

Nanoscale thermal transport

Lecture 3

Riley Hanus

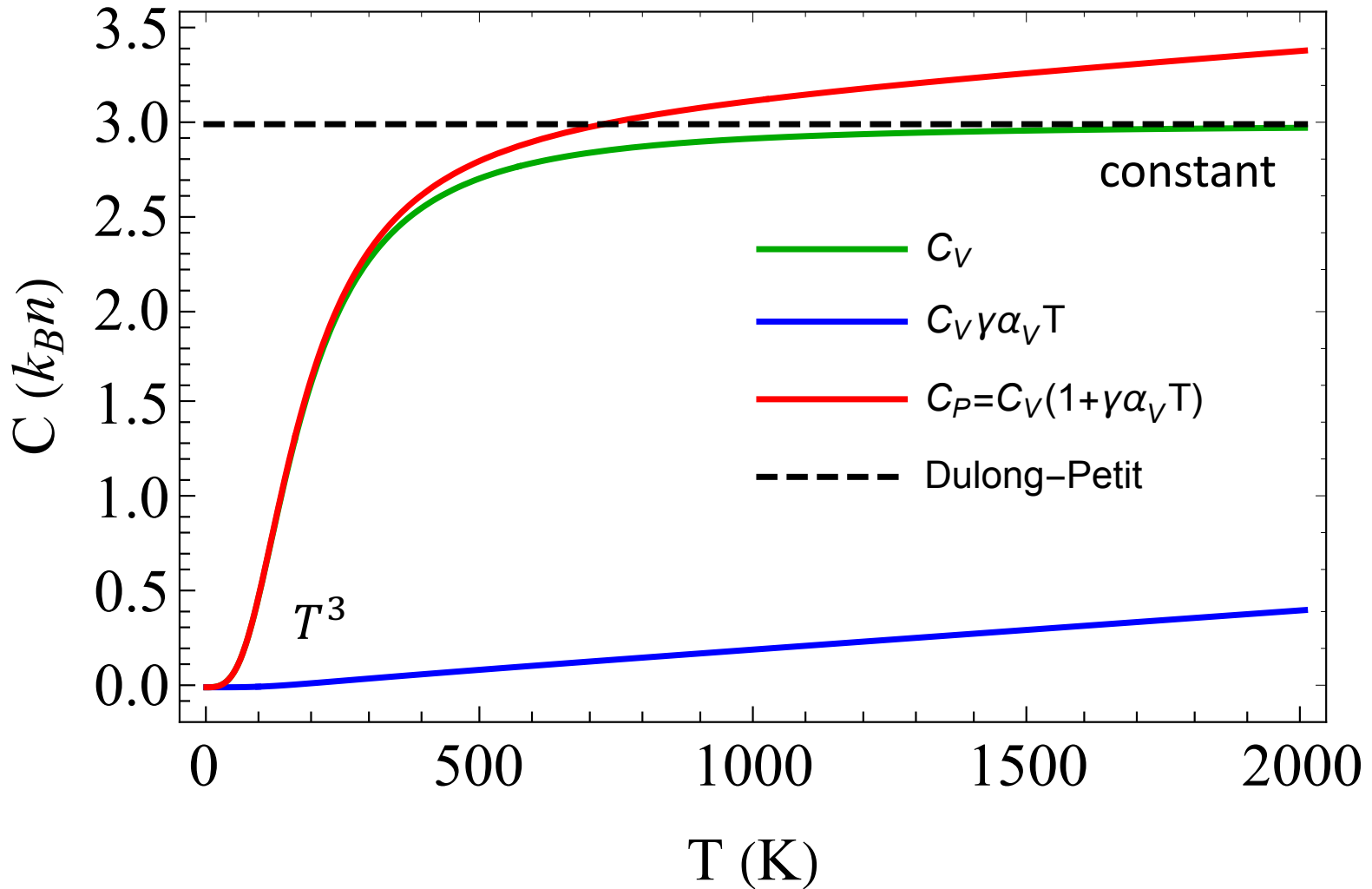
<http://rileyhanus.com/science.html>

1. General discussion about heat capacity
2. Obtain the phonon heat capacity
 - a) examine limiting behavior
 - b) low ω , high T, low T
3. Heat capacity in practice
 - a) Debye level
 - b) Debye temperature
 - c) Speed sound

Heat capacity

Heat capacity is generally a very boring material property.

