

Journal: National Science Review
Article doi: 10.1093/nsr/nwz040
Article title: Thermal conductivity of complex materials
First Author: G. Jeffrey Snyder
Corr. Author: G. Jeffrey Snyder



INSTRUCTIONS

We encourage you to use Adobe's editing tools (please see the next page for instructions). If this is not possible, please list clearly in an e-mail. Please do not send corrections as track changed Word documents.

Changes should be corrections of typographical errors only. Changes that contradict journal style will not be made.

These proofs are for checking purposes only. They should not be considered as final publication format. The proof must not be used for any other purpose. In particular we request that you: do not post them on your personal/institutional web site, and do not print and distribute multiple copies. Neither excerpts nor all of the article should be included in other publications written or edited by yourself until the final version has been published and the full citation details are available. You will be sent these when the article is published.

1. **Licence to Publish:** Oxford Journals requires your agreement before publishing your article. If you haven't already completed this, please sign in with your My Account information and complete the online licence form. Details on how to do this can be found in the Welcome to Oxford Journals email.
 2. **Permissions: Permission to reproduce any third party material in your paper should have been obtained prior to acceptance. If your paper contains figures or text that require permission to reproduce, please inform me immediately by email.**
 3. **Author groups:** Please check that all names have been spelled correctly and appear in the correct order. Please also check that all initials are present. Please check that the author surnames (family name) have been correctly identified by a pink background. If this is incorrect, please identify the full surname of the relevant authors. Occasionally, the distinction between surnames and forenames can be ambiguous, and this is to ensure that the authors' full surnames and forenames are tagged correctly, for accurate indexing online.
 4. **Figures:** If applicable, figures have been placed as close as possible to their first citation. Please check that they are complete and that the correct figure legend is present. Figures in the proof are low resolution versions that will be replaced with high resolution versions when the journal is printed.
 5. **Missing elements:** Please check that the text is complete and that all figures, tables and their legends are included.
 6. **Special characters and equations:** Please check that special characters, equations and units have been reproduced accurately.
 7. **URLs:** Please check that all web addresses cited in the text, footnotes and reference list are up-to-date.
 8. **Funding:** If applicable, any funding used while completing this work should be highlighted in the Acknowledgements section. Please ensure that you use the full official name of the funding body.
 9. **Manuscript tagging:** The information in the table that appears before your manuscript contains the manuscript information that will be captured in the tagging online. Please check that this information is accurate as it cannot be changed after publication. If any of the information is incorrect, please mark the changes onto the table.
-

AUTHOR QUERIES - TO BE ANSWERED BY THE CORRESPONDING AUTHOR

The following queries have arisen during the typesetting of your manuscript. Please answer these queries by marking the required corrections at the appropriate point in the text.

Query No.	Nature of Query	Author's Response
Q1	Author: 'diffusion' changed to 'diffuson'; please check.	
Q2	Author: Please provide volume and page numbers.	

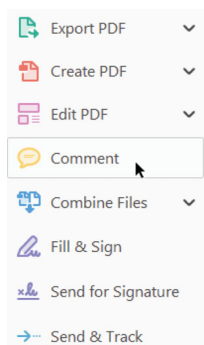
MAKING CORRECTIONS TO YOUR PROOF

These instructions show you how to mark changes or add notes to your proofs using Adobe Acrobat Professional versions 7 and onwards, or Adobe Reader DC. To check what version you are using go to **Help** then **About**. The latest version of Adobe Reader is available for free from get.adobe.com/reader.

DISPLAYING THE TOOLBARS

Adobe Reader DC

In Adobe Reader DC, the Comment toolbar can be found by clicking 'Comment' in the menu on the right-hand side of the page (shown below).

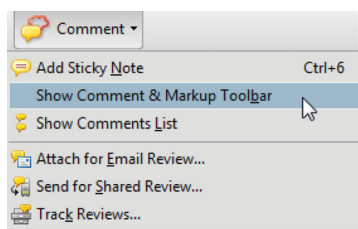


The toolbar shown below will then display along the top.



Acrobat Professional 7, 8, and 9

In Adobe Professional, the Comment toolbar can be found by clicking 'Comment(s)' in the top toolbar, and then clicking 'Show Comment & Markup Toolbar' (shown below).

