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NATIONAL ACADEMIES Sciences Engineering Medicine

Status and Gaps in Thermodynamic Metrology of Materials in Extreme Environments

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Condensed Matter and Materials Research Committee (CMMRC)
National Academies Workshop on, "Frontiers in Data Analytics and Monitoring Tools for Extreme Materials"
Thursday, October 6, 2022; 10:20 AM EST
Keck Center of the National Academies – Washington, DC, USA

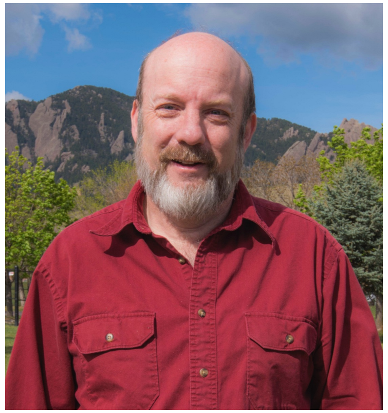
Outline

- Status of Thermodynamic Metrology
  - Measurement: Experimental Techniques
  - Data Availability
  - Data-Driven Models: Equation of State
- Individual Contribution
  - Measurement: High T, High P Liquid Speed of Sound Instrument
  - Data-Driven Model: Creating Fundamental Equation of State
- Gaps + Implications of Gaps → Opportunities
- Open Questions in the Field

Acknowledgements

- Thank you NIST experts who have helped guide my research and give a balanced perspective on the research field
- NASEM for hosting the workshop
- Workshop attendees

Mark McLinden



Eric Lemmon

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Ward Johnson

Carelyn Campbell

Adam Creuziger

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Status of Thermodynamic Metrology: State-Of-The-Art Overview

Elizabeth G. Rasmussen, PhD

What is a thermodynamic property?

- In 1914 P.W. Bridgeman (1946 Nobel Prize in Physics) defined ten fundamental thermodynamic quantities[1]
- Thermodynamic properties are interrelated[2]
- Example with Speed of Sound (SoS), c

$$c = \sqrt{\left(\frac{\partial P}{\partial \rho}\right)_s}$$

P = Pressure
ρ = density
s = entropy

$$c^2 = \left[\left(\frac{\partial \rho}{\partial P}\right)_T - \left(\frac{T}{\rho^2 c_p}\right)\left(\frac{\partial \rho}{\partial T}\right)_P^2\right]^{-1}$$

Independent variables: T, P

$$c^2 = \left[\left(\frac{\partial P}{\partial \rho}\right)_T + \left(\frac{T}{\rho^2 c_v}\right)\left(\frac{\partial \rho}{\partial T}\right)_\rho^2\right]^{-1}$$

Independent variables: T, ρ

TABLE I.

The Fundamental Ten Quantities.

In this table are given the notation and the definition of the fundamental ten thermodynamic quantities. It is to be understood that all the quantities refer to unit amount of the substance. This unit is usually chosen either as 1 gm., or as the quantity that at 0° C. and atmospheric pressure occupies a volume of 1 c.c.

p = pressure per unit area.
τ = temperature on the absolute thermodynamic scale.
v = volume of the unit quantity of the substance.
s = entropy, defined by the integral, $\int dQ/\tau$.
Q = heat absorbed, measured in the mechanical units appropriate to p and v. A physical meaning can be given only to dQ, the heat absorbed during a given change.
W = work done by the substance, in the appropriate mechanical units. Here again, only dW has a physical meaning.
E = the internal energy of the substance in mechanical units. E may be changed by an additive constant without changing its physical meaning. E is one of the thermodynamic potential functions.
$H = E + pv$, the "total heat," also one of the potential functions.
$Z = E + pv - \tau s$, the Gibbs thermodynamic potential.
$\Psi = E - \tau s$, also a thermodynamic potential, the "free energy" of Helmholtz.

1. P. W. Bridgman, **1914** Phys. Rev., 3, 273
2. J.P.M. Trusler and E.W. Lemmon, **2017** J. Chem. Thermodyn., 109, 61-70

Interrelation of Thermodynamic Properties

- In 1914 P.W. Bridgeman (1946 Nobel Prize in Physics) defined ten fundamental thermodynamic quantities[1]
- Thermodynamic properties are interrelated[2]
- Example with Speed of Sound (SoS), c

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Independent variables: T, ρ

Density, ρ

$$\left(\frac{\partial \rho}{\partial p}\right)_T = -\frac{1}{c^2} + \frac{T\alpha^2}{c_p}$$

Isobaric heat capacity, c_p

$$\left(\frac{\partial c_p}{\partial p}\right)_T = -T(\partial^2 v/\partial T^2)_p$$

Isobaric expansivity, α

$$\alpha = -\rho^{-1}(\partial \rho/\partial T)_p$$

Thermodynamic Measurement Techniques

Uncertainty of Measurement

Low (<0.1%) | Medium (~3%) | High (≥10%)

Features of Measurement Technique	Low uncertainty	High uncertainty
Size of Sample	Large	Small
Measurement of Sample Conditions During the Experiment	Direct	Indirect
Time Sample is at Experimental Conditions	Long	Short
Measurement of Property	Absolute	Relative
Uncertainty of State Variables (T, P, V)	Low	High

State Variables: Temperature

- Other workshop speakers discussed a lack of temperature standards in extreme conditions
- There are temperature standards in extreme conditions[1,2] (>1500 K) → Lack of USING standards
- Temperature standards development leadership by US is decreasing as the support for standards involvement diminishes (and people retire)
  - Lack of credit given, although the value is understood
- Knowledge transfer and collaboration between US standards institutions + academic institutions is low
- Dear community, *Do hard things.* Sincerely, The Future
  - Easy = not calibrating thermocouples/temperature measurement equipment
  - Easy = not being aware of standards activities
  - Easy = not completing knowledge transfer to the next generation of scientists (example: how to calibrate a thermocouple)

Eutectic Alloy	Temperature
Rhenium−Carbon	2747.91 ± 0.44 K
Platinum−Carbon	2011.50 ± 0.22 K
Cobalt−Carbon	1597.48 ± 0.14 K

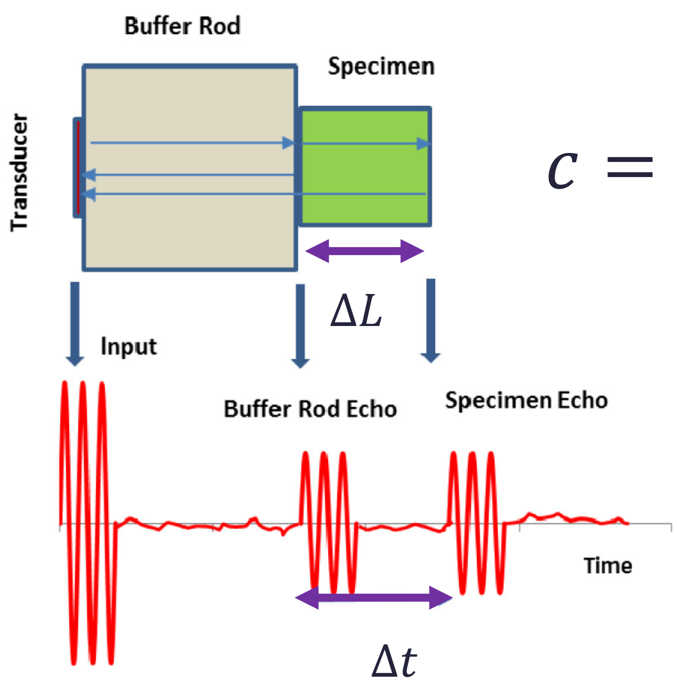
Note: uncertainties at approximately a 95% coverage probability.

