GJI-24-0478

Responses to reviewers and editorial comments

# General Comments

I have now completed the revisions requested by the reviewers. I am grateful to them for their careful and very different comments on the manuscript.

Reviewer 1’s comments clearly demonstrated to me that I had motivated and introduced my study too vaguely, and that I needed to more clearly describe both “classic” Landau theory and the coupled models known as Landau-Ginzburg Theory. As suggested by Reviewer 1, I also needed to demonstrate where existing theories were in error. To be clear, I believe Landau Theory to be correct. I have provided a new Section 2 and supplementary material that I hope will satisfy their concerns.

Reviewer 2’s comments focused mostly on the model description and fitting procedure. I have made most of their suggested changes, refitting the model to more data, and improving the descriptions of the model design and fitting procedure. I have decided not to follow a couple of their suggestions on practical grounds, which I have explained in my line-by-line responses below.

I hope that this modified manuscript meets with the approval of both reviewers and the editors.

Best wishes,

Bob Myhill

I’ve colour coded the reviews and my responses for clarity:

* Reviewer 1
* Reviewer 2
* My responses

# Responses to Reviewer 1

This paper presents a new parameterisation of the effects of the displacive phase transition in stishovite, based on a mix of Landau theory and conventional thermodynamics. The resulting fits to measured variations of atomic positions which scale with the order parameter, lattice parameters and elastic constants as a function of pressure at room temperature allow extrapolation to a wider PT range. The comments presented here are intended as constructive criticism, particularly in relation to what appear to be slight misunderstandings or misrepresentations of the order parameter, q.

Thank you for the summary. I’ll respond to the comments and criticisms below.

The most significant and fundamental aspect of Landau theory is that the order parameter has symmetry determined entirely by the change in space group at a phase transition where there is a group-subgroup relationship between the symmetries of the parent and product phases. This is not mentioned.

I’ve completely rewritten Section 2 to give a more detailed summary of Landau’s derivation. This has allowed me to mention aspects of group theory, as suggested.

In addition, Landau expansions of the type given as Equations 1 and 3 refer to excess energies. This must be clearly stated. Landau expansions only gives the energy difference between the parent and product phases.

I’ve rewritten all the equations in this section to clarify the relationship between the energy of the parent and product phases. I’ve actually written the expressions as total energies, with a reference energy term, to more closely mirror Landau (1935,1937).

p2, line 48: the statement implying that q is an important contributor to the energy of a phase is misleading. The order parameter is a dimensionless quantity. The excess free energy due to a phase transition can be expressed in terms of a series expansion in q but the form of this is subject to strict constraints determined by symmetry.

I’ve removed this from the Introduction, in favour of just talking about the physical phenomena.

For the benefit of clarity, it should be clearly stated that Landau free energies only describe differences between the parent and product phases. They do not provide any information on the free energy of the parent phase which needs to be modelled in a conventional manner if a complete thermodynamic description is being sought.

The section that you refer to (p2, l48) has not yet introduced Landau theory or second order phase transitions, so I haven’t changed this.

p3, line 9: replace "weak" with "weakly". Reference should probably be given to the papers in which this was first discussed (Bacheimer, Dolino ....) rather than the more recent work of Antao.

Done, and done. I’ve added appropriate references to Bacheimer and Dolino.

p3, line 22: Reference should be given to the original work by Jackson et al (2004) rather than the more recent work of Reynard et al.

I’ve made this change.

p3, line23: Reference should be given to the original work by Kingma et al rather than the more recent work of Carpenter et al.

I’ve made this change.

p3, line 35: reference is made to existing methods being restricted to a single temperature. What does this mean and which specific temperature is being referred to?

I’ve removed this in favour of calling the

p5, line28: what are the "metastable equilibrium points" being referred to here?

q=0 below the transition temperature. I’ve completely rewritten this section, as neither you nor the other reviewer found the text very clear.

p5, line 36, 37: this is an incorrect statement. Elements of the strain tensor are not additional order parameters. For most phase transitions there is only one order parameter. Other properties, such as strain, vary in proportion to the order parameter, the square of the order parameter or in some other manner that depends on the symmetry of the order parameter and the symmetry of the strain.

