suggestion. We have added a new test case (Test 9) for the advection of entropy anomalies with sharp boundaries at a non-constant velocity in 2-D. We show that energy is conserved and the solutions converge with expected rates. We originally did not include such a test, because the numerical methods for solving the advection equations are discussed in previous publications on ASPECT's numerical methods (Kronbichler et al., 2012; Heister et al., 2017) and we now refer to them in the description of this new test.

- The two demonstration calculations at the end of the manuscript are interesting, though the difference between them is arguably not very large. The authors are attempting to make an important point about how phase change affects the dynamics, and hence the overall stirring of the mantle. But they limit themselves to a very restricted set of only two scenarios that differ only in the number of "components" which I think means the number of phases. But an

advantage of numerical models is that parameters can be varied at whim. So it would be nice to look at the effect of a single parameter (say A) that controls the dynamic importance of the phase change and test the sensitivity of the model to that parameter. The the authors could plot a relevant metric, say the Nusselt number Nu, versus A. What is d Nu / d A? Or something along those lines that enables a more vivid depiction of the sensitivity. I love figures 12 and 10, but to me the leading-order observation is that the Mechanical Mixture and the Single Component Pyrolite are essentially the same.

In this paper we use these application cases only as a proof of concept for our new method, which demonstrate (1) the feasibility of using our new approach in realistic models and (2) the importance of using a realistic equation of state when modeling mantle dynamics. Although the mechanical mixture and the single-component pyrolite cases are not dramatically different in terms of global metrics of convection, the results demonstrate that differences in phase relations can lead to systematic variations in the morphology and dynamics of slabs and plumes. We have modified the text to avoid overstatement and to better clarify the purpose of the application cases.

We agree that a systematic investigation of how individual thermodynamic parameters affect mantle dynamics would be an interesting and important direction for future work. However, we think such an analysis to be beyond the scope of this manuscript, which focuses primarily on the development and validation of the new methodology, and is already quite long.

Line-specific comments

- line 13: I don't see major differences in convection patterns. I think this is an overstatement.

We have rephrased it as “distinct slab and plume morphologies, influencing mantle convection patterns”.

- line 31 "compositional differences in phase relations" this phrase is confusing.

We rephrased the sentence to be more specific. It now reads “For example, how does the subduction of a slab with basaltic crust and harzburgitic lithosphere differ from a pyrolitic slab?”

- line 98: this is where the enthalpy method and the entropy formulation are very closely aligned in terms of motivation.

We have added a reference and brief description to the enthalpy method in this section.

- line 123: better not to start sentences with mathematical symbols

Fixed.

- line 124: probably you mean provoking or instigating or something else. "invoking" doesn't make sense here.

Changed to “provoking”.

- eqn (7): if Xi is a mass fraction and the theory has non-zero divergence, then I think this equation is missing the term X_i div(u)

Thank you for carefully examining the equations. The X_i in Eqn (7) are indeed the mass fractions of our chemical compositions. We use a form that is common in geodynamic applications (for example, given in Ricard et al., 2015, Treatise on Geophysics: Physics of Mantle Convection, Equation 158). We assume the Eulerian form of the equations, neglecting diffusion and reactions between chemical compositions. The velocity **u** is the velocity of the center of mass. We have added these points to the manuscript.

- eqn (8): why incorporate q_eq,i into this equation and then solve the equation without this term? a bit misleading.

We agree that this was not clear in the manuscript. $q_{eq,i}$ represents the heat exchange associated with the thermal equilibration among bulk compositions. The energy conservation will not hold without this term. However, it has to be calculated separately, because we need to know the entropies of all bulk compositions to calculate their thermal equilibration. Therefore, in each nonlinear iteration, we solve the energy equation without q_{eq} to get S_i, then we calculate the thermal equilibration q_{eq} and treat it as an instantaneous reaction (by using an operator splitting scheme). So in the end, we do solve the equation with this term (it is included in the nonlinear loop), we just use a numerical method that splits up the equation.

We have added more detail in Section 3.2 to clarify this.