Material	Volumetric heat capacity at 25 C C_V (J/K cm ³)
Liquid Hg	1.9
Liquid water	4.2
Cu	3.45
Glass	2.1
Al	2.4
Graphite	1.53
Diamond	1.8



n : number density of atoms

γ : Gruneisen parameter

α_V : volumetric thermal expansion ($\alpha_V \cong 3\alpha_L$)

Derivation set-up

Heat capacity is the change in energy with temperature

We will look for the *spectral* heat capacity *per unit volume*

$$C(\omega) = \frac{d E(\omega, T)}{dT}$$

$$\text{Energy density: } E(\omega, T) = \hbar\omega n(\omega, T)$$

$$\text{Number density of phonons: } n(\omega, T) = g(\omega) n_{\text{BE}}(\omega, T)$$

Note:

- $g(\omega)$ is the number of possible states per unit volume. Here, we say it doesn't change with temperature (i.e. the quasi-harmonic approximation). In reality things get softer with increasing temperature so $g(\omega)$ will shift down in ω as T increases.
- $n_{\text{BE}}(\omega, T)$ is the occupation number (can think of it as an occupation probability), of a state at frequency/energy ω , and temperature T .

$$\frac{d E(\omega, T)}{dT} = \hbar\omega g(\omega) \frac{d n_{\text{BE}}(\omega, T)}{dT}$$

Derivation

$$n_{\text{BE}} = \frac{1}{e^{\frac{\hbar\omega}{k_{\text{B}}T}} - 1}$$

Crazy triple chain rule

$$\frac{dn_{\text{BE}}}{dT} = \frac{(-1)}{\left(e^{\frac{\hbar\omega}{k_{\text{B}}T}} - 1\right)^2} \times e^{\frac{\hbar\omega}{k_{\text{B}}T}} \times \frac{(-1)\hbar\omega}{k_{\text{B}}T^2} = \frac{\hbar\omega}{k_{\text{B}}T^2} \frac{e^{\frac{\hbar\omega}{k_{\text{B}}T}}}{\left(e^{\frac{\hbar\omega}{k_{\text{B}}T}} - 1\right)^2}$$

$$C(\omega) = \hbar\omega g(\omega) \frac{dn_{\text{BE}}}{dT} = \hbar\omega \times \frac{3}{2\pi^2} \frac{\omega^2}{v_{\text{p}}^2 v_{\text{g}}} \times \frac{\hbar\omega}{k_{\text{B}}T^2} \frac{e^{\frac{\hbar\omega}{k_{\text{B}}T}}}{\left(e^{\frac{\hbar\omega}{k_{\text{B}}T}} - 1\right)^2}$$

$$C(\omega) = \frac{3}{2\pi^2} \frac{\omega^4}{v_{\text{g}} v_{\text{p}}^2} \frac{\hbar^2}{k_{\text{B}}T^2} \frac{e^{\hbar\omega/k_{\text{B}}T}}{\left(e^{\hbar\omega/k_{\text{B}}T} - 1\right)^2}$$

Heat capacity per volume

$$C = \int_0^{\omega_{\text{max}}} C(\omega) d\omega$$

Limiting behavior

Let's look at the low ω (and high T) behavior

$$C(\omega) = \frac{3}{2\pi^2} \frac{\omega^4}{v_g v_p^2} \frac{\hbar^2}{k_B T^2} \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2}$$

If I just plug in $\omega = 0$, $C(\omega) = 0/0$.