I’ve rewritten the section to clearly distinguish between natural, internal and conjugate variables.

p5, line 47: the statement that "Ciko may additionally be a function of q" is incorrect. By definition, Ciko refers to elastic constants of the parent structure without any influence from the phase transition.

I’ve made this change.

p5, line 47: what do the quotation marks refer to?

“…” refers to the … in Equation 3. I’ve changed this to say “the first three terms”.

p5, line50: the statement that "The penultimate term allows changes in the structure parameters q to "drive" structural strain" is incorrect.

This is a quote from many papers, e.g. Carpenter et al. 2000 “Here Q is the driving order parameter…”. But I agree with you, so I’ve removed this text.

The order parameter does not really "drive" anything, though in common parlance people sometimes refer to the driving order parameter in the context of symmetry. In addition, no mention is made of the fact that the form of all the terms in Equation 3 depend on symmetry, as expressed in formal group theoretical rules. All physical and structural properties at a phase transition with groupsubgroup relationships vary in a manner that depends on variations of the order parameter.

I’ve added a more detailed description of Landau theory and its modifications to Section 2.

The driving mechanism might be a soft phonon, a soft acoustic phonon, cation order, etc.,

I can see two sides of this (which makes me happy that I don’t have to confront this one):

* Your comment describes the physical manifestation of phase transitions.
* I think the driving mechanism is always minimisation of the appropriate thermodynamic potential.

As an analogy, I guess your comment is akin to saying that the sound of the engine (soft phonon) or the gas pedal moving downward (cation order) drives the car to the shops, whereas mine is more akin to saying that my urge to pick up groceries drives the car to the shops.

in which changes in structure depend on symmetry as defined by the irreducible representation of the order parameter. (As an aside: mention is made on page 2 of the order parameter for electronic spin state. This is fundamentally different from the order parameter for the transition in stishovite, say, because there is no change in symmetry. The order parameter for high spin/low spin transitions has the symmetry of the identity representation and Landau theory, as originally envisaged, does not apply).

This is a fair point. My view would be that the “fundamental aspect” of Landau theory is the minimization of a thermodynamic potential over one or more internal variables. But I acknowledge that there’s more to the 1937 papers than this narrow reading.

I’ve added some words to this effect.

p5, line 52: The order parameter for the ferroelectric phase transition considered by

Devonshire has three components by symmetry. Any phase transition with the same change in space group would have the same order parameter. Devonshire was free to relate any aspect of the low symmetry structure to the order parameter and chose to use polarisation because this was the property of principal interest.

Thanks for this information.

p6, line 9: the statement that "Landau minimisations treating them as free parameters will generally be thermodynamically inconsistent" is rather sweeping and should be justified. It is true the strain and polarisation are not independent variables because they both depend explicitly on the order parameter. The minimisations usually applied are designed to find minima in particular directions of a multiparameter space and, hence, to define relationships between properties which are coupled with the order parameter.

In rewriting Section 2, I’ve been much more careful in stating the conditions of a consistent theory. I’ve also added an example from Carpenter et al. (2000) to the Supplementary Materials to demonstrate the effect of thermodynamic inconsistency:

A graph of a function

Description automatically generated

1. The excess Gibbs energy due to the stishovite-post-stishovite transition as given by Carpenter et al. (2000).
2. The volume of the high symmetry tetragonal phase derived from the standard state volume from Andrault et al. (2003) and the tetragonal moduli reported by Carpenter et al. (2000) (blue dotted line), and the volume of the equilibrium phase determined by adding the change in volume calculated from the excess Gibbs energy (orange dashed line).
3. The bulk modulus of the tetragonal phase (blue dotted line) and the equilibrium phase (black solid line) as calculated from the reported moduli of Carpenter et al. (2000), and the equilibrium phase (orange dashed line) as calculated from the equilibrium volumes in (b), themselves calculated from the Gibbs expression of Carpenter et al (2000).