> **"It is proposed that these values could be used as the basis of thermodynamic temperature measurement at high temperatures (above 1300 K)."**
> - 11 International Metrology Institutes, including NIST[3]

1. E R Williams *et al* **2015** Phil. Trans. R. Soc. A. 374 004420150044
2. A D W Todd *et al* **2021** Metrologia 58 035007
3. D H Lowe *et al* **2017** Metrologia 54 390

Speed of Sound via Pulse Techniques

Example: Pulse-Echo Method



$$c = \frac{2\Delta L}{\Delta t}$$

Figure from: B. Li, and R. C. Liebermann, *Physics of the Earth and Planetary Interiors, 2014*, 233, 135-153

Current Operation Limits of Method

- Upper Temperature Limit: 1900 K
- Upper Pressure Limit: 0.1 MPa
- Measurement Uncertainty: 0.1 - 1%

Uncertainty of Measurement

Features of Measurement Technique	Low (<0.1%)	Medium (~3%)	High (≥10%)
Size of Sample	Large		Small
Measurement of Sample Conditions During the Experiment	Direct		Indirect
Time Sample is at Experimental Conditions	Long		Short
Measurement of Property	Absolute		Relative
Uncertainty of State Variables (*T*, *P*, *V*)	Low		High

Type K Thermocouple

Speed of Sound via Diamond Anvil Techniques

Example: High-Pressure, High-Temperature Diamond Anvil Cell

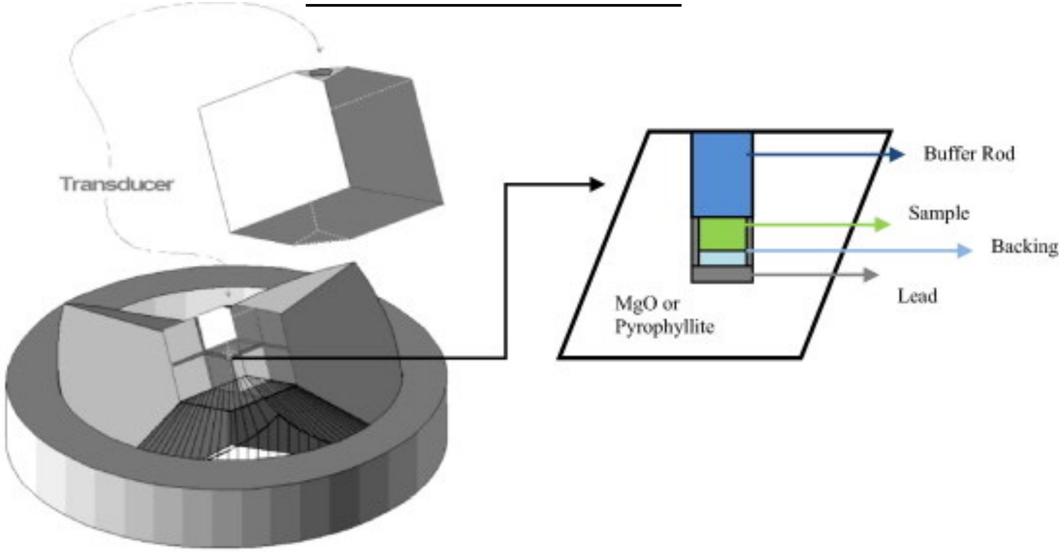


Figure from: B. Li, and R. C. Liebermann, *Physics of the Earth and Planetary Interiors, 2014,* 233, 135-153

Current Operation Limits of Method

- Upper Temperature Limit: 6,000 K
- Upper Pressure Limit: 500 GPa
- Measurement Uncertainty: 3-10%

Uncertainty of Measurement

Features of Measurement Technique	Low (<0.1%)	Medium (~3%)	High (≥10%)
Size of Sample	Large	→	Small
Measurement of Sample Conditions During the Experiment	Direct	→	Indirect
Time Sample is at Experimental Conditions	Long	→	Short
Measurement of Property	Absolute	→	Relative
Uncertainty of State Variables (*T*, *P*, *V*)	Low	→	High

Data Availability

- Know the difference: Collected vs. Calculated vs. Curated

Collected: Repository; burden of growth on community, minimal oversight on data quality (missing method information is tolerated)

Calculated: From theory (DFT, ML, AI, CALPHAD, etc.) or simulation

Curated: Experimental data focus, assigned uncertainty associated with data, differentiates between measured data and calculated data

Data Availability

NIST

- Know the difference: Collected vs. Calculated vs. Curated
- Many materials databases exist
  - Most are collections or calculations databases

Database Name	Lead Country	Description
Materials Project	USA	open web-based access to computed information on known and predicted materials
Nomad materials data	Germany	input and output files of all important computational materials science codes
Atomwork Advance	Japan	crystal structure data, X-ray diffraction data, material properties data, and phase diagram data collected from literature published up to 2014
AFLOW	USA	globally available database containing inorganic materials with calculated properties through high-throughput calculations
Computational Materials Repository	Sweden/ Denmark	infrastructure to enable collection, storage, retrieval and analysis of data from electronic-structure codes
Open Quantum Materials Data	USA	database of DFT-calculated thermodynamic and structural properties of inorganic materials
2D Material Encyclopedia	Singapore	computed properties of 2D materials obtained by exfoliation of existing layered materials and chemical substitution from 2D materials
Material Cloud	Colaboration in Europe	open science platform offering educational, research, and archiving tools; simulation software and services; and curated and raw data.
JARVIS (Joint Automated Repository for Various Integrated Simulations)	USA	repository designed to automate materials discovery and optimization using classical force-field, density functional theory, machine learning calculations and experiments

Data Availability

- Know the difference: Collected vs. Calculated vs. Curated
- Many materials databases exist
  - Most are collections or calculations databases
- Few curated databases exist[1]
  - NIST Alloy Database[2]
    - Part of the Materials Genome Initiative, MGI
  - NIST Structural Ceramics Database[3] (WebSCD)
    - Also known as NIST Ceramics WebBook, or NIST Ceramics Data Portal
  - ACerS-NIST Phase Equilibria Diagrams Database[4]
- Standard Development Organizations (SDOs): ASME, API, ASTM, AVS, ISO, etc.

Standard Reference Data Act [P.L. 90-396; 15 U.S.C. 290-290f]

"To provide form more effective integration and coordination of standard-reference data activities, the Secretary, in consultation with other interested Federal agencies, shall prescribe and publish in the Federal Register such standards, criteria, and procedures for the preparation and publication of standard reference data as may be necessary to carry out the provisions of this Act."

"Standard reference data conforming to standards established by the Secretary may be made available and sold by the Secretary or by a person or agency designated by him. To the extent practicable and appropriate, the prices established for such data may reflect the cost of collection, compilation, evaluation, and publication, and dissemination of the data, including administrative expenses; and the amounts received shall be subject to the Act of March 3, 1901, as amended."

In 1968, Congress passed the Standard Reference Data Act, a law that authorized and directed the Secretary of the Department of Commerce to provide or arrange for the collection, compilation, critical evaluation, publication, and dissemination of SRD. The definition of SRD was limited, and in 2017 Congress passed the Standard Reference Data Act Update with an expanded definition of SRD.