Not super helpful, what we really want is the limiting behavior.

Define: $x = \frac{\hbar\omega}{k_B T}$ Taylor expand e^x about $x = 0$. $e^x \approx 1 + x + \dots$

$$C(\omega) = \frac{3}{2\pi^2} \frac{\omega^4}{v_p^2 v_g} \frac{\hbar^2}{k_B T^2} \frac{(1)}{(1 + x - 1)^2} = \frac{3}{2\pi^2} \frac{\omega^4}{v_p^2 v_g} \frac{\hbar^2}{k_B T^2} \left(\frac{k_B T}{\hbar\omega}\right)^2 = k_B \frac{3}{2\pi^2} \frac{\omega^2}{v_p^2 v_g}$$

At high T and or low ω

$$C(\omega) = k_B g(\omega)$$

which means $C \rightarrow \text{cst}$ at high T

and $C(\omega) \propto \omega^2$ when the dispersion is linear

Limiting behavior

Let's look at **low** T behaviorConvenient to convert the integral to be over the dimensionless parameter x .

$$x = \frac{\hbar\omega}{k_B T}$$

$$d\omega = \frac{k_B T dx}{\hbar}$$

$$x_{\max} = \frac{\hbar\omega_{\max}}{k_B T}$$

$$C = \frac{3}{2\pi^2} \frac{\hbar^2}{k_B T^2} \int_0^{\omega_{\max}} \frac{\omega^4}{v_g v_p^2} \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} d\omega$$

$$C = \frac{3}{2\pi^2} \frac{k_B^4 T^3}{\hbar^3} \int_0^{x_{\max}} \frac{x^4}{v_g v_p^2} \frac{e^x}{(e^x - 1)^2} dx$$

At low T :

1. only low frequency modes are populated, $v_g = v_p = v_s$
2. $x_{\max} \rightarrow \infty$

$$\int_0^{\infty} \frac{x^4 e^x}{(e^x - 1)^2} dx = \frac{4\pi^4}{15}$$

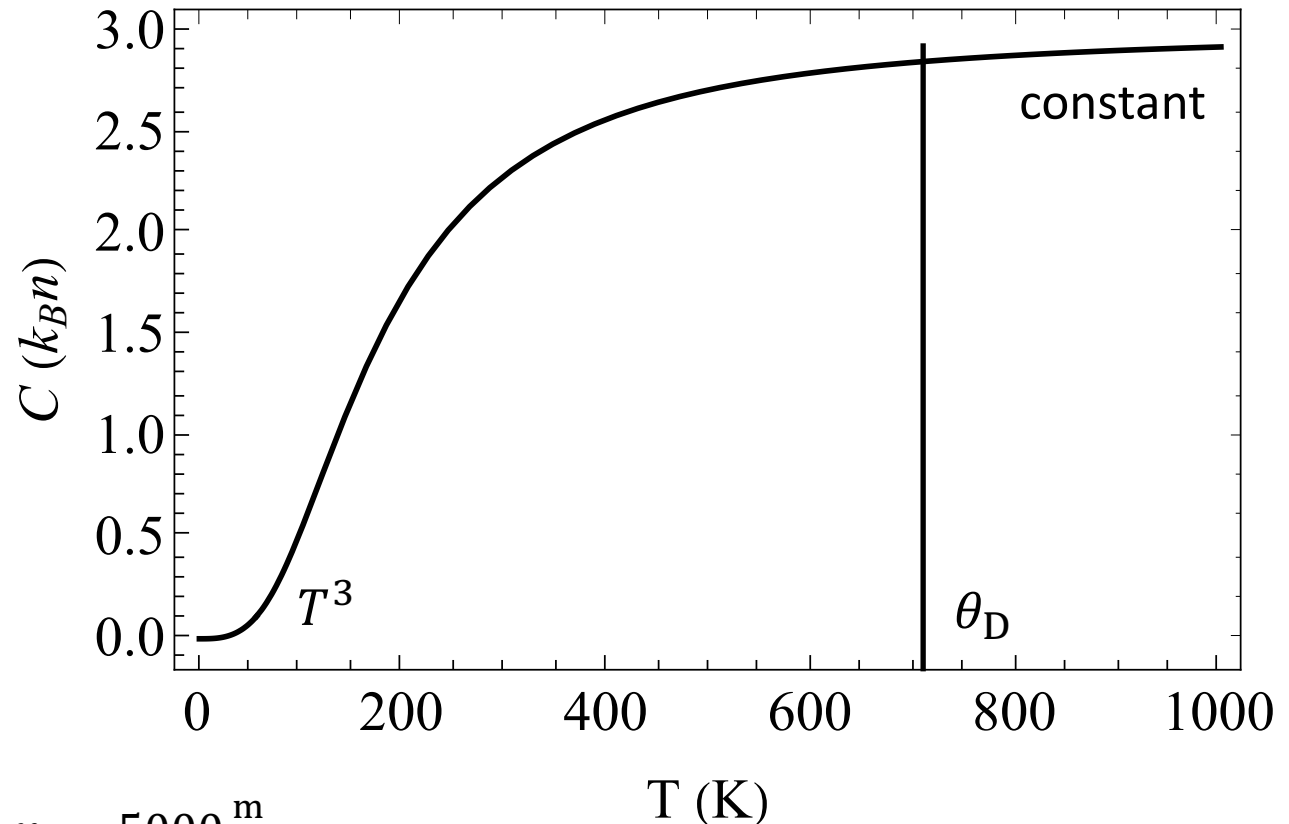
$$C = \frac{3}{2\pi^2} \frac{k_B^4 T^3}{\hbar^3} \left(\frac{4\pi^4}{v_s^3 15} \right)$$