Note that the orange dashed and solid black line in c are *not the same*. This is the thermodynamic inconsistency I was talking about.

p6, line17-24: These standard requirements of how the bare elastic constants vary must apply, of course. Landau theory has nothing to say about this because the only consideration is of excess properties which depend on the order parameter. For a complete description of the thermodynamic properties it is necessary to model both the bare properties, ie those of the material in the absence of the phase transition, and the additional changes due to the transition. Landau gives only the latter and no minimisation of a Landau expansion would give information about the bare elastic constants.

This comment is addressed in the rewrite of Section 2.

p6, line 25-32: this appears to be a self-evident truism. For the treatment of spontaneous strains, it is necessary to use a reference state - ie the lattice parameters of the parent structure without influence of the phase transition. For a treatment of the full response of a crystal to external stress, it is necessary to include both the response of the reference structure and the the excess property of the product structure. Landau only gives the latter.

Yes, my point is that the high symmetry / parent structure at a given P, T can sometimes differ significantly from the actual structure under the same conditions. That difference is sufficiently large that small strain approximations to the excess properties are inaccurate.

The rewrite of Section 2 addresses this comment.

p6, line 34-37: The author appears to be implying that Landau theory does not meet the challenge of thermodynamic consistency. If I understand correctly, what he really means is that for a complete thermodynamic description of the properties of any material it is necessary to include the properties of the reference phase, whereas Landau only gives the excess properties. For elastic properties it is necessary to have a correct description of the bare elastic constants, Ciko, as well as the influence of the strain/order parameter coupling on them.

Hopefully the example analysis of Carpenter et al. (2000), above and in the revised manuscript, makes my point more clearly. Having a correct description of the bare elastic constants is important, but the model formalism also has to be thermodynamically consistent.

p7, line 37: If I understand correctly, the reference to "hyperelasticity" is included to imply that strains are a non-linear function of stress. Elsewhere (page 6, line30) the claim is made that the spontaneous strains at a phase transition are large and so are not relevant to the consideration of infinitesimally small strains for thermodynamic calculations. The spontaneous strains are only those which arise at the phase transition. They are usually represented by a series expansion in q. Experimental data show that the series expansion can be truncated so that they vary with q or q^2. There is no evidence that the coupling coefficients are anything other than constant, even for infinitesimally strains close to the transition point, other than in systems with higher order terms are known, such as quartz. This is completely different from saying that the strain response of the crystal as a whole is a linear function of stress. The bulk behaviour of the crystal as a whole may be hyperelastic but the spontaneous strains are elastic.

I apologize for any confusion. My point was that over reasonable values of q, the spontaneous strains can be large. I shouldn’t have used the term hyperelastic. Instead, I should have emphasized that small strain approximations are not applicable when the difference between the parent structure and equilibrium structure are significant. The rewrite of Section 2 addresses this point.

p14, line 22: The analysis of elastic constants by Carpenter et al was quantitative. Improved parameterisation has allowed calculated values to more accurately reproduce observed values.

Thanks, I’ve changed the text to be clearer.

p14, line 56: If I understand correctly, the statement that "Parameters for the Q = 0 and Q =1 states are fit to the data with the equation of state of Stixrude and Lithgow-Bertelloni" is at the heart of the "alternative Landau formalism" proposed in this paper. In essence, the model depends ultimately on conventional parameterisation of the reference structure (Q = 0) which is not considered in a Landau description. For a non-expert, this would be very difficult to pick out as the abstract and introduction seem to imply that some kind of post-Landau theory is being proposed.

Yes, using distinct endmembers for Q=0 and Q=1 is part of the modified approach in the paper.

The more major modification is to use the anisotropic equation of state of Myhill (2024a) that self-consistently defines M and CT. This means that the small strain approximation no longer needs to be made for the symmetry breaking strain (because symmetry breaking strain is no longer a parameter in the model).