1. H. G. Semerjian and D. R. Burgess, **2022** J. Phys. Chem. Ref. Data 51, 011501
2. B. Wilthan, *et al.* **2017** Calphad 56, 126-138
3. NIST Structural Ceramics Database (SCD) Database (NIST Standard Reference Database 30), NIST, **2021**
4. Phase Equilibria Diagrams Database (NIST Standard Reference Database 31), ACerS and NIST, **2021**

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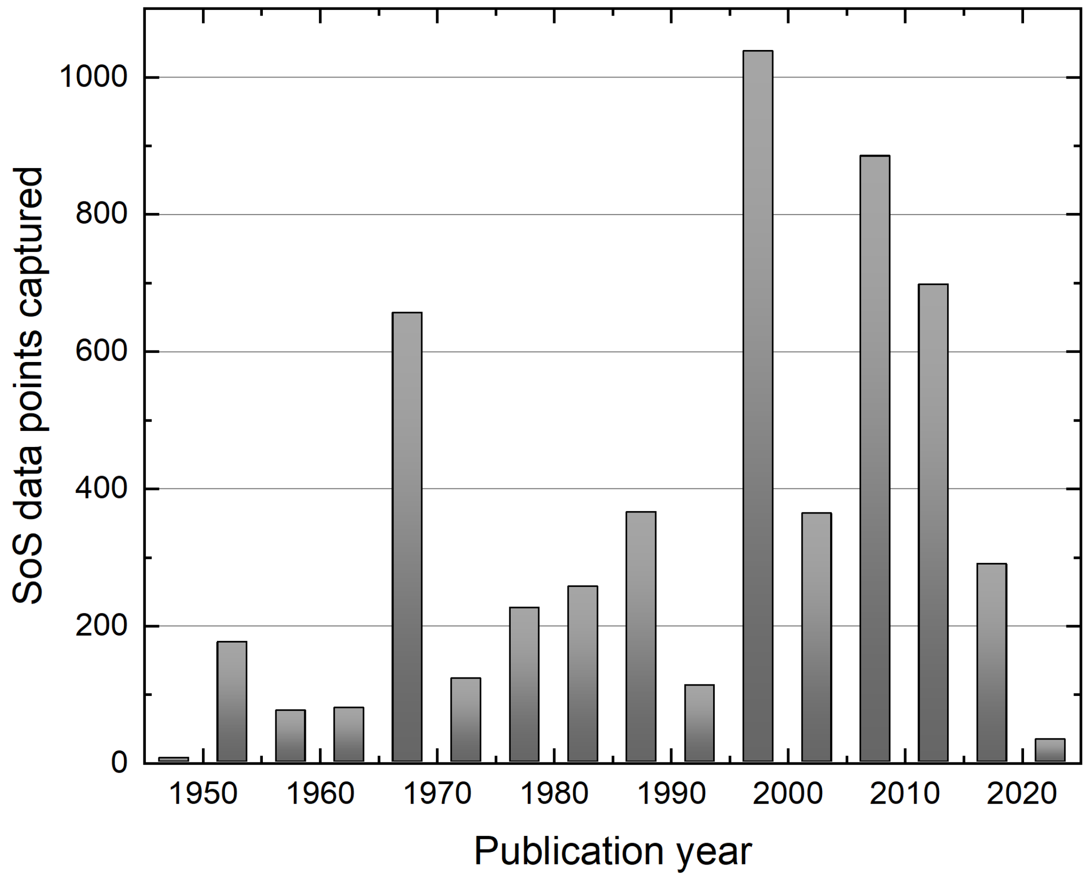
SoS Measurements in Curated NIST Alloy Database



1. H. G. Semerjian and D. R. Burgess, **2022** J. Phys. Chem. Ref. Data 51, 011501
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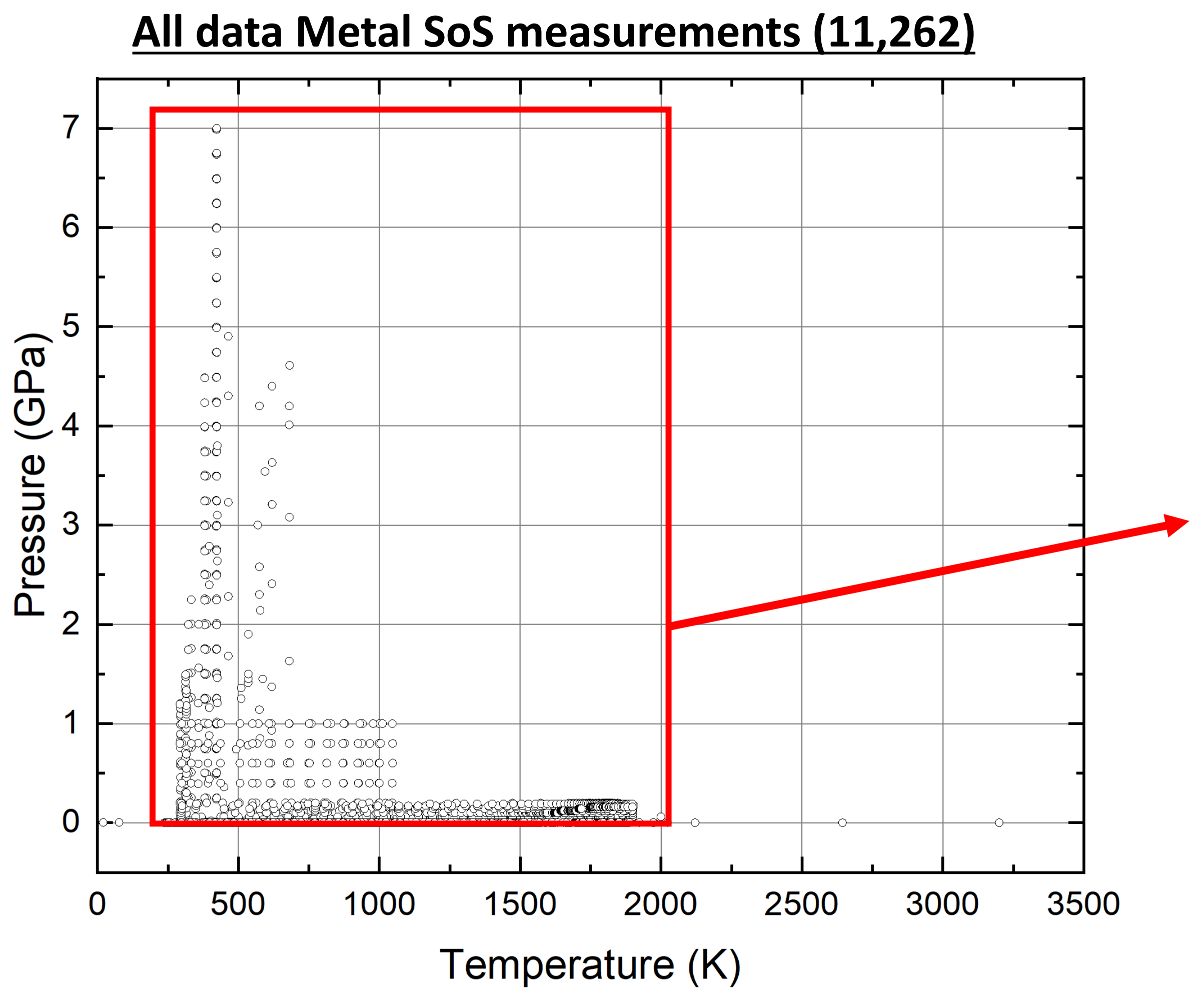
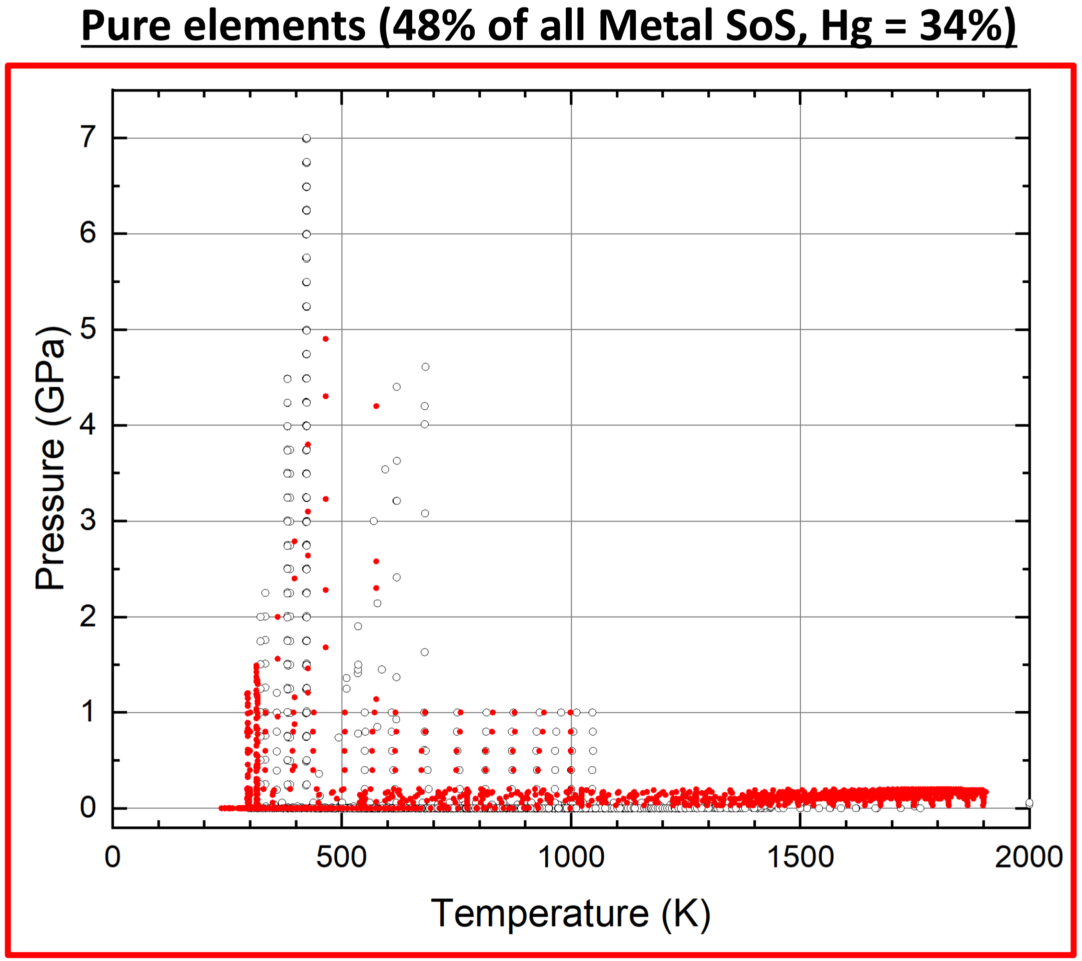
Data Availability: SoS of Metal Elements

