Second sound driven by a modulated temperature field

Luciano Colombo

Department of physics – University of Cagliari (Italy)

A talk based on:

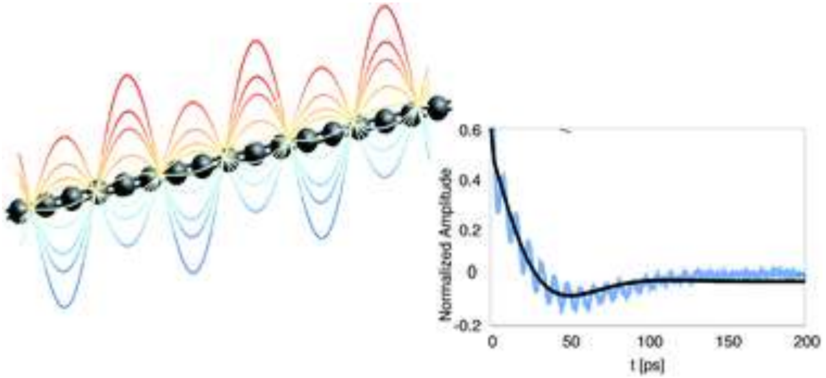
Sci. Adv. **7** (27) eabg4677 (2021)

Phys. Chem. Chem. Phys. **35**, 15275 (2021)

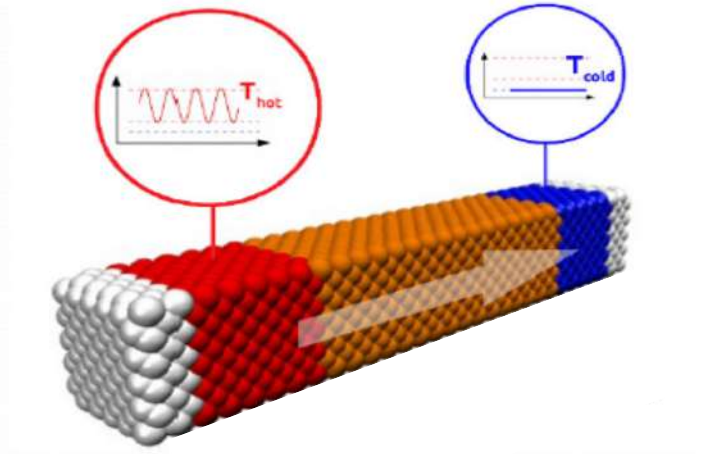
Outline

- Second sound: A synopsis
  - conceptual framework and definitions
  - basic theory

- Second sound generated by a **space-periodic thermal excitation**
  - this talk: **molecular dynamics simulations** exploiting a gedanken-experiment on **1D cumulene @ room temperature** inspired by real laser-induced transient thermal gratings measurements on bulk graphite



- Second sound generated by a **time-periodic thermal excitation**
  - this talk: **molecular dynamics simulations inspired by** laboratory evidence in **bulk germanium @ room temperature** as observed by frequency-domain optical reflectance pump-and-probe experiment



Second sound: a synopsis

- Conceptual framework and definitions

  - **second-sound**: spatio-temporal propagation of the temperature field in the form of **waves**

    Memo: «first sound» is ordinary acoustic sound, driven by mechanical lattice waves

  - fingerprint of a possible heat transport **beyond Fourier** regime (**anomalous** thermal transport)

    Fourier eqn.

    $$\vec{J} = -\,\kappa\,\vec{\nabla}T$$

    - **good** for describing steady-state heat transport in bulk materials
    - **questionable reliability** for low-dimensional systems (infinitely-long ranged ballistic transport, that is: **divergent thermal conductivity**!)
    - **unsuitable** for non a steady-state regime

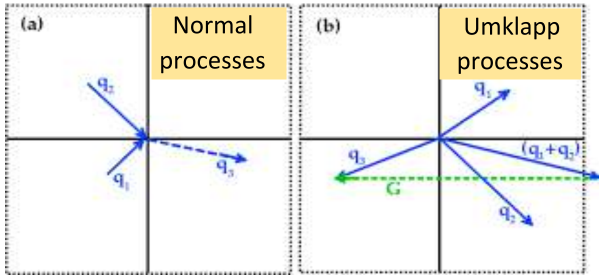
    • Nat. Commun. **5**, 1 (2014)
    • Phys. Rev. B **87**, 125424 (2013)
    • Phys. Rev. Mater. **2**, 015603 (2018)

  - many ongoing efforts aimed at unravellig (i) the physical properties of thermal waves (ii) the conditions for their observation

    • Rev. Mod. Phys. **84**, 1045–1066 (2012)
    • Nature **503**, 209–217 (2013)
    • Appl. Phys. Rev. **1**, 011305 (2014)
    • Phys. Rev. Lett. **125**, 265901 (2020)

More on anomalous behaviors

- Different thermal transport regimes explained by the dominance of **different phonon scattering mechanisms**

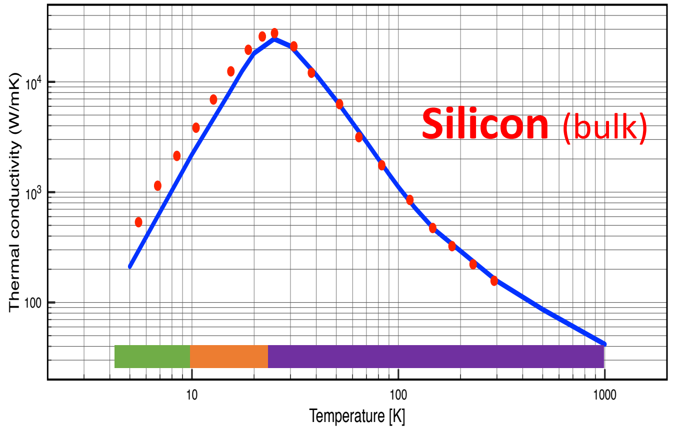


Brillouin zone   Brillouin zone

Total momentum is **conserved** in **normal N processes**
Total momentum **is not conserved in resistive R processes**

more specifically: boundary **B** scattering
Umklapp **U** scattering
defect **D** scattering

- **Thermal transport regimes**:



ballistic transport	when B ≫ N or U
hydrodynamic	when N ≫ B ≫ U ←
diffusive (or kinetic)	when U ≫ N or B

- **Second sound**: a hydrodynamic transport regime

$N \gg B \gg U$ dominance of momentum conserving phonon scattering with respect to resistive scattering is the **key physcal mechanism**

  - N-processes preserve the heat flux **creating a correlation among phonons**
  - **collective phonon-excitation** are thus generated
  - phonons can develop a **nonzero drift velocity** when subjected to a temperature gradient