At low T
where dispersion is linear:

$$C \propto T^3$$

Example model

$$C = \frac{3}{2\pi^2} \frac{\hbar^2}{k_B T^2 v_s^3} \int_0^{\omega_{\max}} \frac{\omega^4 e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} d\omega$$



speed of sound:

$$v_s = 5000 \frac{\text{m}}{\text{s}}$$

volume per atom:

$$V_{\text{at}} = \frac{V_{\text{UC}}}{N_{\text{at}}} = 9 \text{ \AA}^3 \quad (V_{\text{UC}}: \text{volume of unit cell}, N_{\text{at}}: \text{\# atoms in unit cell})$$

max k-vector (isotropic):

$$k_{\text{max}} = \left(\frac{6\pi^2}{V_{\text{at}}} \right)^{1/3} = 1.87 \text{ \AA}^{-1}$$

Debye frequency:

$$\omega_D = \omega_{\text{max}} = v_s k_{\text{max}} = 93.7 \text{ THz}$$

Debye temperature:

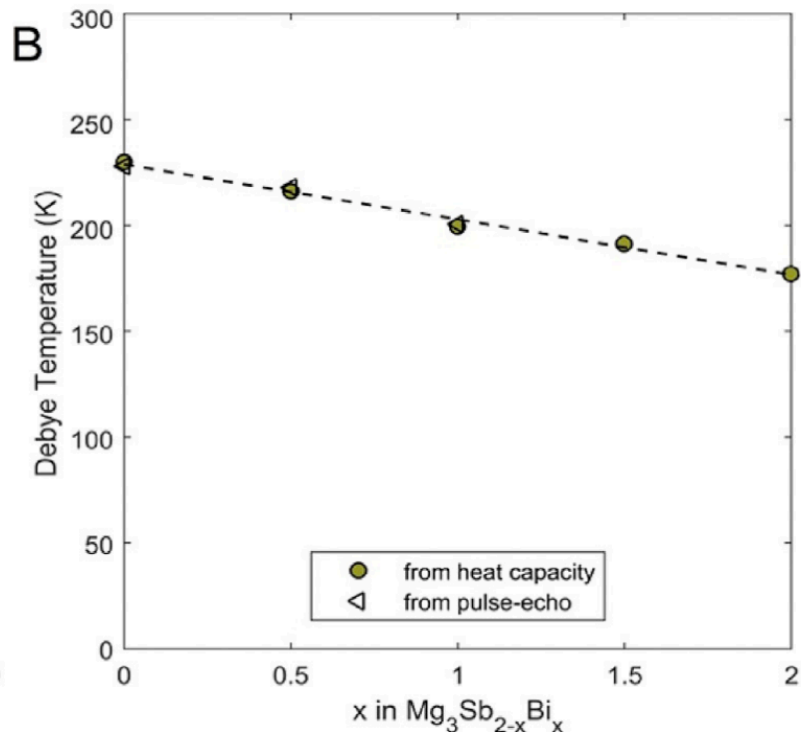
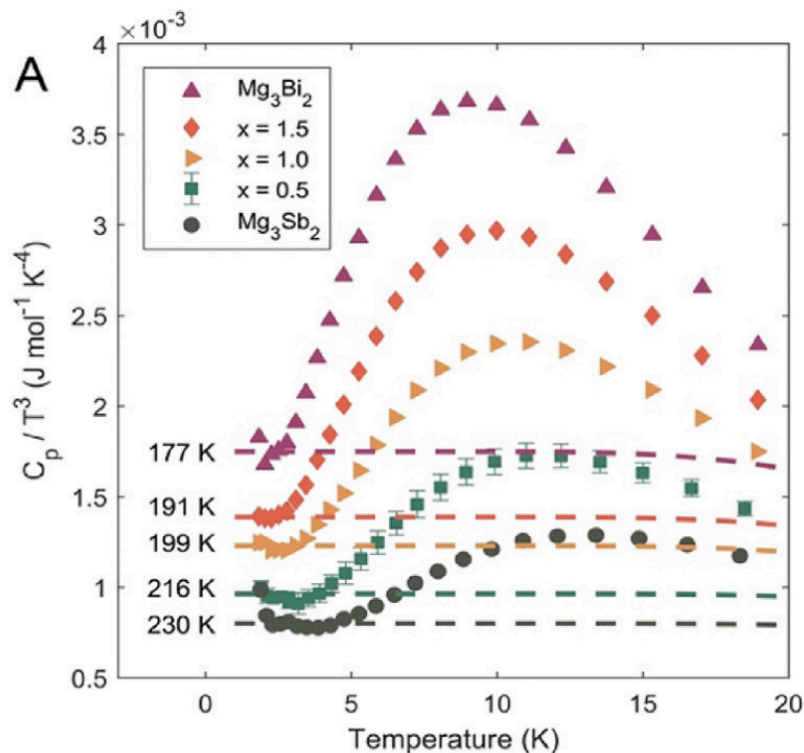
$$k_B \theta_D = \hbar \omega_D \quad \theta_D = 715 \text{ K}$$