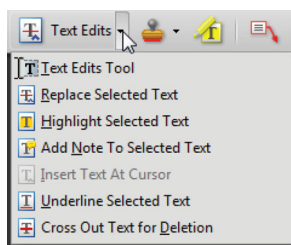


The toolbar shown below will then be displayed along the top.



USING TEXT EDITS AND COMMENTS IN ADOBE ACROBAT

This is the quickest, simplest and easiest method both to make corrections, and for your corrections to be transferred and checked



1. Click **Text Edits**
2. Select the text to be annotated or place your cursor at the insertion point and start typing.
3. Click the **Text Edits** drop down arrow and select the required action.

You can also right click on selected text for a range of commenting options, or add sticky notes.

SAVING COMMENTS

In order to save your comments and notes, you need to save the file (**File, Save**) when you close the document.

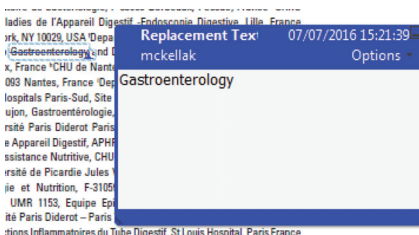
USING COMMENTING TOOLS IN ADOBE READER

All commenting tools are displayed in the toolbar. You cannot use text edits, however you can still use highlighter, sticky notes, and a variety of insert/replace text options.



POP-UP NOTES

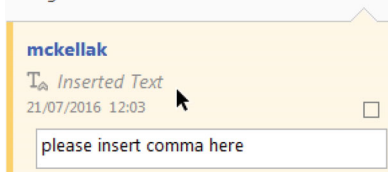
In both Reader and Acrobat, when you insert or edit text a pop-up box will appear. In **Acrobat** it looks like this:



In **Reader** it looks like this, and will appear in the right-hand pane:

Page 1

3 ^



DO NOT MAKE ANY EDITS DIRECTLY INTO THE TEXT, USE COMMENTING TOOLS ONLY.

Element	Included in this paper
Manuscript category	MATERIALS SCIENCE
Funder ID	None
Orcid IDs	http://orcid.org/0000-0003-1414-8682
Contributors	G. Jeffrey Snyder, Matthias T. Agne, Ramya Gurunathan
Supplementary data files cited	None
Related article(s)	
Corresponding author	G. Jeffrey Snyder
Title	Thermal conductivity of complex materials
Keywords	None
Collection ID	

MATERIALS SCIENCE

Thermal conductivity of complex materials

G. Jeffrey Snyder , Matthias T. Agne and Ramya Gurunathan

In the discussion and analysis of thermal properties (e.g. heat capacity, thermal conductivity) the Debye approximation is typically used to describe the collective behavior of lattice vibrations (phonons) in solid materials. Because the Debye model has been successful in explaining many properties of materials, particularly in contrast to the non-dispersive model considered by Einstein, the Debye model is often the starting point of introductory textbooks in solid state physics. Yet the more we learn about the full spectrum of lattice vibrations, and now can calculate detailed phonon dispersion relations for almost any crystalline solid, the more surprising it is that the linear dispersion Debye model works as well as it has for so long. A real density of vibrational states, for example, appears qualitatively different from the Debye model

for all of the many optical branches and even half of the acoustic phonons (Fig. 1g).

In a recent work published in NSR by Chen *et al.*, ‘Rationalizing phonon dispersion for lattice thermal conductivity of solids’ [1], the effect of a non-linear ‘Born–von Karman’ (BvK) dispersion, which can still be manipulated analytically, is examined on thermal conductivity models. Keeping the speed of the acoustic vibrations (where the Debye model works well) a constant, the result is a subtle decrease in the energy and velocity of the predicted vibrational states (compare Fig. 1a–d with Fig. 1e and f) that leads to a lower predicted thermal conductivity more consistent with experimental values.

The analytic model developed by Chen *et al.* [1] can be compared to a

number of simple estimates for the thermal conductivity of complex materials. The ‘Debye–Slack’ model [2]

overestimates the thermal conductivity because optical vibrations are treated as acoustic vibrations (Fig. 1a and b). The ‘Debye–Snyder’ (Fig. 1c and d) model [3] treats the optical modes using the Cahill model for the thermal conductivity of a glass and still overestimates the thermal conductivity (note that the minimum optical frequency of $\omega_D n^{-1/d}$, mentioned by Toberer *et al.* [3], refers to the limits of integration for optical vibrations that range from $\omega_D n^{-1/d}$ to ω_D , for d -dimension considerations).