    (very much like the viscous flow of a fluid driven by a pressure gradient)
  - **heat propagates as a wave** ⟶ **second sound**
  - **thermal waves eventually dampened** on longer timescales by the resistive processes

- **Second sound**: a fascinating, but elusive phenomenon

  - hard to detect experimentally since the typical experimental observation time τ_{expt} must be
    - **longer** than normal phonon scattering times τ_N allows for momentum redistribution
    - **shorter** than resistive phonon scattering times τ_R prevents phonons to decay into equilibrium distribution *(thermal waves)*

$$\tau_N < \tau_{expt} < \tau_R$$

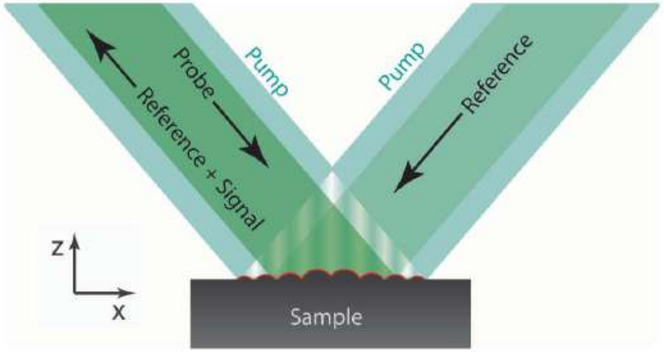
  - this makes the **use of conventional thermal sensors unsuitable**
  - better strategy: **looking for second sound occurring in «modulated phenomena»**

- **Second sound**: experimental setups that inspired this MD investigations (outline)

Laser-induced transient thermal gratings (TTG) - **space-modulated temperature field**

- two crossing laser pulses focused on the system surface
- thermal expansion gives rise to a surface modulation
- **transient decay of the amplitude of the temperature profile** sampled *via* diffraction of a probe laser beam
- **System**: graphite @ T>100K

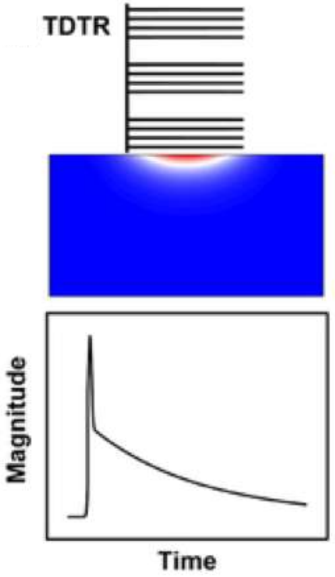
Science **364**, 375 (2019)



Time domain thermo-reflectance (TDTRR) – **time-modulated temperature field**

- time-modulated laser pulses used to heat the system surface
- induced variation of the surface temperature
- corresponding change in reflectivity measured by a probe laser
- temperature change @ surface detected as phase lag between pump and probe
- **System**: bulk Ge @ T=300K

Science Advances **7,** eabg4677 (2021)



Picture taken from:
J. Appl. Phys. **126**, 150901 (2019)

Second sound: basic theory

- Simplest equation describing **wave-like heat transport**

$$\tau_{ss}\frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} - \alpha\nabla^2 T = \frac{1}{\rho C}\left[S(\vec{r},t) + \tau_{ss}\frac{\partial S(\vec{r},t)}{\partial t}\right]$$

α:	**thermal diffusivity**
τ_{ss} :	**thermal relaxation time**
ρ:	**mass density**
C:	**specific heat**
$S(\vec{r},t)$:	**external power heat source**

Maxwell-Cattaneo-Vernotte eqn.

- describes the **propagation of a temperature wave with a damping term** given by $\partial T/\partial t$ and a **propagation velocity** v_{ss} = $(\alpha/\tau_{ss})^{1/2}$
- describes the **delayed response** between temperature gradient and heat flux
- describes **different heat transport regimes** depending on the time-/space-length scales under

- Key to unlock the different regimes: the **thermal inertial term** $\tau_{ss}\frac{\partial^2 T}{\partial t^2}$

if large enough, **the temperature field exhibits a wave-like behavior**

Second sound generated by a space-periodic temperature profile

- Limitations of present TTG experiments
  - **reduced spatial resolution** limiting TTG technique to spatial periods lower than a few mm
  - **reduced time-resolution ~ns** limiting the frequencies of the detectable second sound signal to just a few GHz

- Limitations even more severe when dealing with 1D materials
  - 1D systems worth of investigation thermal conductivity $\kappa(L)$ could eventually diverge for $L \rightarrow \infty$
  - 1D systems ideal test cases for better understanding the condition for the non-validity of the Fourier law

- This work: **cumulene** prototypical 1D system - highest lattice thermal conductivity - negligible electronic contribution

carbine isomers

cumulene

single-bond sequence
stable up to 499K

polyyne

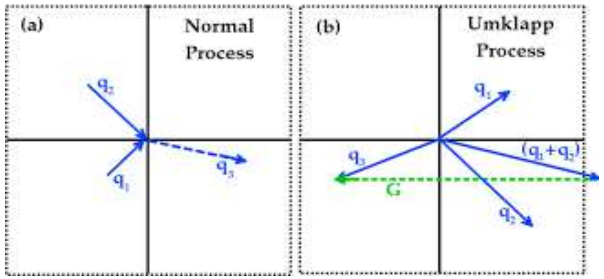
- *«Thermal Transport in Carbon-Based Nanomaterials»* (Elsevier, 2017)
- *«Carbyne and Carbynoid Structures»* (Springer Science, 1999)
- J. Phys. Chem. C, **119**, 21605 (2015)
- J. Phys. Chem. C, **119,** 24156 (2015)

- **Our goal** — cumulene as a **molecular dynamics** Gedanken experiment **inspired to TTG** to identify critical features for **observing second sound**

Memo: phonon momentum conservation is the key factor for the anomalous behaviour

- **Need a predictive theory**
  - good description of harmonic prts — phonon frequencies and group velocities
  - good description of anharmonic prts. — phonon scattering rates and lifetimes

need to **reproduce accurately phonon dispersion relations** throughout the full BZ to mimic the actual momentum and energy conservation conditions associated with each scattering event



CLASS II force field $E_{total} = E_b + E_\theta + E_{b,b'} + E_{vdW}$

valence terms:

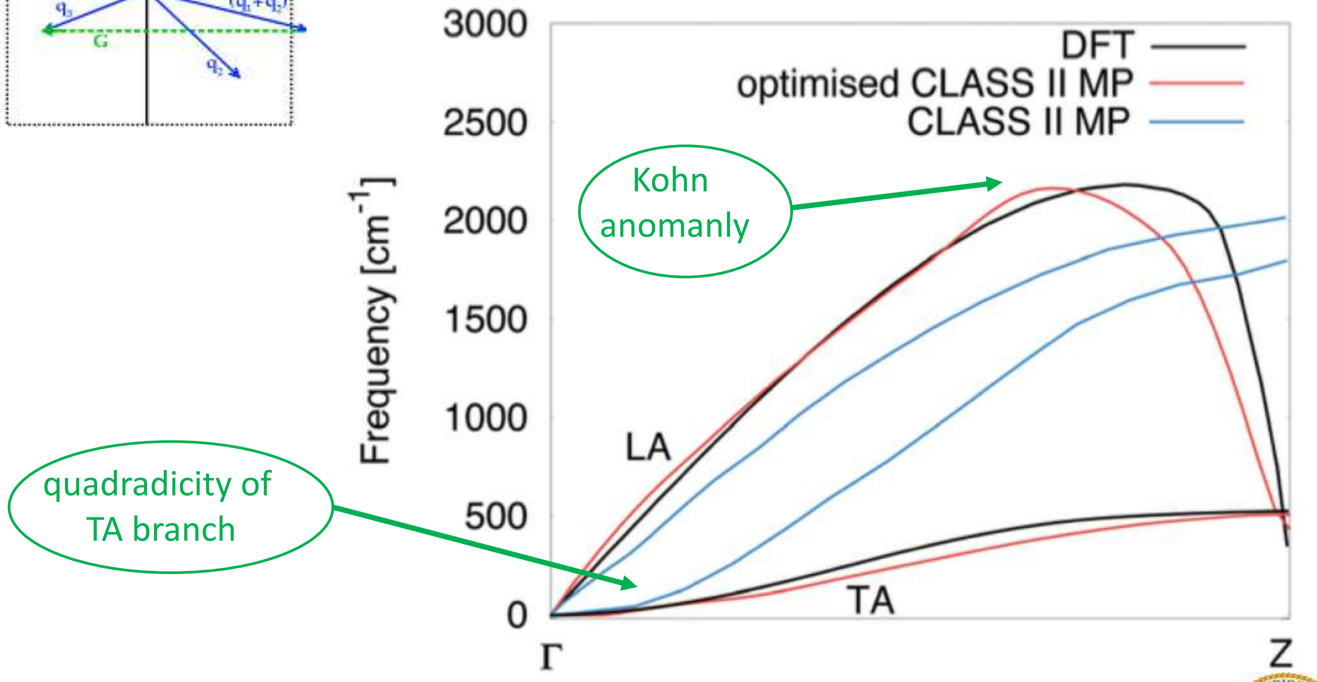
$$E_b = \sum_b k_{b1}(b-b_{eq})^2 + k_{b2}(b-b_{eq})^3 + k_{b3}(b-b_{eq})^4$$

$$E_\theta = \sum_\theta k_{\theta 1}(\theta-\theta_{eq})^2 + k_{\theta 2}(\theta-\theta_{eq})^3 + k_{\theta 3}(\theta-\theta_{eq})^4$$

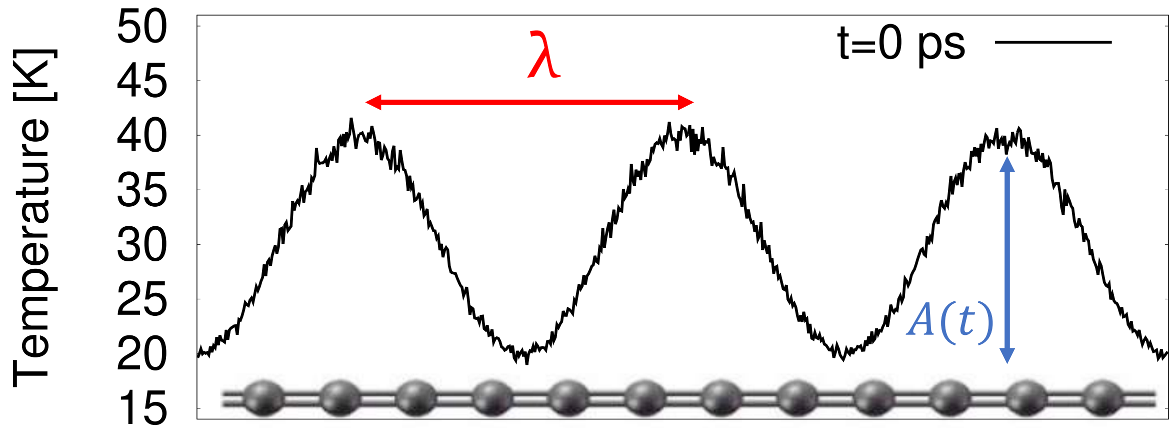
$$E_{b,b'} = \sum_{b,b'} k_{b,b'}(b-b_{eq})(b'-b'_{eq})$$ ← Kohn anomaly

non-bonding term:

$$E_{vdW} = \sum_{i<j} 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$



- Simulation protocol of the **MD gedanken experiment**



Step 1: modulated temperature field imposed

$$T(x,t) = T_0 - A_0 \cos(qx)$$

$q = 2\pi/\lambda$	wave vector
λ	space period
A_0	initial profile amplitude = 10.0 K
T_0	average temperature

white thermostatting:
- system divided in segments (PBC adopted)
- all vibrational modes excited by a Langevin thermostat at a local temperature value
- local temperature varied periodically along the chain