- line 144: "individual chemical components do not chemically react with each other" is ambiguous but important and should be clarified. I think that what this means is that phases can undergo phase-change, but there is no exchange of mass between, co-existing phases that have differing compositions. Or something like that.

We now have rephrased the sentence to “there is no chemical reaction or mass exchange among the individual chemical compositions i”. As noted before, we have also replaced the term "component", which caused ambiguity, by “(bulk) composition”.

- line 164: odd to call the energy conservation equation the "advection equation" because it is much more than just advection.

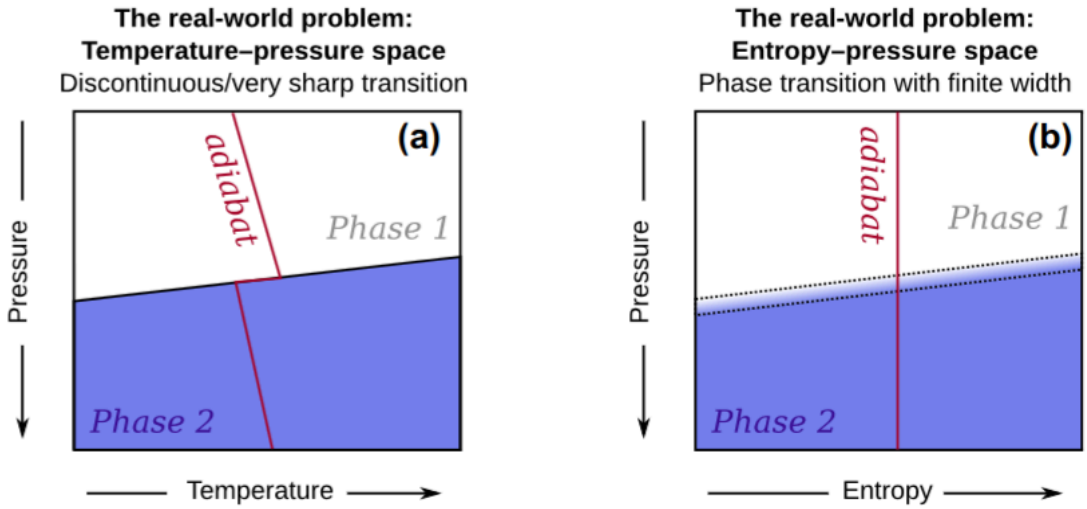
We have changed the wording to “energy balance equation” here and throughout the manuscript.

- line 168: what is the convergence criterion?

We have added more detail. Specifically, “After solving all equations, we check for convergence by comparing the nonlinear residual of each equation to a prescribed tolerance (typically 10^{-5}). We define the nonlinear residual of an equation as the ratio between the residual of the equation using the current best guess for the solution and the residual of a representative reference solution (in particular, a constant entropy, no velocity, and an adiabatic pressure). If all equations fulfill this criterion, we stop iterating over the equations; otherwise, we loop back to solving for thermal conduction with T_{eq}.”

- It is somewhat unclear to me how Figure 2 shows that the "partitioning of entropy between the compositions becomes undefined" and generally it is surprising that the entropy approach doesn't distribute the phase change over a range of entropy such that there is no step. So I think a bit more explanation is needed here. If a Gaussian filter is really needed, then it is imperative to note the parameters and their values that are entailed in the smoothing, and how those parameter values are chosen.

Thank you for this comment. You are correct that in the entropy approach, phase transitions occur over a range of entropy values rather than as a discontinuous step. Figure 3 in Dannberg et. al (2022), which we have reproduced here, shows the general concept.



This gradual change can also be seen in Figure 6 (Test 7b) in our manuscript. In the middle row, we plot the temperature change over the model evolution time; in the bottom row, we plot the entropy change over model evolution time. The model is heated with a constant rate, and the material crosses a univariant phase transition as the entropy increases. During the phase transition, the temperature change is step-like (with the temperature staying constant during the transition) while the entropy increases linearly.

