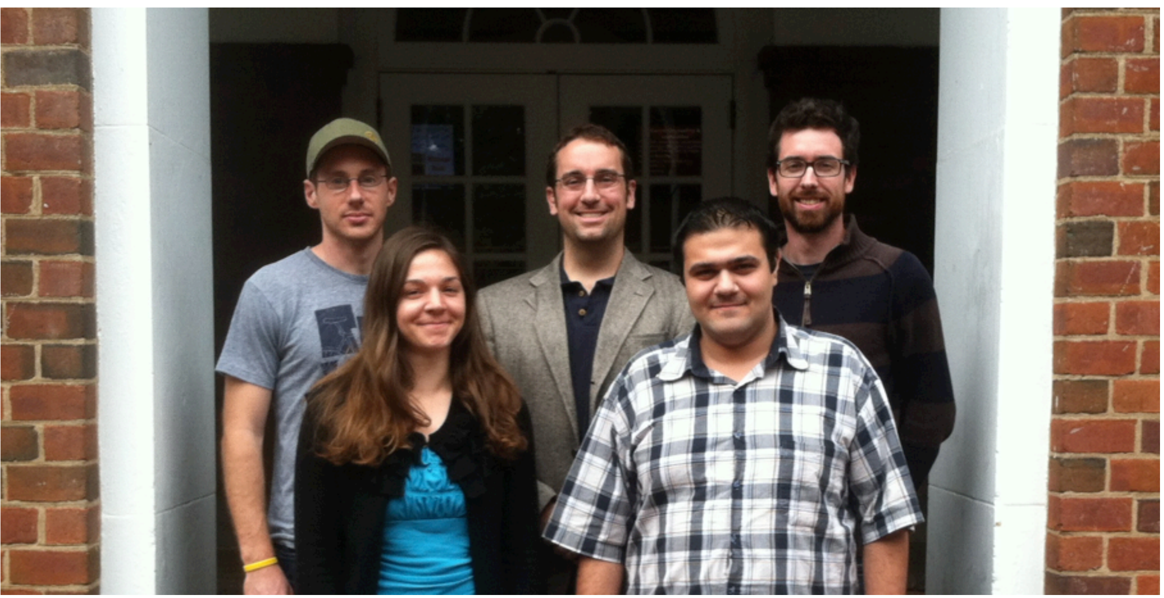
School of Engineering & Applied Science
University of Virginia

Energy transfer processes in nanosystems: phonon transport in metals, interfaces, and polymers



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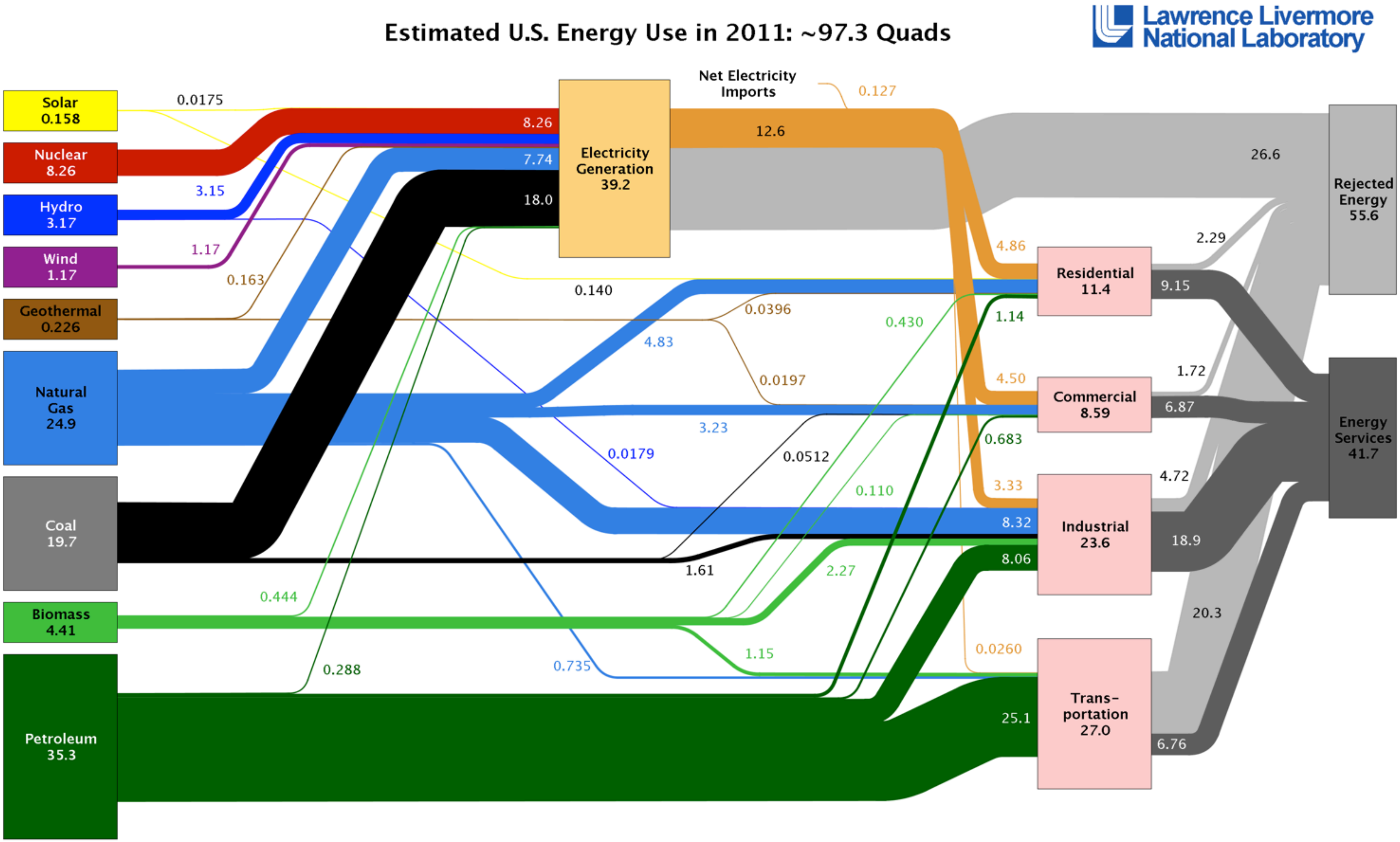
patrickehopkins.com