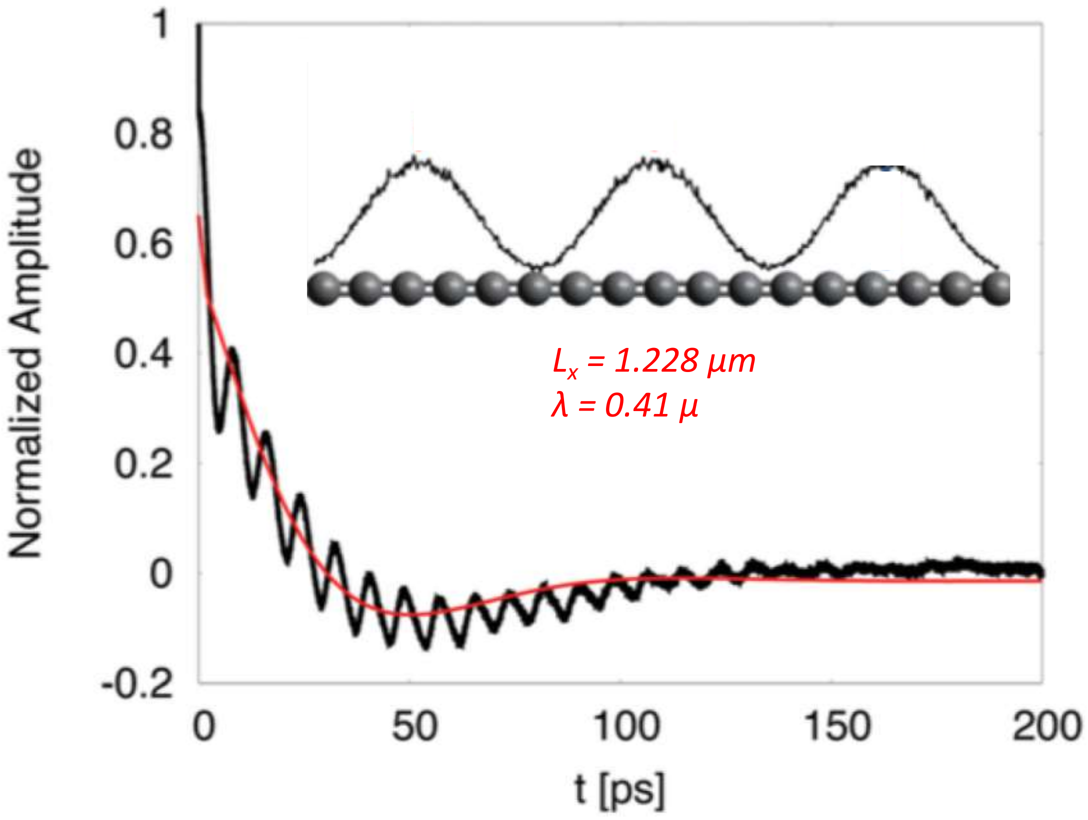
Step 2: removal of Langevin thermostats

Step 3: transient relaxation of the cumulene chain monitored

Time evolution of **amplitude** $A(t)$
temperature field $T(x,t)$

- very small time resolution (10 ps)
- microcanonical run

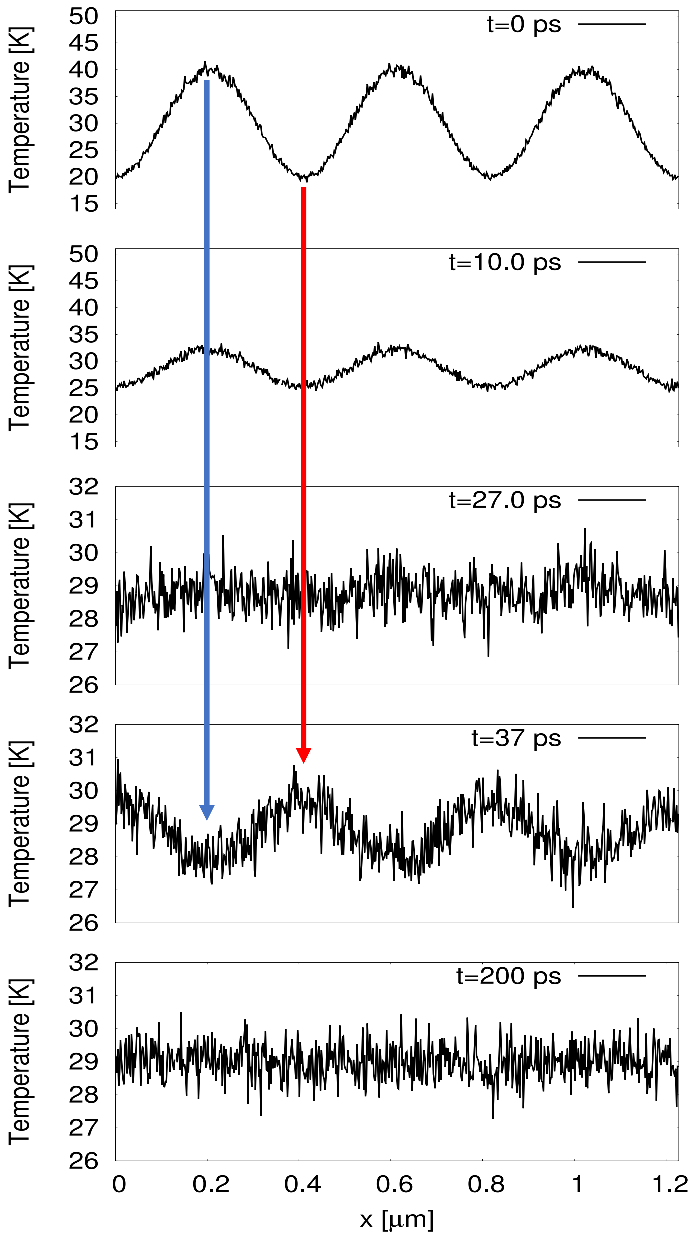
- Very intense computational burden
  - a number $40 < N < 1600$ atomic trajectories used to average statistical fluctuations
  - several space periodicity investigated: λ = 0.0409, 0.409, 4.090, 40.90 μm
  - system length set at: $L_x = 3\lambda$
  - number of atoms: 10^3, 10^4, 10^5, 10^6



- Key features
  - plot of the normalized amplitude $A(t)/A_0$
  - dumped oscillations
  - **sign flip after ~ 27 ps**

↓

space phase of the initial sinusoidal T-profile shifted by π

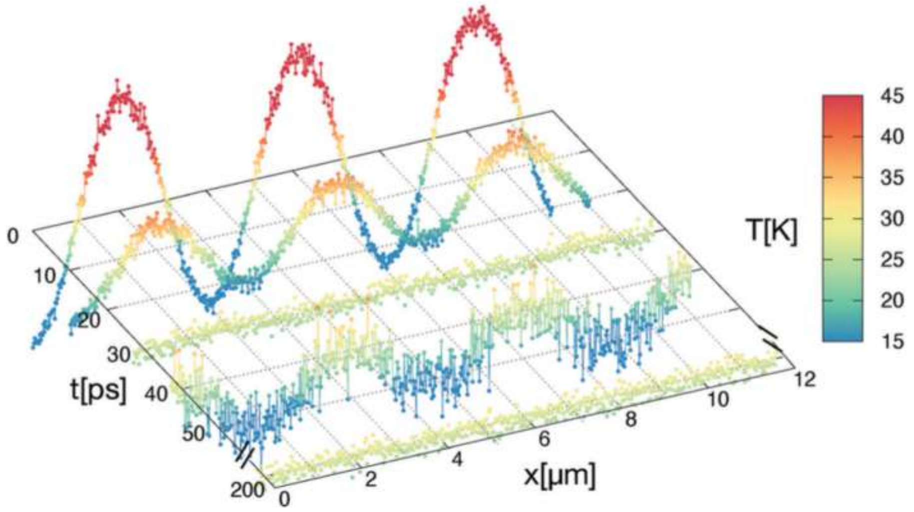


Local temperature maxima converted into minima (and *vice versa*)

This is the fingerprint of a wave-like propagation

Science **364**, 375 (2019)