Hopefully the rewrite of Section 2 has made this clearer.

p19, line 32: "q appears to have a negligible role in determining the length of c-axis" is a slight misrepresentation. The order parameter determines only the form of coupling with e3, through the constraints of symmetry. The strength of coupling is a material property and, in this case, the coupling coefficient is small.

In the Landau-Ginzburg-Devonshire-style approach, your description is correct. However, within the context of the approach presented in this paper, I believe my wording accurately describes how the value of q influences the value of e3​.

Section 5 as a whole: This section does not add anything to the paper beyond the fact that Landau theory works well for excess properties. It could be cut without loss of impact of the paper as a whole.

I’ve cut this section.

p26, line 10: Landau theory is also thermodynamic. The only important parameter is the order parameter which depends on symmetry and not on details of the crystal structure.

See my comments and the manuscript changes described above.

p26, line 26: The fact that all measurable changes in properties at the displacive transition stishovite can be described by a single order parameter implies that the Landau description provides an accurate description, both qualitatively and quantitatively, of the influence of coupling with strain. In essence it works firstly because Q has explicit symmetry properties and, secondly, because strain fields are long ranging and therefore ensure that the overall pattern of behaviour conforms to mean field. In materials when this is not the case, the usual explanation is that there is more than one order parameter or that there are fluctuations which are not accounted for by a static order parameter.

Hopefully the changes described above resolve your concerns. Please let me know if you’d like me to make any more changes.

p26, lines 26-50: this section adds nothing to the paper. It merely provides descriptions of terminology used elsewhere in the literature that is not used in the present paper.

I understand your concern. I have shifted a couple of points into the introduction and have deleted the rest to streamline the paper.

p26, line 56: This statement is incorrect. Many materials, such as quartz, have spontaneous properties that are not ferroic. The term ferroic is an accident of history because it was first used for magnetism. A ferromagnet is one in which a magnetic dipole can be switched from + to - by an applied magnetic field. A ferroelectric material is one in which an electric dipole can be switched from + to - by an electric field. A ferroelastic material is one in which a strain can be switched from + to - by an applied stress. Ferroic means switchable by an external field.

Thanks for pointing out that I’d missed the concept of switching! I appreciate your clarification on the term "ferroic" and its historical context. I’ve removed the section from the text.

section 5.2: this section adds nothing to the paper. The statement that the terms pseudoproper, proper and improper are not particularly insightful should be cut as it implies that there is something wrong with the underpinning of symmetry. Properties scale with the order parameter in a manner that is determined by symmetry, as set out in equations 68-70.

I apologize if my previous statement suggested that the formalism in equations 68–70 produces incorrect symmetries. My intention was to highlight that minimizing F by varying y, when y is a derivative of F with respect to its natural variables, is inconsistent with the laws of thermodynamics. This section has been cut, and Section 2 should make my points more clearly.

page 29, lines 7-12: this claim is misleading. The Landau free energy expansion only provides information about excess properties related to the order parameter. Minimising it in the standard manner is perfectly valid,

I agree that Landau's original formulation is fundamentally sound.

otherwise 80 years of physics would be wrong.

My point, now explained in more detail in Section 2, is that there are a few papers that abuse Landau theory.

page 29, lines 14-20: this statement is also misleading. It is possible to use the proposed new parameterisation for stishovite because there are high quality experimental data available for all the important properties. The same approach could be used for a phase transition in troilite, say, but only if an equivalent set of data was available.

I apologize for any confusion; I assumed the need for high-quality data was implicit. This section has been removed.

page 29, line 15: It is incorrect to state that more than one order parameter is needed to describe the a-b transition in quartz. Perhaps the author is referring to the incommensurate structure?

I appreciate your feedback and have removed this comment, saving it for a later paper. As you noted, only one order parameter is required to model the alpha-beta transition in quartz. However, this single-order parameter model cannot fully explain the volume and bulk modulus anomalies observed above the transition (see figures in Angel, 2017).