The ‘BvK–Pei’ model [1] expands on the ‘Debye–Snyder’ model using the BvK rather than the Debye dispersion to give a $\sim 30\%$ lower estimate due to the lower frequencies and phonon group

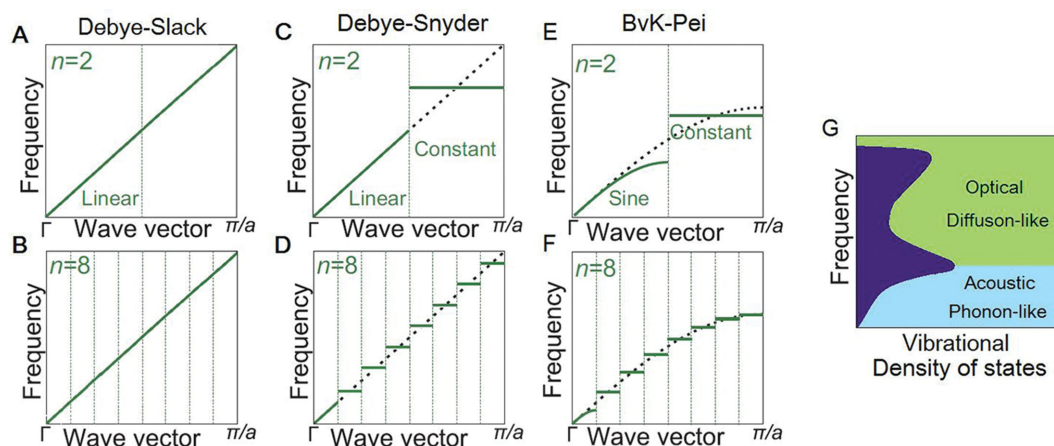



Figure 1. Schematic for a 1D dispersion model used to predict thermal conductivity according to (a) the Debye dispersion used by Slack [2] for a two-atom primitive unit cell and (b) an eight-atom primitive unit cell; compared with (c) the Debye dispersion used by Toberer *et al.* [3] for a two-atom primitive unit cell and (d) an eight-atom primitive unit cell; compared with (e) the BvK dispersion used by Chen *et al.* [1] for a two-atom primitive unit cell and (f) an eight-atom primitive unit cell. In panels c–f, the acoustic branch is treated as phonon-like, whereas the optical branches are treated as more diffuson-like, as illustrated in (g) a schematic vibrational density of states.

velocities. Alternatively, one could use a *diffuson* model [4] to account for the optical modes similar to [5], which would also result in a lower estimate for the thermal conductivity.

One possible takeaway from all of this is that maybe Einstein was not as wrong as we make it seem in introductory textbooks. That is, high-frequency optical vibrations in real materials at and above room temperature have a small, but non-negligible, contribution to thermal conductivity. These optical vibrations might actually be better described as more spatially localized (diffuson-like) vibrations [6] than fully delocalized

collective (phonon-like) vibrations (Fig. 1g). At high temperatures, despite these profound philosophical differences for the nature and speed of the vibrations, the predicted thermal properties are remarkably similar [4].

G. Jeffrey Snyder , Matthias T. Agne and Ramya Gurunathan
Department of Materials Science and Engineering,
Northwestern University, USA
*Corresponding author. E-mail:
jeff.snyder@northwestern.edu

REFERENCES

1. Chen Z, Zhang X and Lin S *et al. Natl Sci Rev* 2018; **5**: 888–94.
2. Slack GA. *J Phys Chem Solids* 1973; **34**: 321–35.
3. Toberer ES, Zevalkink A and Snyder GJ. *J Mater Chem* 2011; **21**: 15843–52.
4. Agne MT, Hanus R and Snyder GJ. *Energy Environ Sci* 2018; **11**: 609–16.
5. Slack GA In: Seitz F, Turnbull D and Ehrenreich H (eds). *Solid State Physics*, Vol. 34. New York: Academic, 1979, 1–71.
6. DeAngelis F, Muraleedharan MG and Moon J *et al. Nanoscale Microscale Thermophys Eng* 2018; doi: 10.1080/15567265.2018.1519004.