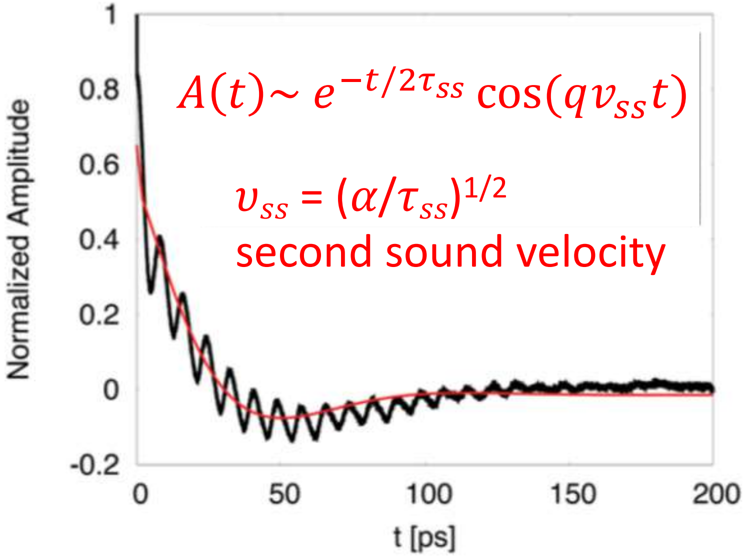
In the **diffusive regime** maxima and minima **could not switch** just because the heat moves only from hotter to colder regions



Specific form of the Maxwell-Vernotte-Cattaneo eqn.

$$\tau_{ss}\frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} - \alpha\nabla^2 T = 0$$

Its solution for the 1D case with PBC →



λ (μm)	T (K)	v_{ss}(Km/s)	τ_{ss} (ps)
4.090	30	2.47±0.18	75.87±11
4.090	300	3.23±0.23	138.37±23
0.404	30	2.74±0.31	14.2±8
0.404	300	3.54±0.43	18.2±9

- Increase of v_{ss} and τ_{ss} with temperature as observed also in graphene
  Nature communications **6**, 6290 (2015)
  Nature communications **6**, 1 (2015)
- v_{ss} marginally affected by space period
- v_{ss} much lower than sound speed (~36 Km/s)

An independent check
Phys. Rev. B **2**, 1193 (1970)

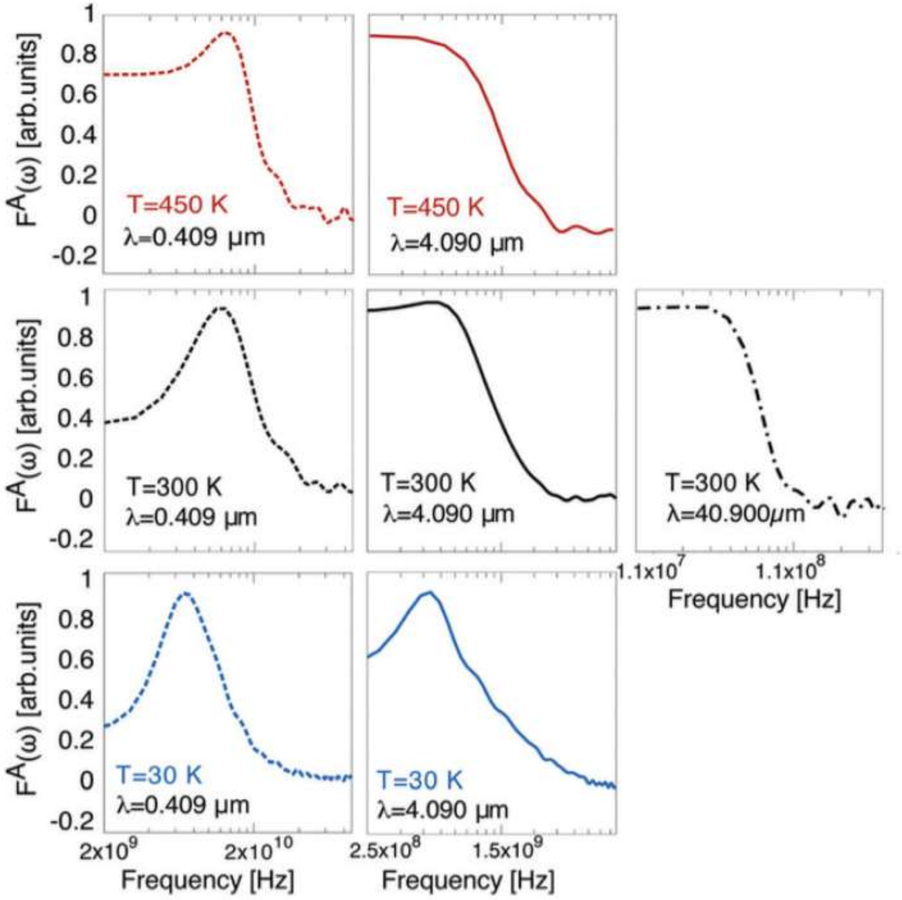
$$(v_{ss})^2 = (C_0 V^{-1})\sum_k \frac{dn_{k,0}^{(eq)}}{dT_0}\hbar\omega_k \frac{1}{3} v_k \cdot v_k$$

v_{ss}=2.538 Km/s

• Hydrodynamic-to-diffusive transition

- **tool**: calculate the Fourier transform $F^A(\omega)$ of time-dependent $A(t)$
  three temperatures 30K, 300K, 450K
  three space periods λ=0.404 μm , λ=4.090 μm , λ=40.900 μm

second sound peak



- found a second-sound peak at ~0.6 GHz like in graphite

  Science **364**, 375 (2019)