Energy efficiency = heat transfer problem

57% of energy consumed in the United States is wasted as **HEAT**

Let's look at a simple graph…

Energy usage in the United States



Source: LLNL 2012. Data is based on DOE/EIA-0384(2011), October, 2012. If this information or a reproduction of it is used, credit must be given to the Lawrence Livermore National Laboratory and the Department of Energy, under whose auspices the work was performed. Distributed electricity represents only retail electricity sales and does not include self-generation. EIA reports flows for non-thermal resources (i.e., hydro, wind and solar) in BTU-equivalent values by assuming a typical fossil fuel plant "heat rate." The efficiency of electricity production is calculated as the total retail electricity delivered divided by the primary energy input into electricity generation. End use efficiency is estimated as 80% for the residential, commercial and industrial sectors, and as 25% for the transportation sector. Totals may not equal sum of components due to independent rounding. LLNL-MI-410527

Making energy usage more efficient?

Lighting has already experienced a paradigm shift

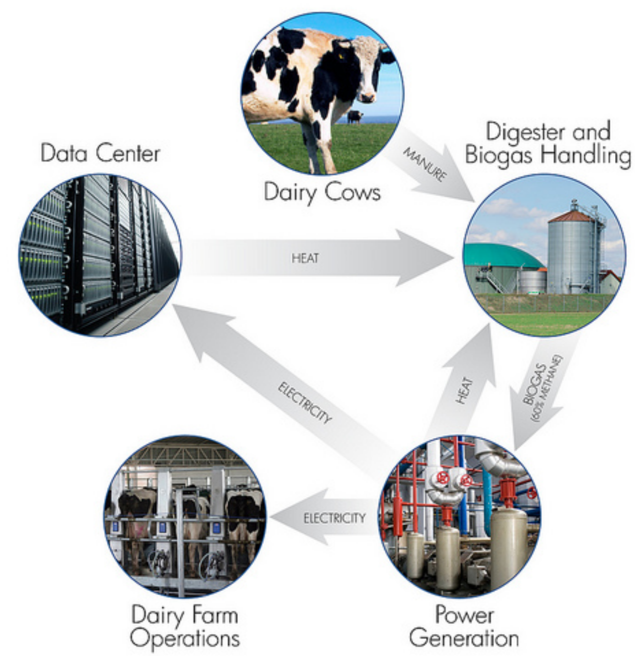
The Light Emitting Diode (LED)!

Making energy usage more efficient?