I will show in a future paper that introducing a second parameter can accurately reproduce these high-symmetry anomalies, which reflect thermal disorder, as demonstrated by the results of the Cambridge group from the early 2000s.

The proposed thermodynamic model is valid in the sense that it includes an equation of state for the reference structure. It is therefore specific to the material being investigated and the parameterisation depends entirely on the amount and quality of experimental data available. I was not able to work out from the text exactly how many fit parameters have been used. It would be insightful to compare the number of fit parameters that have been used to generate the calculated elastic constants in comparison with the number of fit parameters used by Zhang et al. and to include this comparison in the text and in the abstract.

I’ve now added a short section comparing the number of fit parameters with the model of Zhang et al.

As noted above, these comments are intended to be constructive criticisms. Rather than dwelling on perceived inadequacies of Landau theory it would be much better to state that the proposed model includes a thermodynamic description of the reference phase. As a result, parameterisation to fit available experimental data provides a robust description of the properties of the crystal as a whole and not just of the properties that depend on the order parameter.

Hopefully the rewritten Section 2 addresses this comment.

For the benefit of readers who are unfamiliar with the topic, it is probably essential to include a clear statement not only of the fact that the most important property of the order parameter is that it has symmetry, but also that the Landau free energy expansion applies only to the excess free energy due to the transition.

Hopefully the rewritten Section 2 addresses this comment.

# Responses to Reviewer 2

Isochemical transformation (e.g., displacive, order-disorder, electronic, etc.) occur in many common rock-forming minerals, such as quartz, feldspars, garnet and pyroxenes, and can significantly affect the thermodynamic, elastic, and transport properties of crustal and mantle rocks. Thermodynamic models based on Landau theory have been often used to calculate anomalies in the physical properties of minerals across these transformations. However, bulk properties thus modelled have been either inconsistent with the anisotropic properties or ignore the effects of temperature or pressure.  
  
Here, the author proposes a new internally consistent thermodynamic formalism for the treatment of isochemical transformations in anisotropic materials where scalar properties are entirely derived from an anisotropic model. As an example, the anisotropic equation of state of SiO<sub>2</sub> stishovite - a major mineral phase in subducted metabasalt undergoing a ferroelastic transition in the mid-lower mantle - is obtained from the analysis of high-pressure and high-temperature X-ray diffraction data and high-pressure and room-temperature sound velocity measurements reported in previous studies.  
  
I think the author did a excellent job at deriving the model presented here. The fit of the experimental data from previous study is also satisfactory and proofs that this could indeed be a useful tool for mineral physicists, seismologists and geodynamicists interested in isochemical reactions in the deep Earth.

Thanks for the compliment!

My main complaint about this article is that the derivation of the formalism is often difficult to follow. Many thermodynamic relations between variables are defined throughout the manuscript, but the actual working equations, where dependent variables are explicitly written as a function of the independent variables and fit parameters (e.g., relaxed and unrelaxed <i>C</i><sub>ijkl</sub> as a function of <i>ψ</i><sub>ijkl</sub>) are often not presented. I believe this can be a huge obstacle for scientists (and students) interested in the model but not willing to spend days deriving all the equations they need to fit their experimental data.

On the other hand, I believe that models such as the one of Stixrude and Lithgow-Bertelloni (2005, 2011, 2024), although not fully internally consistent for anisotropic materials, would be much more appealing to them exactly because all the equations show the explicit dependence of the dependent variables on volume (or strain), temperature, and fit parameters.

Although I understand that it takes time to do so, I would encourage the author to add at least the most relevant expressions for the anisotropic model. I believe that this will significantly improve the model usability.

I completely agree with the reviewer, simple expressions are nice. But I’m also aware of how easy it is to make mistakes (the Zhang papers have incorrectly copied the Stixrude and Lithgow Bertelloni equation), which is why I made all the code available in the BurnMan project.