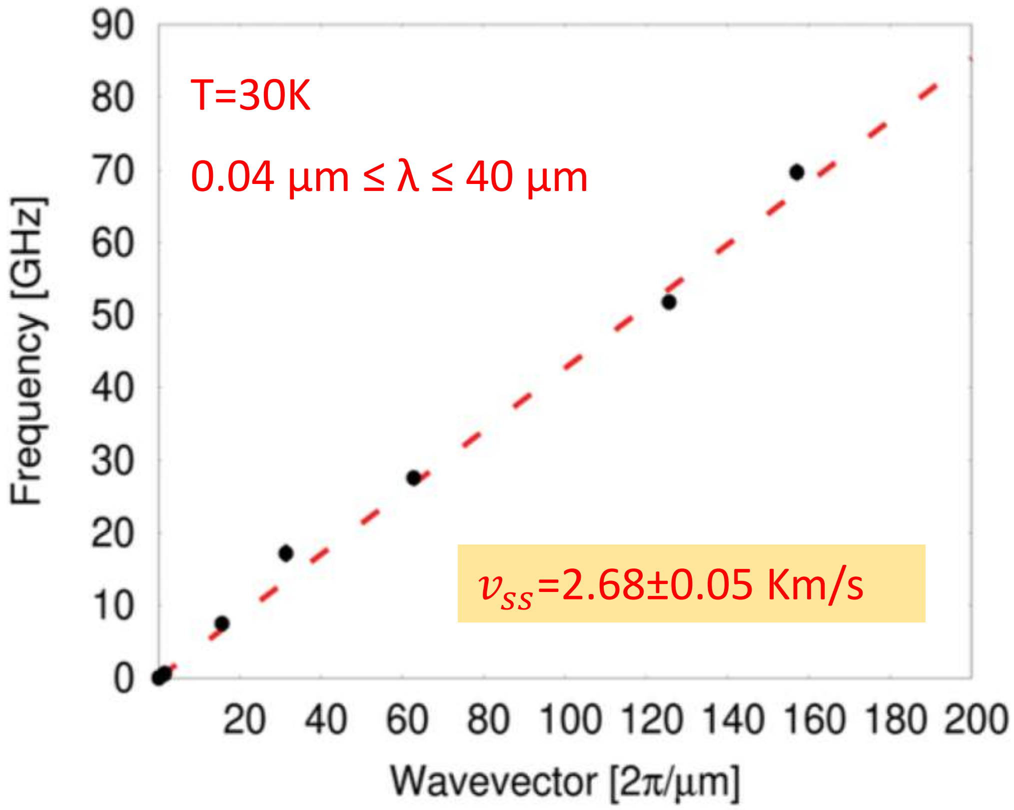
- second-sound peak largely affected by increasing temperature

- at large-T values $F^A(\omega) \sim \frac{a}{a^2+\omega^2}$ ⟶ Fourier transform of $e^{\alpha t}$

  simple exponential decay of a
  purely diffusive transport regime

- **second sound** occurs **in cumulene at T = 300 K** for a **suitably short modulation** of the initial temperature profile

- From peak frequency to velocity



Excellent agreement for v_{ss} @ 30K with previously estimated second sound velocity

1. Fitting $A(t)$

λ (μm)	T (K)	v_{ss}(Km/s)	τ_{ss} (ps)
4.090	30	2.47±0.18	75.87±11
4.090	300	3.23±0.23	138.37±23
0.404	30	2.74±0.31	14.2±8
0.404	300	3.54±0.43	18.2±9

2. Solving the kinetic eqn.

$$(v_{ss})^2 = (C_0 V^{-1}) \sum_k \frac{dn_{k,0}^{(eq)}}{dT_0} \hbar\omega_k \frac{1}{3} v_k \cdot v_k$$

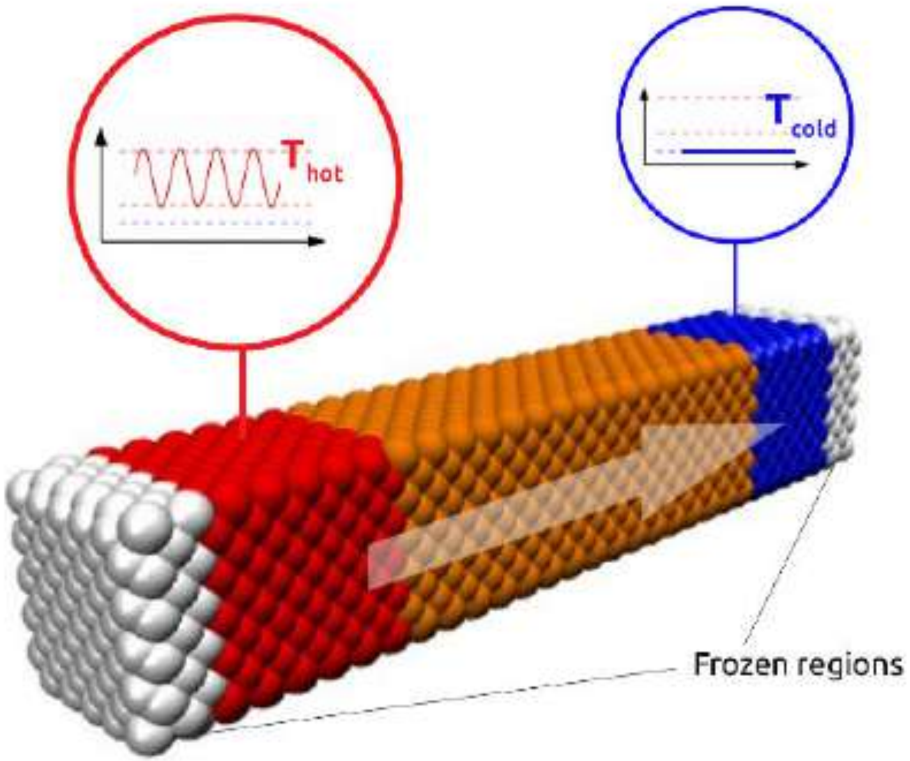
v_{ss}=2.538 Km/s

Second sound generated by a time-periodic temperature profile

- A simulation protocol mimicking a TDTR measurement
  - a Ge sample at first **ketp under thermal bias @ T_{ave}=300K** by NEMD for 2 ns
  - Tersoff force field
  - Nosé-Hoover thermostatting (no simulation of the light-matter interaction)

- Oscillatory heat flux imposted
  - hot thermostat temperature varied as $T_{hot}(t) = T_0 + \Delta T \sin(\nu t)$
  - ΔT=90K and 70 $MHz \leq \nu \leq$ 30 GHz choosen so to assure heat flux from hot to cold thermostat ⟶ **inward heat flux condition**
  - Data accumutated over 20+ ciclyes

- Heat flux vs. local temperature
  - time derivative of the work performed by the hot thermostat $W_{AC}(t)$
  - no need to implement a microscopic formulation of the heat flux