A key strength of the entropy method, whether it involves a single bulk composition or multiple bulk compositions, is that there is a unique mapping from [total entropy+pressure] to [temperature] where there is not a unique mapping from [temperature+pressure] to [entropy]. There is also usually a unique mapping from [entropy+pressure] to [phase proportions], and therefore to [density].

Nevertheless, there are residual edge-cases in the entropy method that we deal with by smoothing the enthalpy and then defining other thermodynamic properties by partial differentiation. We describe three cases below, and they are described in similar detail in the text.

Entropy partitioning

Consider two lookups with bulk compositions corresponding to a subducted basalt and a subducted sediment. In the deep upper mantle, both compositions are expected to contain a free silica phase that transforms from coesite to stishovite. At known total entropy and pressure, the temperature and *total amount* of stishovite across the two compositions are known. However, the *proportion* of stishovite within each bulk composition is *not* known - it is thermodynamically valid for the phase transition to be partitioned unevenly between bulk compositions. Consequently the *partitioning of entropy* between the two bulk compositions is also non-unique. In this study, we propose restoring uniqueness by applying a *minimal* smoothing to the enthalpy lookup table for each bulk composition, and deriving from that smoothed table the thermodynamically self-consistent temperature and density by partial differentiation. This smoothing results in a unique mapping from total entropy to the entropy of each bulk composition at fixed pressure. We note that while this smoothing also yields a unique mapping from [temperature+pressure] to entropy, the entropy formulation remains much more computationally robust than the temperature formulation. We emphasize that this smoothing only needs to be large enough to provide a unique temperature for every entropy; the actual differences in temperatures across a univariant reaction can be extremely small and thus have an insignificant influence on the physics.

In our initial version, we have already mentioned all parameters of the Gaussian smoothing in the Appendix A: Construction of lookup tables. In the revised manuscript, we have added a short summary of this explanation to the caption of Figure 2.

Invariant reactions

Invariant reactions buffer both temperature and pressure, and therefore an exact thermodynamic lookup table with entropy and pressure as independent variables cannot capture the progress of such reactions. A unique mapping can be obtained by using entropy + density as input variables, but geodynamic problems are not amenable to formulation with density as a natural variable. Smoothing the enthalpy table spreads out the effect of invariant reactions over a finite pressure range.

Diffusively controlled problems

The entropy method works particularly well in advection-controlled problems, with or without radiogenic heating. This is because entropy is expected to vary smoothly in these problems, even where there can be abrupt temperature jumps. This makes it particularly well-suited to many mantle convection problems, where thermal diffusion is often slow relative to advection.

Nevertheless, there are situations in which thermal diffusion dominates the evolution of parts of complex convecting systems - for example, the thermal relaxation of stagnant slabs.

In problems controlled by thermal diffusion, we meet a set of problems related to the classical Stefan free-boundary problem. In this problem, a univariant phase change takes place in a static material as a result of external heat addition. The phase change takes place across a narrow moving front, with reactants on one side, and products on the other. The temperature on both sides of the front is buffered by the reaction, which means that the entropy is discontinuous, with the jump across the transition equal to the difference between the entropy of the reactants and products.

In ASPECT, we require the entropy field for each bulk composition to be spatially smooth, which is not consistent with the solution to the Stefan problem. There are a number of ways to mitigate this problem, including:

- Smoothing the thermodynamic tables
- Limiting the maximum heat capacities used in the conductive part of the energy balance equations.
- Damping changes in entropy on the spatial grid
- Applying artificial stabilisation (e.g., by increasing the artificial viscosity in the entropy viscosity formulation)

In this paper, we focus on smoothing (see Appendix in the revised manuscript for the effect of this smoothing). ASPECT also has functionality for directly limiting the heat capacity. We reiterate that smoothing is performed in entropy space, not temperature space. Even after smoothing, univariant and near-univariant reactions still effectively buffer the temperature.