- Using NIST Alloy Database[1], all phases, all compositions

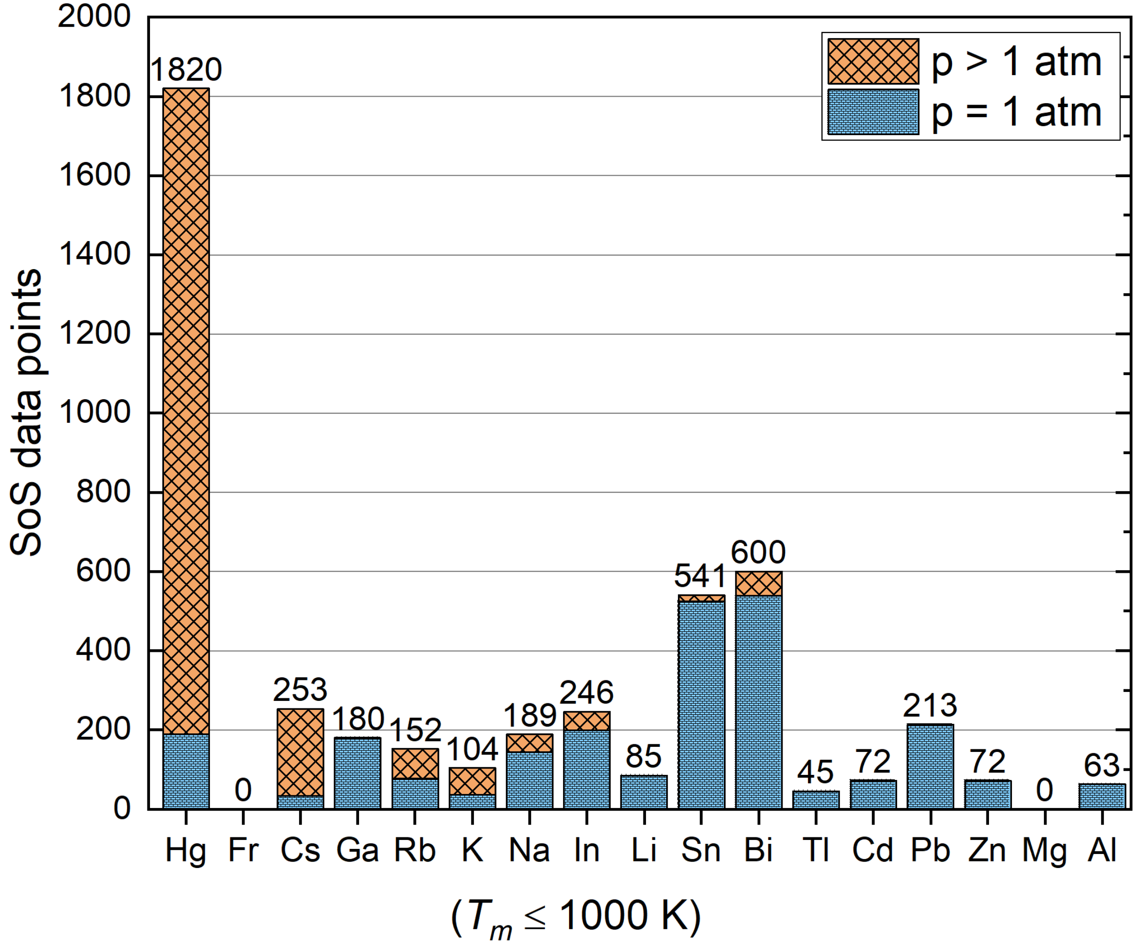


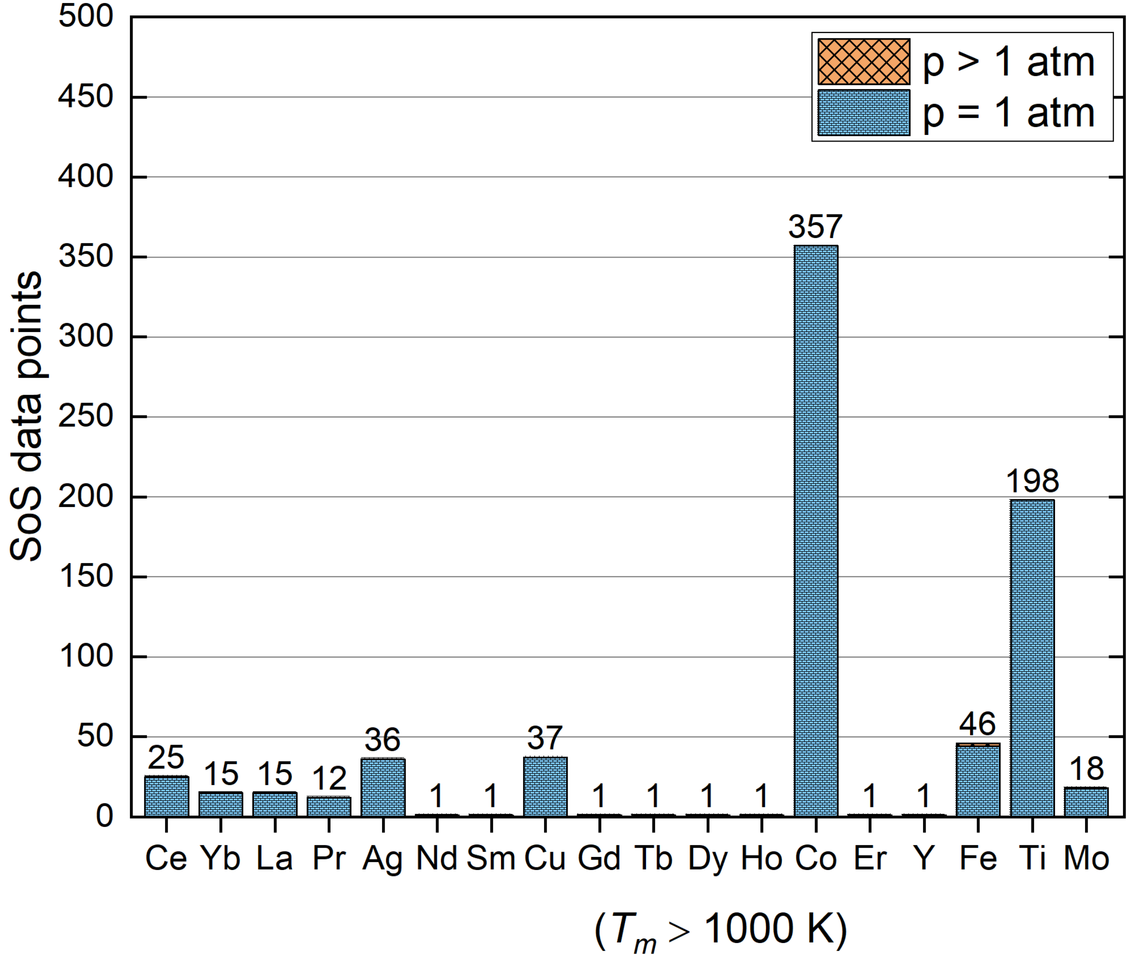


1. B. Wilthan, NIST alloy data, National Institute of Standards and Technology Public Data Resource, **2019**

Data Availability: SoS of Metal Elements

- Using NIST Alloy Database → Single-Component Metal Elements[1]



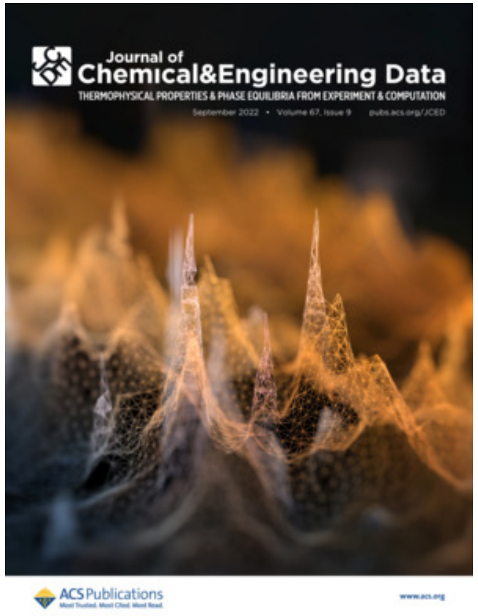


1. E. G. Rasmussen, B. Wilthan, In Preparation.

Data Reporting + Accountability

- State-of-the-art for materials in extreme environments is in the early stages of development
- As data availability grows, a challenge is holding authors accountable for good publishing practices (what, where, how)
- An example of setting publishing requirements can be seen in ACS's JCED Editor in Chief J. Ilya Siepmann[1]
- Increased outlining in detail journal requirements is needed
  - A potential issue is researchers migrate away from such journals and submit to more "hot topic" journals that do not have such rigorous requirements
- Note: JCED is 1 of 5 journals directly connected with NIST data curation efforts[2]

J. Ilya Siepmann



JCED: Three Things We Want Authors to Know

J. Ilja Siepmann
3 months ago

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The *Journal of Chemical & Engineering Data's* Editor-in-Chief, Ilja Siepmann, would like to highlight three items all prospective *JCED* authors should know, but may be underappreciated, as part of the journal's efforts to continuously improve.

GUIDELINES DOCUMENTS

Author Guidelines simply should *not* be viewed as something that can be ignored. *JCED* has both general guidelines applying to all manuscripts *and* guidelines specific to the topical section(s) appropriate for your manuscript's content. As some are aware, five thematic sections were introduced for *JCED*'s table of contents in 2022. Your efforts to align with these guidelines will not only expedite the review process for your manuscript and increase the likelihood of acceptance for publication in *JCED*, but will ultimately lead to your research publications providing accurate, precise, reproducible, and consequential data that will have a greater impact. For example, *JCED* requires a chemical sample table for *all* manuscripts. Forgetting to include the sample table is the clearest signal to an editor that authors have neither read the *JCED* guidelines nor utilized the 1-page submission checklist as a cheat sheet. You would be amazed to know the fraction of manuscripts submitted without a chemical sample table and the rather low acceptance rate for these manuscripts.