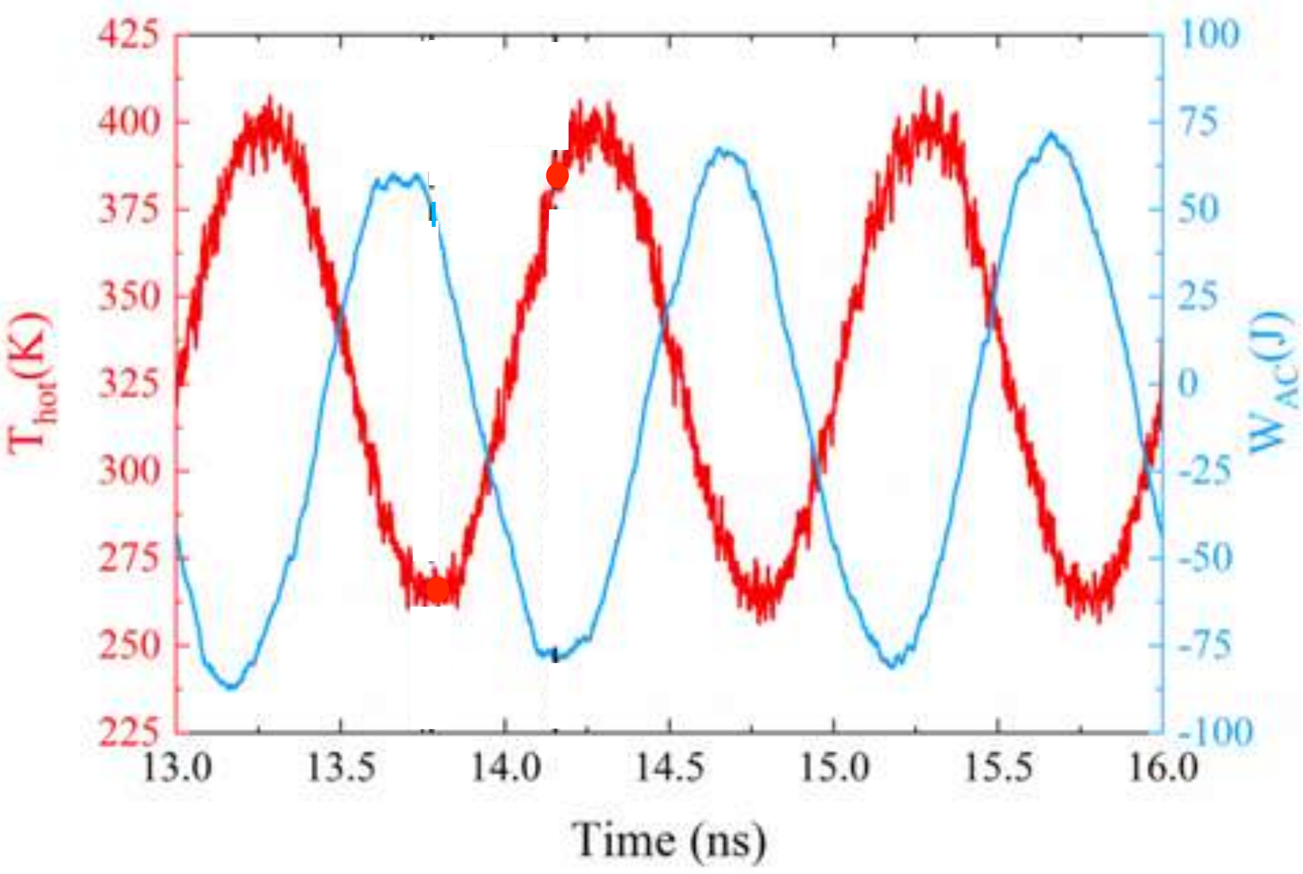
Indeed a **very critical** issue: Phys. Rev. B 92 094301 (2025)