For instance, it would be useful to have:

- Expressions for the elastic stiffness tensor (<i>C</i><sub>ijkl</sub>) and thermal stress tensor (<i>π</i><sub>ij</sub>) as a function of <i>M</i>, <i>T</i>, and <i>n</i> and derivation from the anisotropic state tensor (<i>ψ</i><sub>ijkl</sub>)

The anisotropic equation of state provides expressions for the elastic stiffness tensor and thermal expansivity tensor (from which the thermal stress tensor can be calculated). These equations are already provided in the companion paper (Myhill, 2024a).

- Expressions for the scalar thermal properties, such as internal energy (<i>E</i>), heat capacities (<i>c</i>), entropy (<i>N</i>), etc. (are these calculated from a Debye model?);

They can be determined from any scalar equation of state. I’ve added a comment to this effect to Section 3.

- Expressions for the relaxed isochemical relaxation vector (<i>q</i>\*), relaxed stiffness tensor (<i>C</i>\*<sub>ijkl</sub>), and relaxed thermal stress tensor (<i>π</i>\*<sub>ij</sub>) as a function of <i>ε</i>, <i>T</i> and <i>x</i>.

I have provided the relaxation vector for the stishovite model as a function of P, T in Section 4.2.1.

I could potentially define the other properties as a function of V, T and x for the stishovite model, but they would be complicated equations and not relevant for any other model.

Some more line to line comments

Page 2 Line 28. A structure can be flexible without necessarily changing symmetry. What about <i>structural distortion</i> instead?

I’ve added a line at the end of this list to say “This flexibility can result in displacive symmetry-breaking phase transitions, as in the case of a-b quartz or stishovite to post-stishovite.”

Page 2 Line 32. I think it would be appropriate to either define <i>p</i> or reference Table 1.

Done.

Page 2 Line 43-44. Please use either CaCl<sub>2</sub>-structured phase or CaCl<sub>2</sub>-structured post stishovite. Stishovite only refers to the tetragonal phase.

Done

Page 2 Line 59. Cell lengths → crystal elongation

I’ve changed this to say “unit cell volume”.

Page 4 Line 18. Why is entropy <i>N</i> and not the more commonly used <i>S</i>?

I’ve now changed all references to entropy from N to S.

Page 4 Line 21. Should be ln(<i>V</i>/<i>V</i><sub>0</sub>)

That was true of the endmember anisotropic equation of state paper, but in the three companion papers submitted here, f is the absolute logarithmic volume ln V. I’ve explained this in the first of the companion papers.

Page 4 Line 37. The symbols for heat capacity is upper case here and lower case in most of the text (except for the left hand side of equation 35). Please choose one of the two and use it consistently.

Thanks. I’ve changed them all to upper case to differentiate them from the parameter c in the Landau expressions.

Page 5 Line 28-29. I can intuitively understand what the author is trying to say, but I find their phrasing confusing. Is the change in concavity as a function of pressure, temperature, etc. only relevant at <i>Q</i> = 0 to determine which phase is stable? And are the equilibrium points not in the concave up region, where the minima of the <i>Φ</i> curves are located?

I agree that this was poorly worded. I’ve reworded the text to say “Continuous symmetry-breaking phase transitions (Wadhawan, 1982) naturally occur where ∂2Φ/∂q∂q changes sign from positive to negative along a particular vector δq”

Page 6 Line 7. Strains → spontaneous strains?

This section (Section 2) has been completely rewritten to satisfy Reviewer 1.

Page 8 Table 2. Is it really necessary to have four different identifiers? For example, is temperature not the same for all the potentials? This was quite confusing when I first read it.

Yes, it is always necessary when taking partial derivatives to specify both the variable that is changing and the variables that are being held fixed.

Even if temperature is common across different potentials, the other variables (such as pressure or volume) may differ, and this affects how the partial derivatives are interpreted.

For example, differentiating entropy with respect to temperature while holding pressure constant is different from differentiating entropy with respect to temperature while holding volume constant (this is the origin of the difference between C\_p and C\_v).