Analyzing low-T data

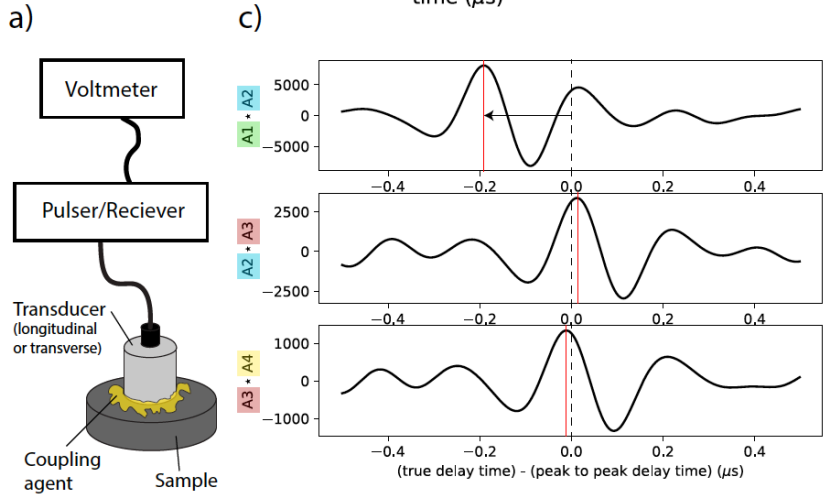
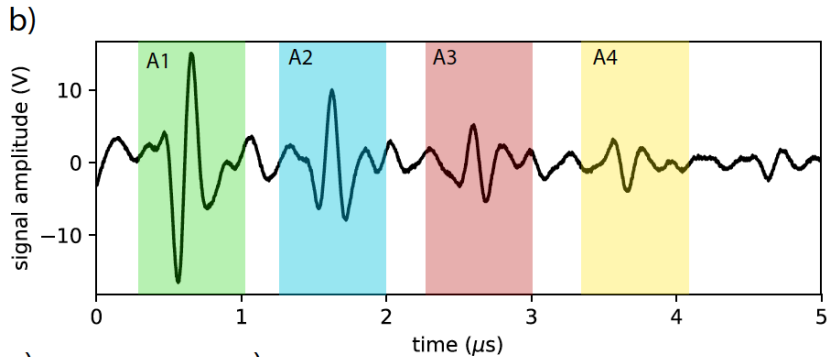
$$C = \frac{3}{2\pi^2} \frac{k_B^4 T^3}{\hbar^3} \left(\frac{4\pi^4}{v_S^3 15} \right)$$

$$\frac{C}{T^3} = \left(\frac{2}{5} \right) \frac{\pi^2 k_B^4}{\hbar^3 v_S^3} = \beta \xrightarrow{\text{good exercise}} \theta_D = \left(\frac{12\pi^4 n k_B}{5 \beta} \right)^{1/3}$$