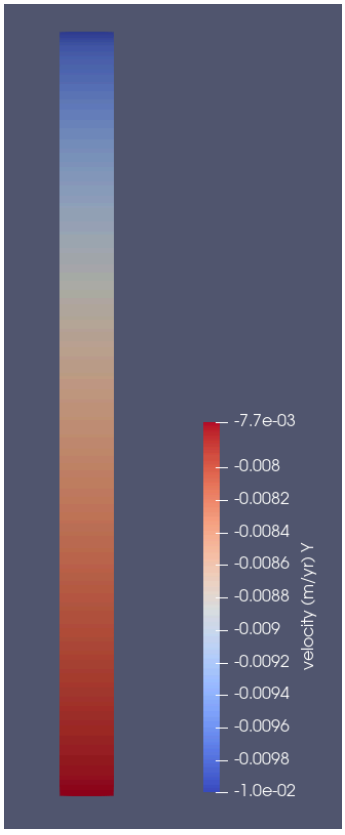
-line 228 and elsewhere: why should you need a boundary condition on stress when the velocity is prescribed?

We either prescribe the stress or the velocity. In this test (and elsewhere) only the normal component of the velocity to the boundary is prescribed while the horizontal component can evolve freely and is not prescribed (so we prescribed a zero stress for that component). For this test, there is no flow, so it does not make a difference. But in other cases (like the side boundaries in Test 6), we want to enable flow along the boundaries but no in- or outflow and therefore choose free slip conditions.

- line 243: "both sides" should probably be both ends, as a cylindrical pipe doesn't have two sides. And since this model has variations in density, it is surprising that the velocity (ie the volume flux) is identical at both ends of the pipe. The mass rate should be identical by conservation.

Thank you for catching this! We actually prescribed the velocity only at the top of the pipe. Our original description was inaccurate and we have corrected the text accordingly. The velocity at

the bottom is therefore indeed different from the prescribed top boundary velocity due to the change in density (see below).
But to clarify: our model geometry is a 2-D rectangular channel and not a cylindrical pipe. We have changed ‘pipe’ to ‘channel’ in the text to avoid confusion.



- line 264. The thermal diffusion problem can be solved analytically by periodic extension and Fourier series.

In our cases, we use a thermodynamic table to look up the density and specific heat. Since both properties are pressure- and entropy-dependent, we cannot calculate an analytical solution. We have clarified this in the manuscript.

- line 207. What is the order of accuracy of the time-stepping scheme?

We now explicitly say that the BDF2 time-stepping is second order, but its initialization phase is first order.

- line 313. thermal equilibrium with no density change is hardly an "extreme" case -- perhaps an endmember case.

Yes, that makes sense. We changed it to the endmember case.

- FIgure 8. I didn't see where this figure was described or used.

In our original text, we referenced Figure 8 (phase diagram, now Fig. 9 in new version) at the end of Section 5.1.

- line 482. hot thermal instabilities doesn't really make sense. I think you mean hot thermal plumes. But hot thermal is redundant. So how about just hot plumes? An instability is a bifurcation in state space. In this case, the instability leads a laterally uniform system to produce upwelling plumes and downwelling plumes.

Thank you for your suggestion. We changed it to ‘hot plumes’.

- line 534, "even small variations in phase transitions can lead to substantial differences in mantle convection style" -- this is entirely subjective at present, and I think is an overstatement of the actual results. But what is really needed is to quantify the sensitivity so that adjectives aren't needed. Small compared to what? Significant in what sense? There should be a way to answer these questions quantitatively.

We agree that the original statement was not sufficiently supported by a quantitative analysis. Such an analysis would be valuable but is beyond the scope of this manuscript, which focuses on the development and validation of the new methodology. We have revised the text to avoid overstatement and to focus the conclusion more on the qualitative differences in slab and plume morphology (which can be observed in Figures 10 and 12)

Other minor comments

- equations should be treated as part of sentences in terms of punctuation. Use of colons before equations is not good style; commas following equations are needed where the sentence continues.

We went through where the equations are mentioned and changed the punctuations.

- Throughout. For a paper as long as this one, it would be easier to read if the figure references were at the start of sentences, and the main text actually described what the figure shows.

We have modified this throughout the text.