Especially for new JCED authors or previous authors that have not submitted a manuscript during the past year, please read and familiarize yourself with the complete *JCED* Author Guidelines to ensure you are up to date. This will surely increase the likelihood for a smooth peer review process.

1. *J. Chem. Eng. Data* **2016**, 61, 1, 1–2
2. *J. Chem. Eng. Data* **2019**, 64, 10, 4191–4192

Data-Driven Models: Using the data

NIST

- Other speakers will address properties via computation: ML/ AI/ MD-MC/ CALPHAD, or data-driven simulations of the process
  - These methods need (reliable/good) data[1]
- Equation of State (EoS) is an algebraic relationship between pressure, temperature, and volume
  - The simplest form is Ideal Gas Law[2]
  - More complex forms have increased accuracy across larger ranges of temperature, pressure, and states
  - Other properties from thermodynamic relations

Ideal Gas Law

$$PV = RT$$

1. Kattner, U. R. **2020**. High temperatures-high pressures, 49, 1-2
2. Clapeyron, E. **1834**. J. de l'École Polytechnique **XIV**: 153–90, 153–190

Data-Driven Models: EoS Modeling

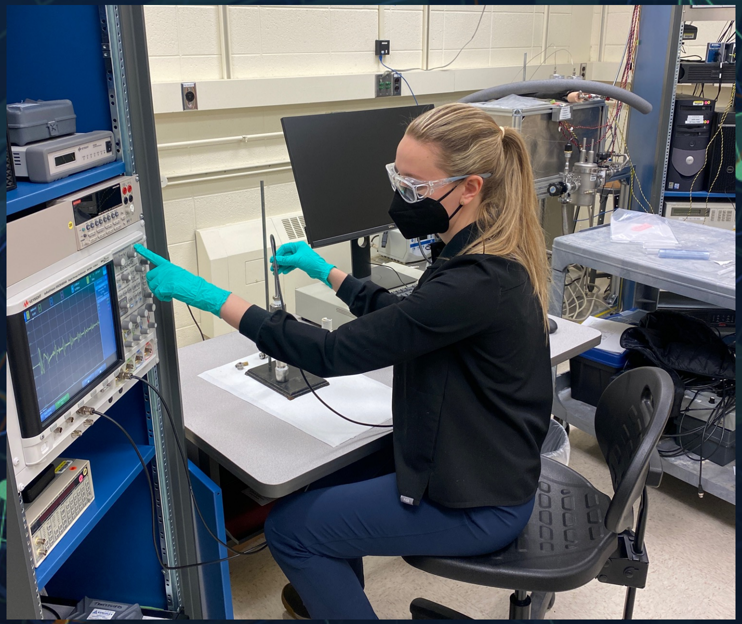
- Equation of State (EoS)
  - Solid Phase in the form of Gibbs Energy, $G = f(T, P)$
    - Metal elements, ceramics
  - Liquid, Gas, Supercritical Phase in the form of Helmholtz Energy, $A = f(T, \rho)$
    - Organic fluids, natural gases, etc.
  - Implementation into commercial multi-physics simulation software like ANSYS, SolidWorks, COMSOL, Aspen‡
- EoS is an empirical ("data-driven") model for thermodynamic properties
- Advancement in EoS modeling only possible with more reference quality experimental data

‡ Any mention of commercial products is for information only; it does not imply recommendation or endorsement by NIST

Individual Contribution:

Measurement: High *T*, High *P* Liquid Speed of Sound Instrument

Model: Creating Fundamental Equation of State



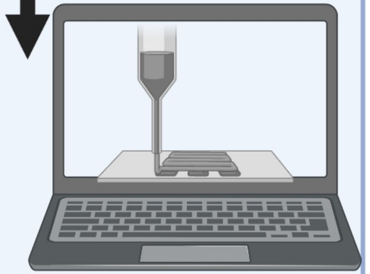
Elizabeth G. Rasmussen, PhD

Motivation for Speed of Sound Instrument

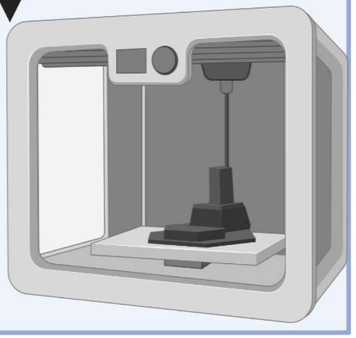
Liquid Metal Material Properties → Ultra Accurate Equation of State