$n = \frac{1}{V_{\text{at}}}$: number density of atoms



Speed of sound

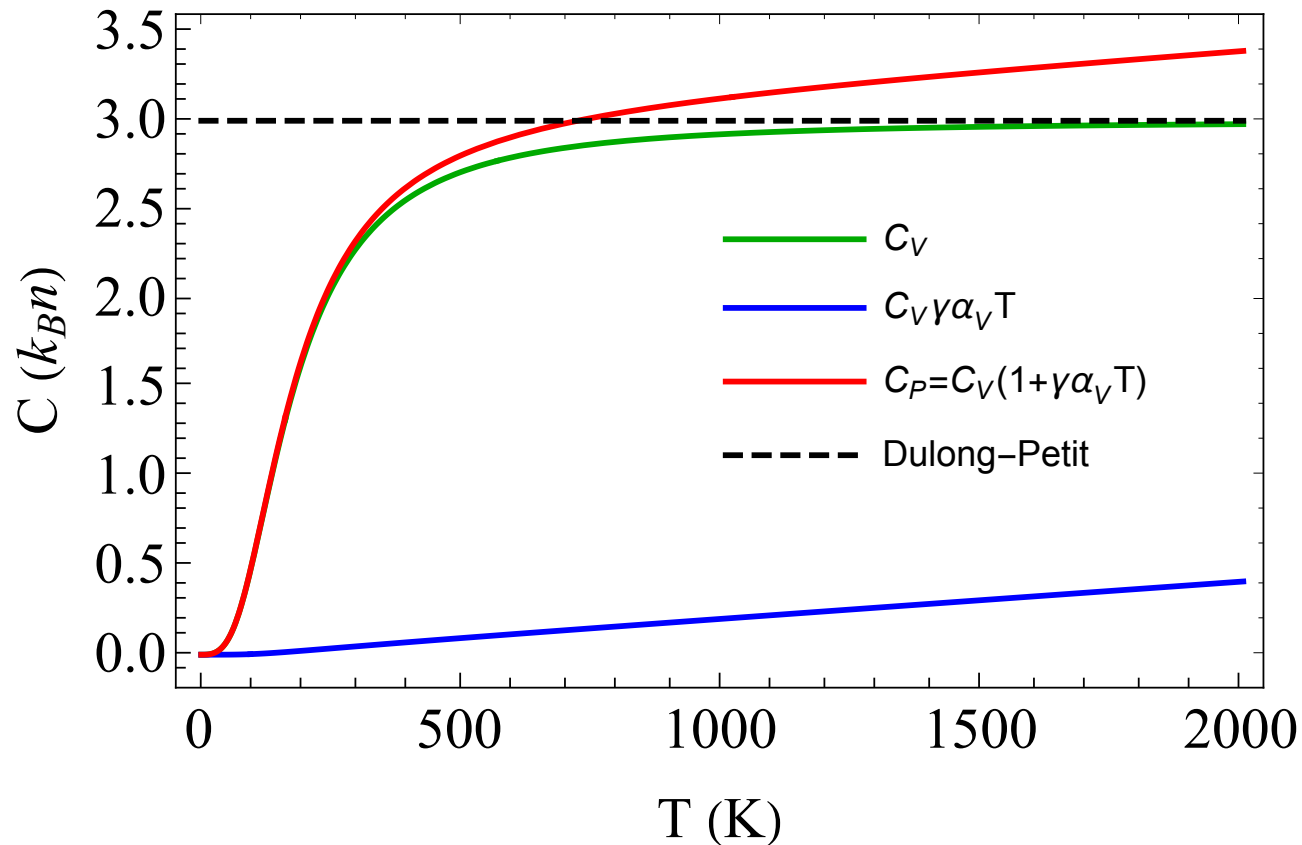


- When the cross-correlation is used to measure the time delay, the error is typically limited by the thickness variation of the sample. Can get better than 1% accuracy, if careful.
- If sample is a randomly oriented polycrystalline, then you are measuring the isotropic average longitudinal and transverse speeds of sound.
- Be mindful of preferred orientation of grains, especially for non-cubic materials.
- Be mindful of sample density. Samples should be very dense, >98%.

The isotropic average speed of sound, used for thermal conductivity modeling, heat capacity modeling, Debye temperature.

$$v_s = \left(\frac{1}{3} \left[\frac{1}{v_L^3} + \frac{2}{v_T^3} \right] \right)^{-1/3}$$