I’ve added a note to this effect in the text.

Page 9 Line 30. I find the name "thermal stress" confusing given how similar it sounds to the more conventional thermal pressure. The thermal pressure is an actual pressure (measured in Pa) whereas <i>π</i> is not (Pa/K). I think it is worth stressing this difference.

I’ve added the sentence: “Note that the thermal stress tensor is not an actual stress, but instead describes how internal stress changes with temperature if deformation is not allowed to occur.”

Page 9 Line 45-47. Can the derivation of these relations (e.g., 21, 24 and 25) be added to the appendix?

Done

Page 14 Line 10. I understand what the author means, but perhaps it is worth explaining what anti-post-stishovite is.

I’ve added a comment that the transition represents a change from Q is slightly positive to Q is slightly negative.

Page 14 Lines 19-20. Is there a reason why the experimental data of Nishihara et al. (2005) and Wang et al. (2012) were not used here? I think they would help to better constrain the thermal parameters of the stishovite phase. [<https://doi.org/10.1007/s00269-004-0426-7>, <https://doi.org/10.1029/2011JB009100>]

Thanks for the recommendation! I’ve now added these two datasets to the fitting procedure, and have updated the Figures and the Tables.

Page 14 Line 20. Ito et al (1974); Fischer et al. (2018) → (Ito et al., 1974; Fischer et al., 2018)

Changed, thanks!

Page 14 Lines 48-58. Is the scalar model used in this study the one of Stixrude and Lithgow-Bertelloni (2005)?

No, the scalar model parameters are refit to the data. I’ve reworded the text to make this clearer.

Why can the volume and temperature dependence of the thermodynamic parameters not be determined from the anisotropic properties?

The Q=1 state cannot be fully characterised because not all states can be investigated experimentally. We only have a single plane of experimental data in the P-T-Q volume. I haven’t modified the text, as I don’t think this point fits neatly into the text.

Page 15 Line 35. At the transition pressure and temperature, the Gibbs free energy of the stishovite and post stishovite phase should be the same. Why is <i>ΔG</i> not equal to zero?

No, at the transition pressure and temperature, d2G/dQdQ = 0 at Q=0. See the figure of the Gibbs energy curve (was Figure 1, now Figure 2). I’ve added a sentence to the caption to make this explicit.

Page 16 Figure 2. Is there an analytical expression for <i>Q</i> as a function of volume (or pressure) and temperature or was it calculated numerically?

Q^\* was calculated numerically. I’ve added this to the caption.

Page 17 Line 24. Personally, I would not rescale the pressure values as it could be seen as a way of massaging the data. Normalizing to the <i>V</i><sub>0</sub> of each dataset would be better as equations of state are usually function of <i>V</i>/<i>V</i><sub>0</sub> and not explicitly <i>V</i>.

Sadly, normalising volumes to V\_0 would not have made the datasets consistent with each other. Normalising volumes to V\_0 only shifts ln(V) up and down, but the discrepancy between XRD and Brillouin datasets requires differences in dln(V)/dP. I’ve made minor changes to the text.

Page 18 Table 3. What are the errors on the fit parameters? Is it really necessary to have that many significant digits? This applies to Table 4 as well.

I have added the uncertainties on the fit parameters and a figure showing the correlation matrix to the Supplementary Information.

I have also added sentences to explain that the number of significant digits is not to indicate that the values are that well known, but to avoid round-off error.

What are <i>a</i><sub>0</sub> and <i>b</i><sub>0</sub>? Are these the unit cell parameters of post-stishovite at 1 bar and 300 K? Please define these parameters

Yes. I’ve now defined these parameters in the Table caption.

Page 19 Table 4. What about the anisotropic properties of tetragonal stishovite? Are they calculated from those of post stishovite? How?

See Section 4.2.2. I’ve added a sentence there.

Page 21 Line 41. Either increasing pressure or decreasing volume.

Thanks for catching this! I’ve changed the text.