Create Cloud Database (like REFPROP)

Empower High-Fidelity Simulations

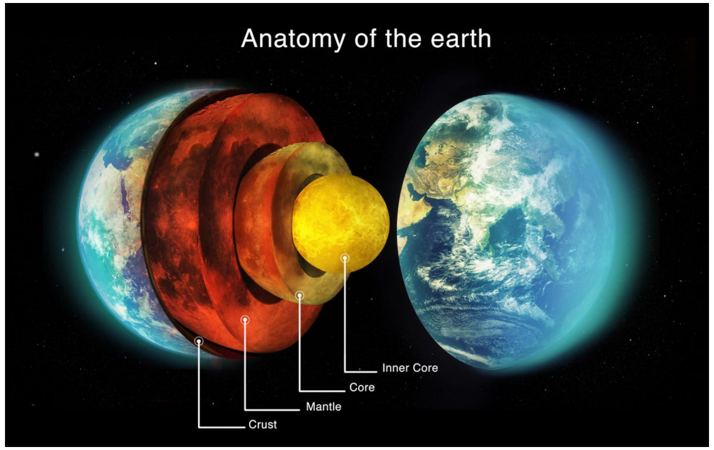


Data-Driven Addative ~~Manufacturing of Metals~~

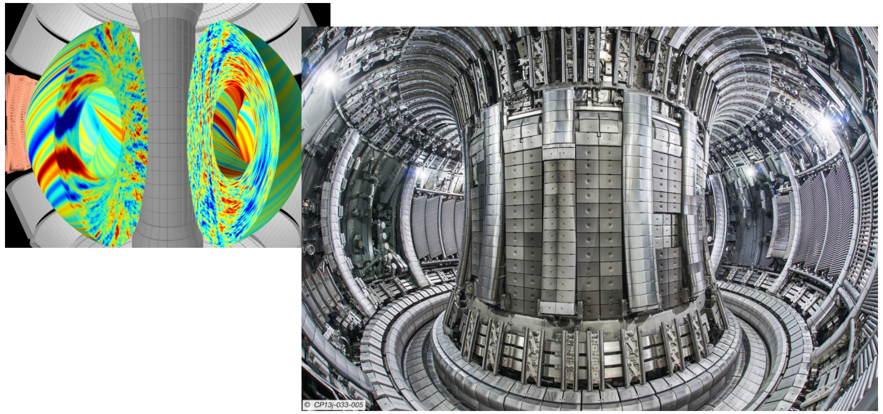


Blast Furnace ("Giga-Scale")

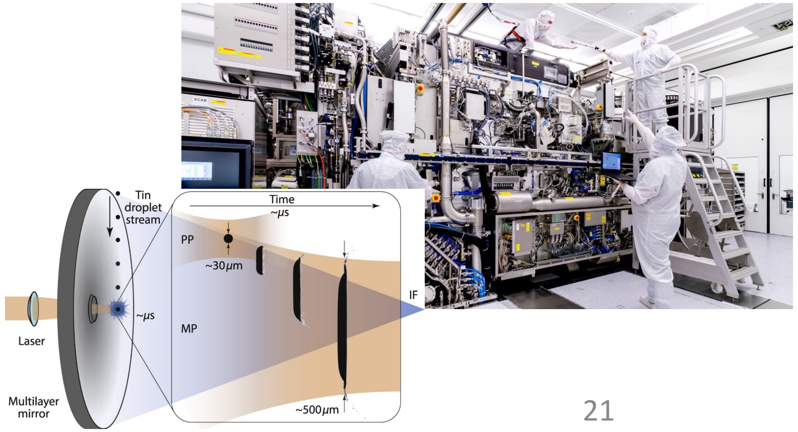
Planetary Exploration



Fusion Energy

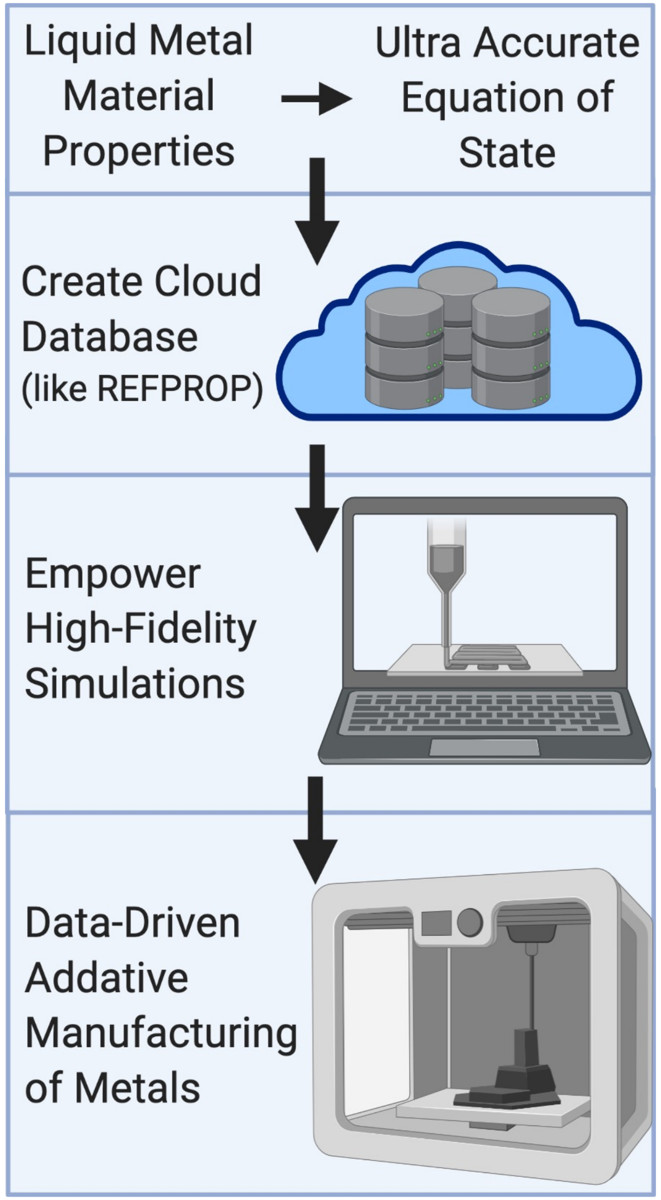


Semiconductor Manufacturing



Status and Gaps in Thermodynamic Metrology of Materials in Extreme Environments

Motivation for Speed of Sound Instrument



From a metrology perspective determining speed of sound can be done rapidly and automatically across wide range of temperatures and pressures with low uncertainty (0.04% for organic materials in our group)

Why speed of sound? A four-for-one property!