• The temperature field calculated along the sample

time variation of the temperature @ z=0

thermostat work

$\upsilon = 1GHz$



Temperature and work fitted by

$$T(z=0,t) = T_0 + \Delta T \sin(\nu t)$$

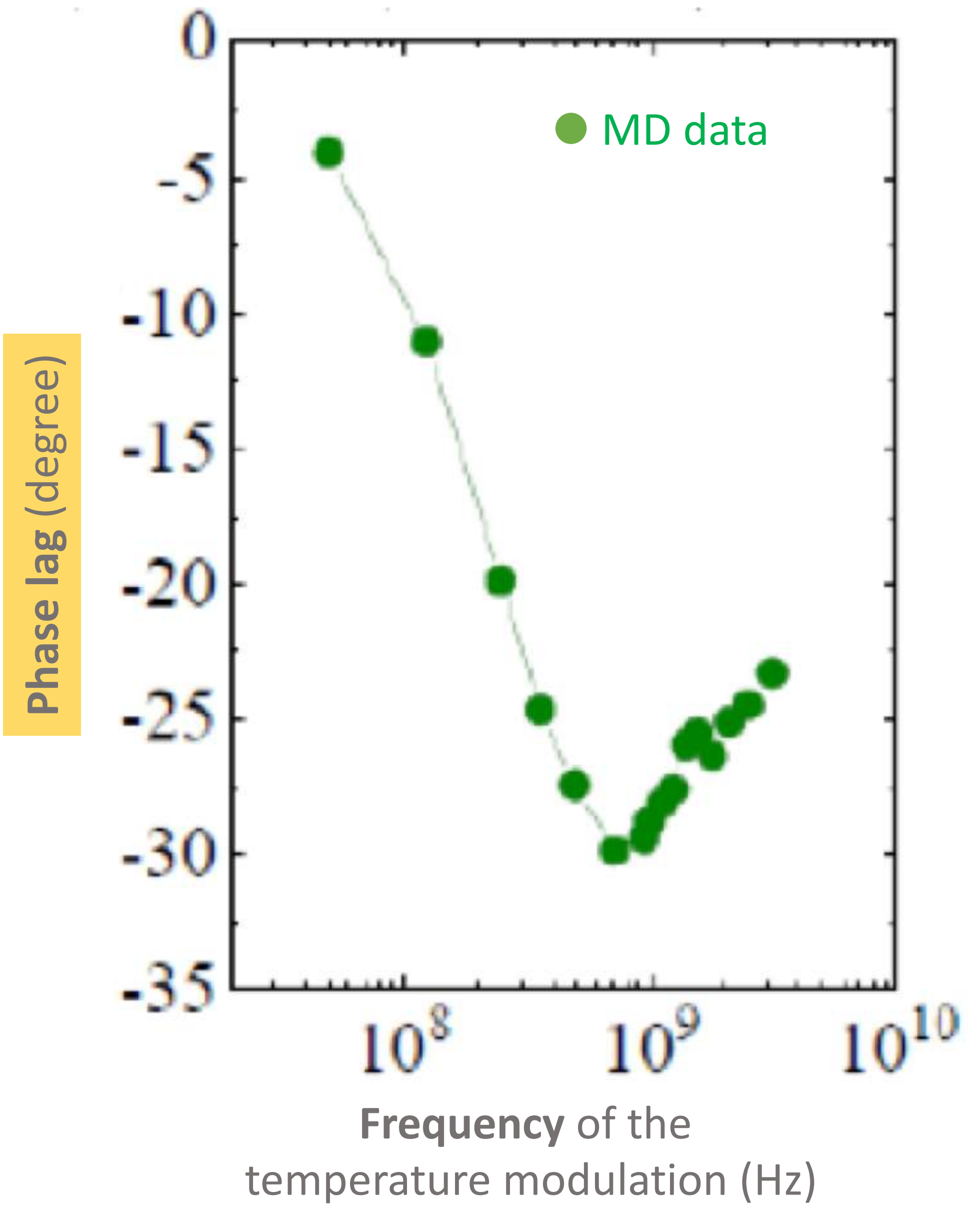
$$W(t) = W_0 + \sin(\nu t + \varphi)$$

dephasing angle

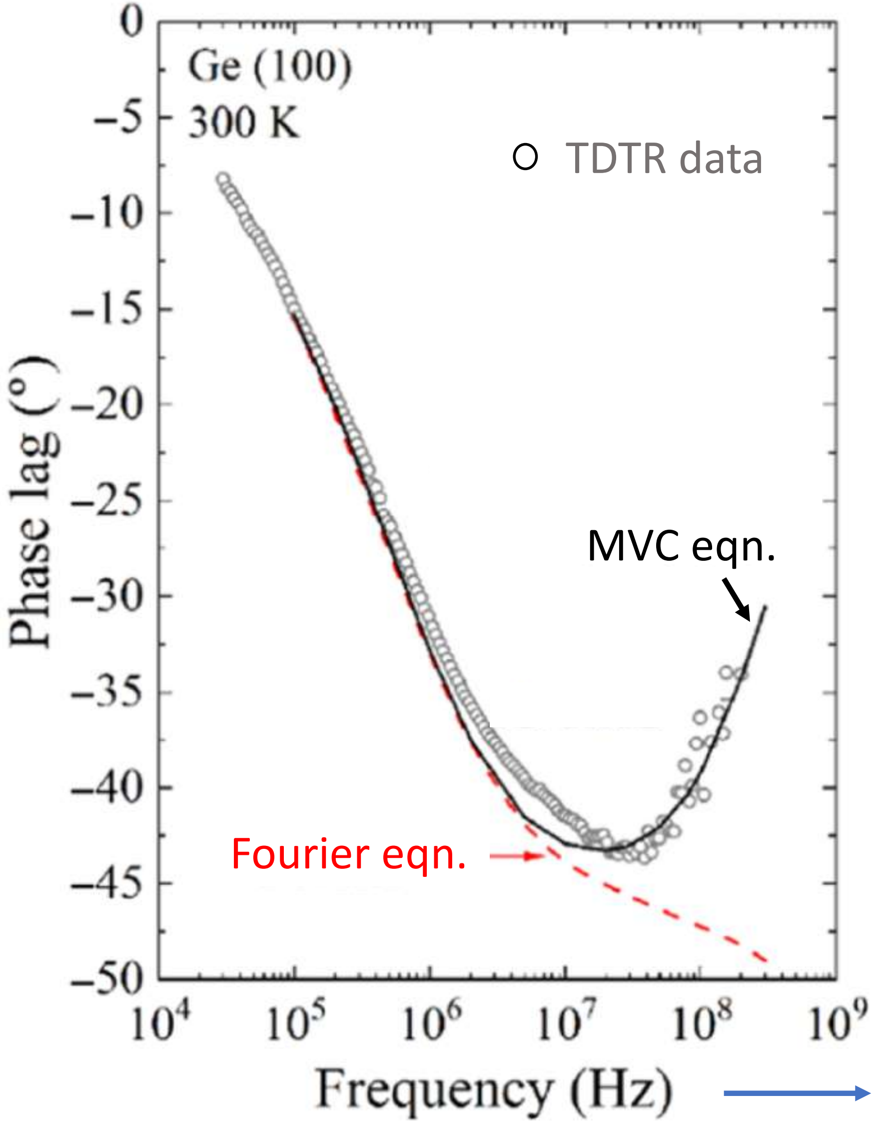
A **phase lag** is observed between the **oscillating thermostat work** and the resulting **oscillating temperature field**

- Predicted phase lag
  - local T-value averaged over 1 ps time
  - simulation repeated at different modulation frequencies
  - **A non-monotonic behaviour is observed**

    - at low frequency the phase lag increases with frequency
    - **at high frequency, the trend is inverted**: the phase lag decreases (absolute value) with increasing frequency



- MD prediction **fully consistent with experimental findings**



→ pump excitation frequency

- Experimental situation matching MVC eq.

$$\tau_{ss}\frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} - \alpha\nabla^2 T = \frac{1}{\rho C}\left[S(\vec{r},t) + \tau_{ss}\frac{\partial S(\vec{r},t)}{\partial t}\right]$$

response temperature field   harmonic thermal excitation

- theory predictions

  - - - - - - - - Fourier solution $\tau_{ss}\frac{\partial^2 T}{\partial t^2} = 0$

  ——— full MVC solution

- Fourier works at low frequency
- deviations from TDTR data start @ 1MHz
- high-frequency trend not consistent with Fourier transport

- fitting MVC eqn. to TDTR data leads to

$$\tau_{ss}^{expt} = 500\ \text{ps} \qquad \alpha^{expt} = 3\times 10^5 \text{m/s} \qquad v_{ss}^{expt} = 250\ \text{m/s}$$

- Elaboration

  - **In both TDTR experiments and MD simulations a non-monotonic phase lag vs. pump frequency** caused by **rapidly time-varying temperature field** although there generated by an unalike physical mechanism

  - The key concept: while reproducing qualitatively the same laboratory situation, the MD simulation is different in that

    (i) there is no optical excitation;
    (ii) there are no electron-holes pairs;
    (iii) there are no electron-related scattering mechanisms;
    (iv) there is no surface, nor any issue related to the penetration depth of whatever perturbation.

    Nevertheless, **a phase-lag signal is observed in both cases**.

  - We argue that **the physical origin of such a commonly observed phase-lag is the rapidly time-varying temperature field**, although differently originated in laboratory or numerical experiments

  - **Phase lag is unambiguously a second sound effect**, associated to the second order time derivative term appearing in the hyperbolic heat equation

Ackowledgements

I presented results obtained in the framework of the following collaborations

second sound in cumulene (by a space-periodic temperature field) - Phys. Chem. Chem. Phys., **23**, 15275 (2021)

- **Giorgia Fugallo**
  LTeN, UMR 6607 CNRS PolytechNantes, Université de Nantes (France)
- **Claudio Melis***
  Department of Physics, University of Cagliari (Italy)

second sound in germanium (by a time-periodic temperature field) - Science Advances **7**, eabg4677 (2021)

- **Abert Beardo, Lluc Sendra, Javier Bafaluy, Juan Camacho, Francesc Xavier Alvarez**
  Departament de Física, Universitat Autònoma de Barcelona (Spain)
- **Luis Alberto Pérez, Maria Isabel Alonso, Riccardo Rurali, Juan Sebastián Reparaz***
  Institut de Ciència de Materials de Barcelona, ICMAB-CSIC (Spain)
- **Miquel López-Suárez, Claudio Melis**
  Department of Physics, University of Cagliari (Italy)

*Correspondig Author