Thermal expansion contribution



n : number density of atoms

$\gamma = B\alpha_V/C_V$: Gruneisen parameter

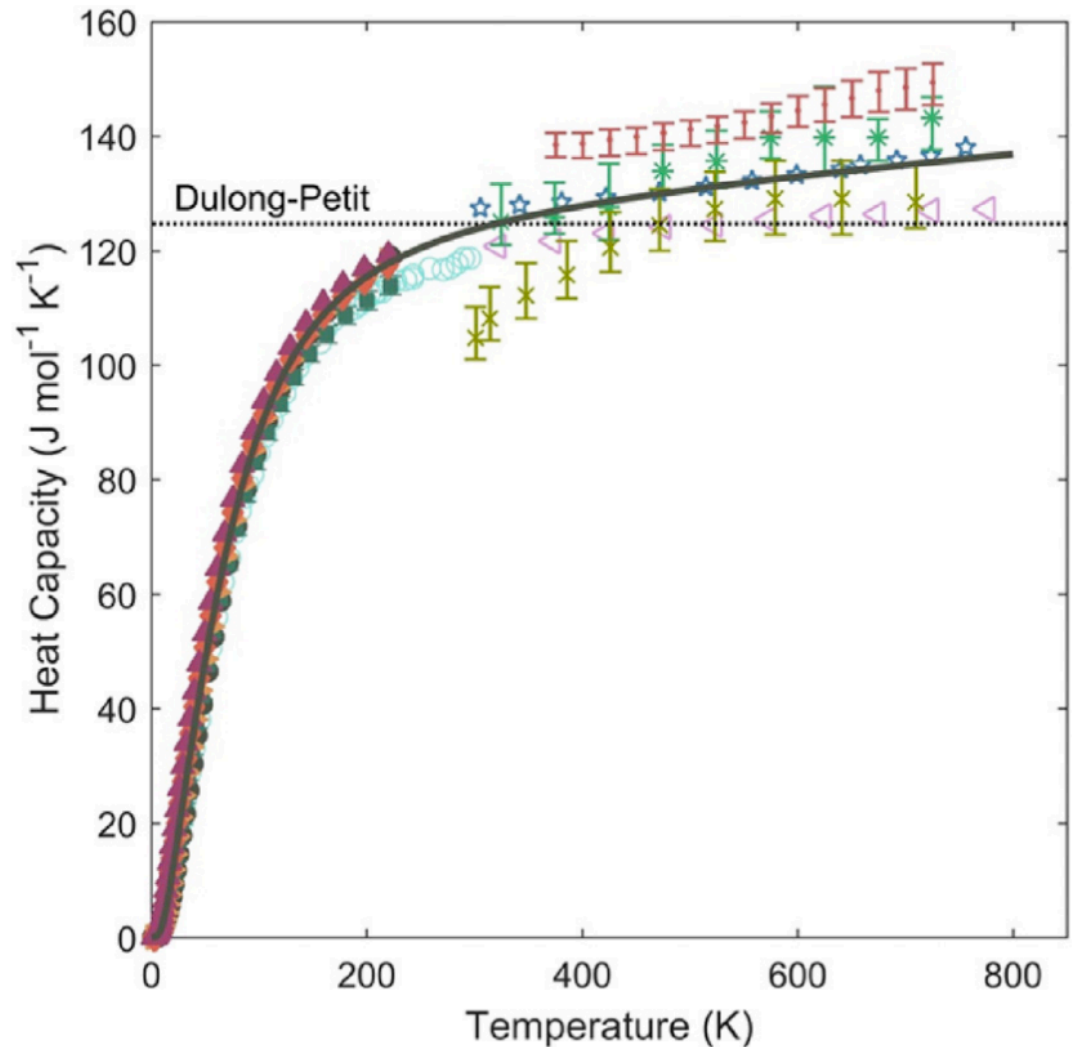
B : isothermal Bulk modulus

α_V : volumetric thermal expansion ($\alpha_V \cong 3\alpha_L$)

$$C_p = C_V(1 + \gamma \alpha_V T)$$

Analyzing high-T data

- Absolute value of high temperature heat capacity is notoriously hard to measure.
- In contrast low-temperature heat capacity can be very accurate (e.g. physical property measurement system [PPMS](#) in heat capacity mode).
- Often times our models are better at predicting it than one given measurement is.
- The slope of Heat Capacity vs. T at high T can be reasonably accurate.



Thermal conductivity considerations

Modeling:

$$\kappa = \int C(\omega) D(\omega) d\omega$$

$$D(\omega) = \frac{1}{3} v_g^2(\omega) \tau(\omega)$$

$C(\omega)$: spectral heat capacity per unit volume

$D(\omega)$: spectral diffusivity

Experiment:

$$\kappa = C_V D = C_P \rho D$$

D : thermal diffusivity measured by, for example LFA

C_V : heat capacity per unit volume

C_P : heat capacity per unit mass

ρ : mass density

$$C_V = \int C(\omega) d\omega$$

$$D = \frac{\int C(\omega) D(\omega) d\omega}{\int C(\omega) d\omega}$$

Heat capacity weighted average diffusivity

$$\kappa = \left(\int C(\omega) d\omega \right) \frac{\int C(\omega) D(\omega) d\omega}{\left(\int C(\omega) d\omega \right)} = \int C(\omega) D(\omega) d\omega$$