Speed of sound, c

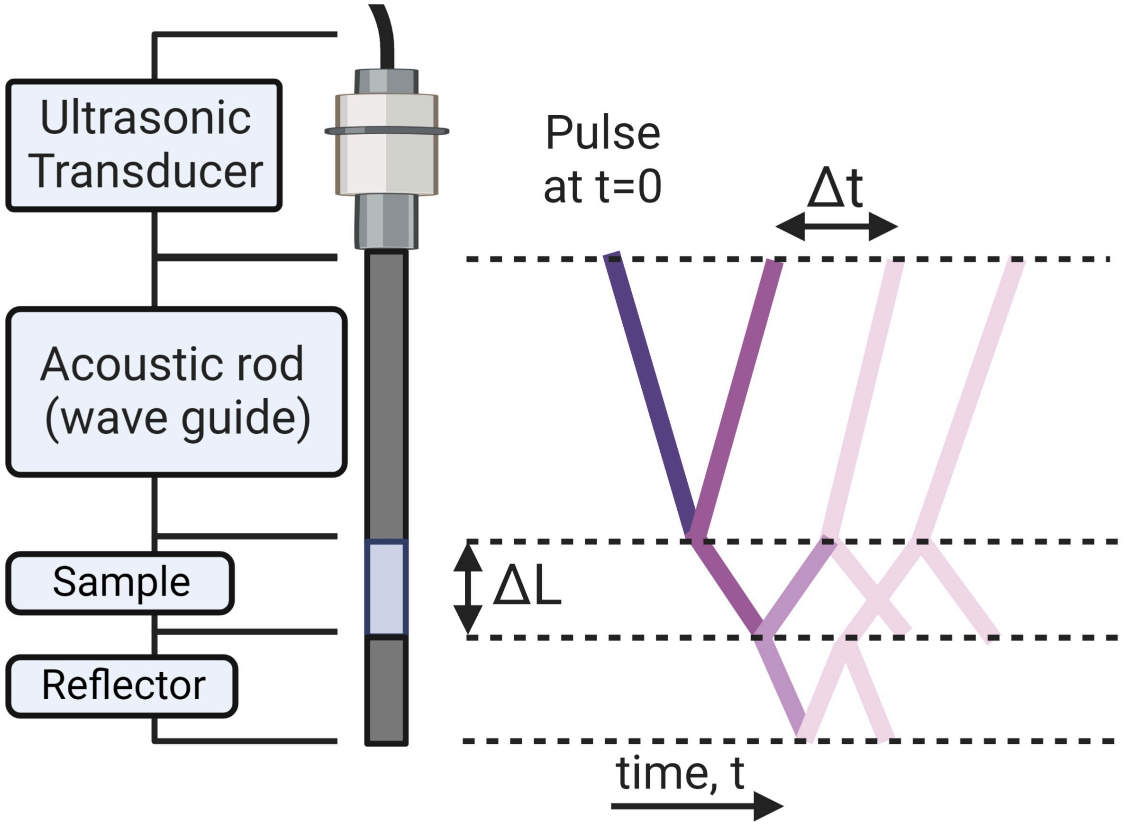
Isobaric expansivity, α

Density, ρ

Isobaric heat capacity, c_p

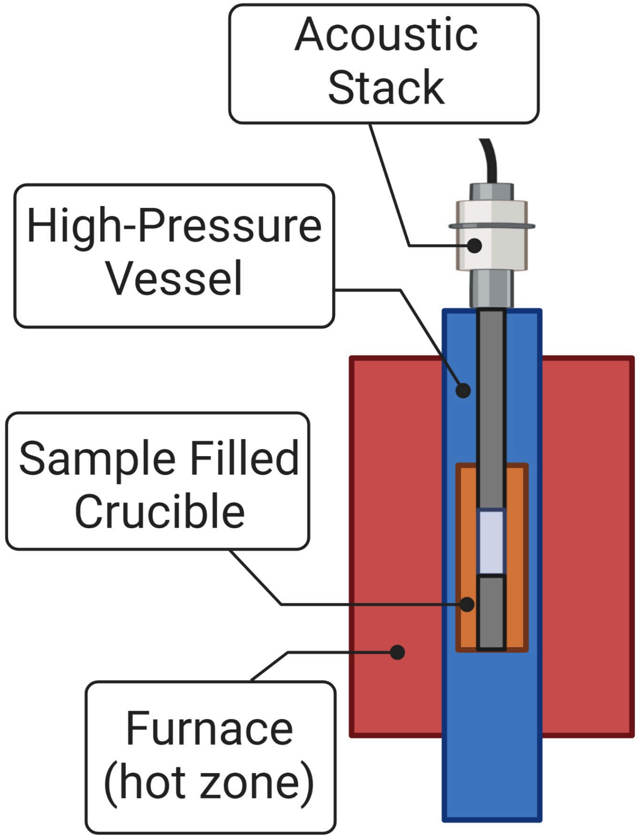
Instrument Overview

Instrument to perform reference quality speed of sound measurements of liquid phase materials up to 1700 *K* and 0.2 *GPa* with ~0.1% uncertainty[1]



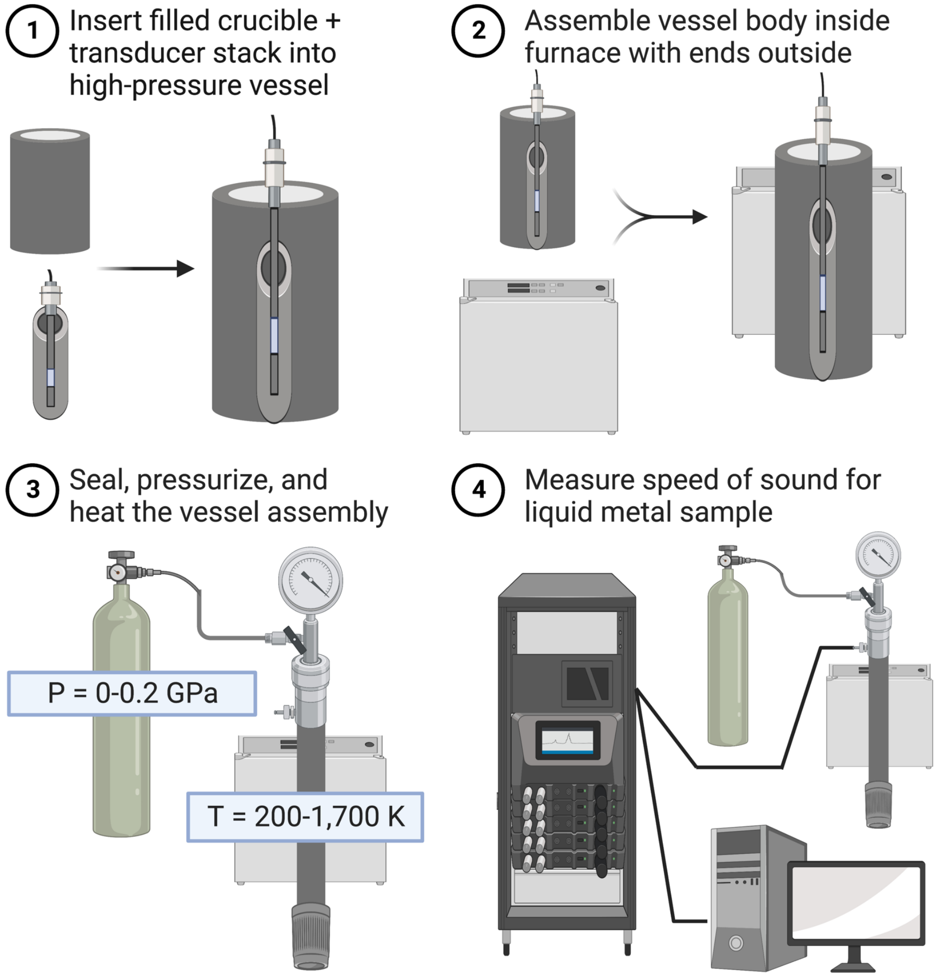
Speed of sound

$$c = \frac{2\Delta L}{\Delta t}$$



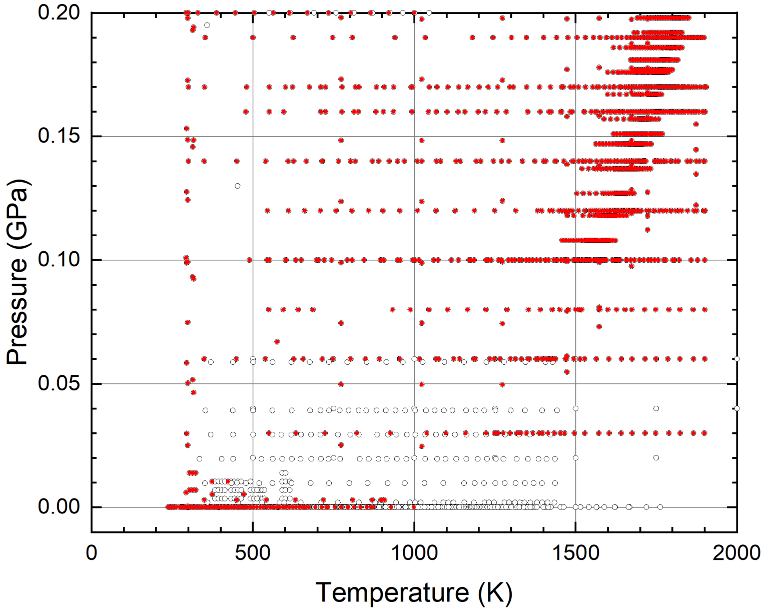
1. E. G. Rasmussen, M. O. McLinden, In Preparation.

Instrument Operation



Schematic of the four-step experiment procedure to collect speed of sound (SoS) reference data of liquid samples using the SoS instrument.[1]

- Instrument and method configured for automated operation via control software
  - Will run for days without needing human intervention
- Built for longevity: Should be operational for 10+ years
- High pressure vessel design inspiration from geology studies by Orville Frank Tuttle[2,3]
- Invention disclosure submitted (I.P. protection)



1. E. G. Rasmussen, M. O. McLinden, In Preparation.
2. W. C. Luth, O. F. Tuttle, **1963** American Mineralogist, 48 (11-12): 1401–1403
3. O. F. Tuttle, **1948** American J. of Sci., 246 (10) 628-635

EoS For Elements

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- With instrument will be able to create new reference data for liquid elements with melting points over 200 *K*
- Given ‘anchor points’ of density and specific heat capacity as a function of temperature from literature, one can calculate all thermodynamic properties in the form of an EoS
- Reference EoS can be useful for Multiphysics simulations
- Few EoS exist for elements, fewer for multi-component systems (alloys, ceramics, compounds, etc.)

Multi-phase equation of state for aluminum

Published online by Cambridge University Press: **17 December 2007**

I.V. Lomonosov

Hide author details

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Abstract

Results of theoretical calculations and experimental measurements of the equation of state (EOS) at extreme conditions are discussed and applied to aluminum. It is pointed out that the available high pressure and temperature information covers a broad range of the phase diagram, but only irregularly and, as a rule, is not thermodynamically complete; its generalization can be done only in the form of a thermodynamically complete EOS. A multi-

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Gaps, Consequences, & Opportunities

1. Techniques
2. Data
3. Theory

Gap 1: Data + Experimental Methods

Gap

1. Few measurement techniques and facilities *globally* to generate reference quality data in extreme conditions
2. Lack of innovation in methods to measure properties

Implication

1. Lack of accurate data available
2. Mindset that we have reached limits of experimental availability so 'have to' generate properties with simulations

Opportunity

- Encourage reference quality experimental pursuits
- Reward high-quality experimental pursuits with a currency of choice (citations, awards, money, promotions, stability)
- Define promote educating standards and instrument innovation

Gap 2: Use of Standards, Understanding Uncertainty

NIST

Gap

1. Lack of community using standards in extreme conditions
2. Lack of understanding implication of uncertainties at extreme conditions

Implication

1. Increased uncertainty in data
2. Decrease to theory computation usefulness

Opportunity

- Where standards exist, use them (carbon eutectic fixed points for *T*)
- Support standards creation at extreme conditions
- Hold each other accountable for uncertainty reporting, calibration, and consideration in computations

Gap 3: Empirical Computations → Simulations

Gap

1. Lack of reference thermodynamic models (EoS) for condensed matter at extreme conditions’
2. Using computed property data to compute property data

Implication

1. Less accurate simulation and models
2. Failure to translate simulations to real world environments

Opportunity

- Advanced thermodynamic theory and modeling from reliable experimental data
- Create data-driven simulations to guide design of systems in extreme environments

Who does what?

National Metrology Institutes (NIST): (1) Innovate in metrology, (2) capture reference-quality data, curate and distribute reference data

Academic Institutes: (1) Train the next generation of scientists on standards, (2) capture high throughput data, and (3) collaborate with NIST on projects to ensure knowledge transfer

Industry: (1) Engage with NIST and Academia to communicate material needs and scalability insights

Funding Agencies: (1) Support metrology pursuits, (2) require publishing in journals collaborating with NIST to support organized data capture in the US, (3) avoid funding research that creates 'new' programs that should operate/collaborate *inside* of current programs (4) support your PI's to use NIST's standard reference data, help us help them to help you

Conclusions and Open Questions in the Field

Elizabeth G. Rasmussen, PhD

Conclusions

<u>Frontier of Materials in Extreme Environments Is Like an Iceberg</u>

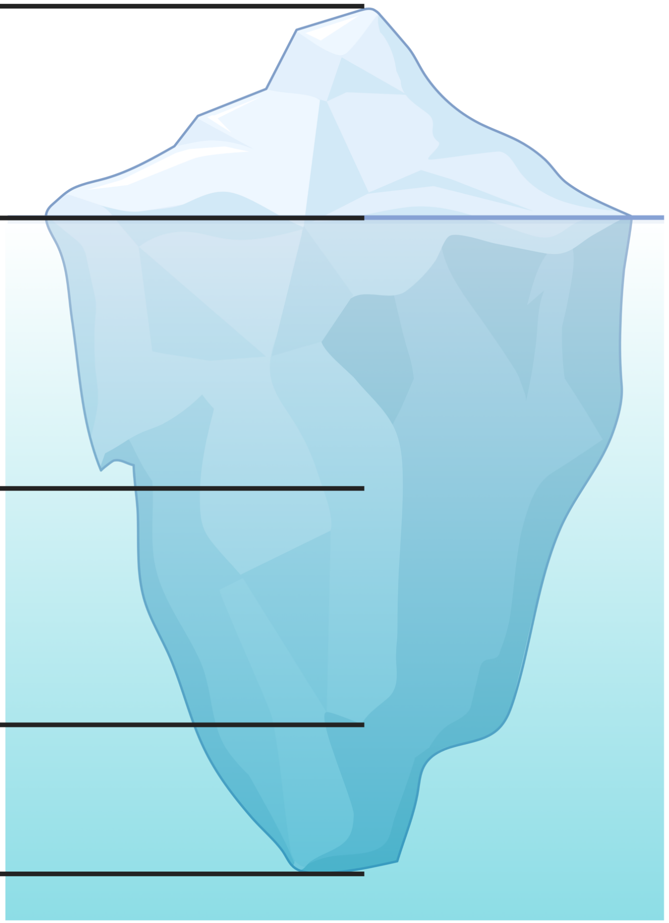
Vision: Execution of Advanced Systems in Extreme Environments

Optimized Advanced System Design: Multiphysics Simulations

Accurate Simulations: Data-Driven/ Empirical Reference Models

Reference Data

Reference Instruments



Accurate measurement instrumentation
enables
the ability to create accurate datasets
which enables
the ability to create data-driven models
which enables
<u>Leadership in materials for extreme environments</u>

Open Questions in Thermophysical Properties in Extreme Environments

1. To what extent do computations base on data with over 5% uncertainty impact advancement in extreme environments?
2. How does one prioritize materials to analyze?
   - For curated databases, calculated databases, and data measurements
3. How will we hold the community accountable to using standards in materials experiments, dissemination, collection, calculation, and curation?
4. How can we eliminate creating (and funding) “parallel programs” or programs that have to claim “novel” standalone product when it would be more appropriate to collaborate with established programs?

Status and Gaps in Thermodynamic Metrology of Materials in Extreme Environments

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Condensed Matter and Materials Research Committee (CMMRC)
National Academies Workshop on, "Frontiers in Data Analytics and Monitoring Tools for Extreme Materials"
Thursday, October 6, 2022; 8:50 AM - 9:15 AM
Keck Center of the National Academies – Washington, DC, USA