Server farms…

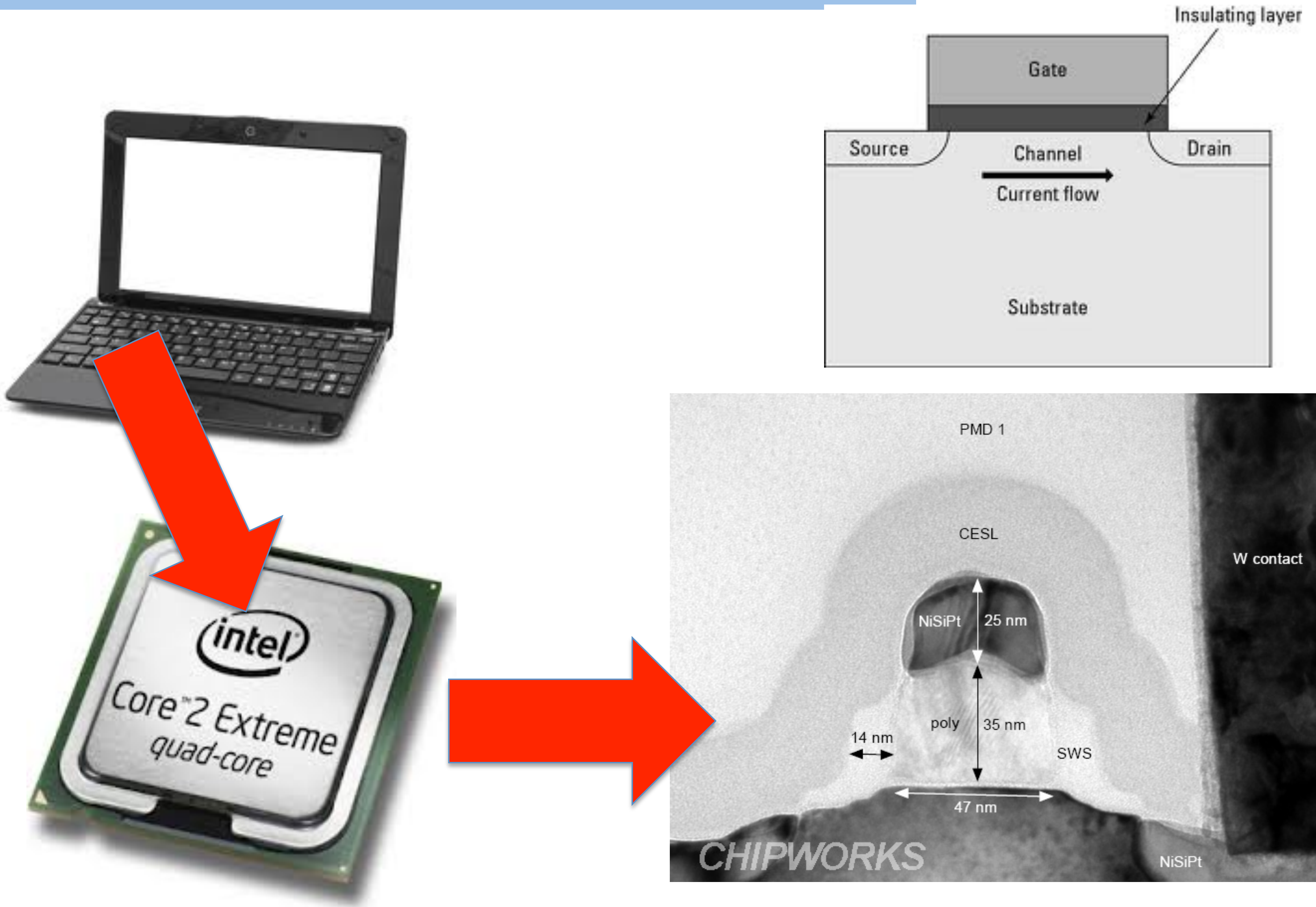
Recycle the wasted heat
(NET energy decrease)

HP Labs Design for a Farm Waste
Data Center Ecosystem



Can we make computers chips more energy efficient?

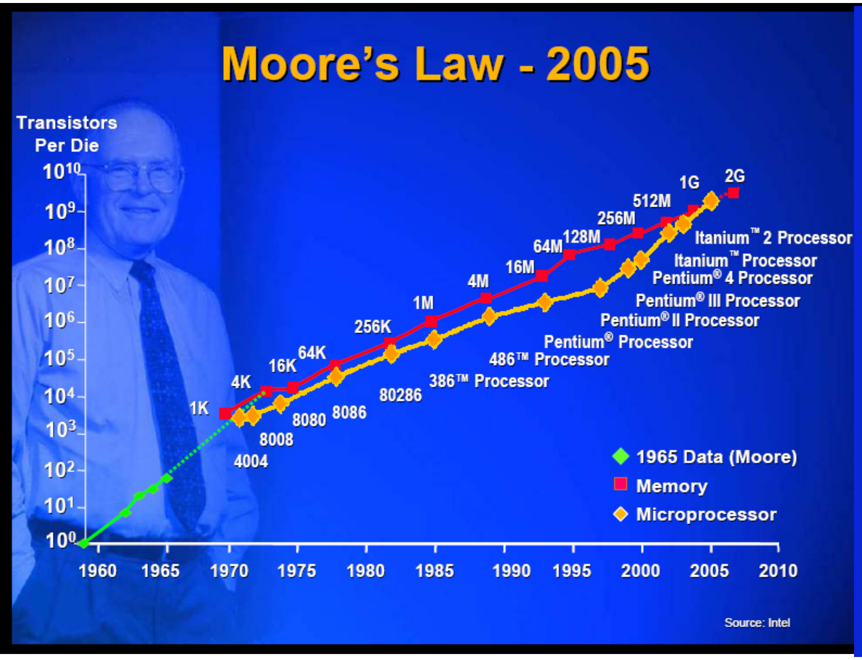
Making computers more efficient

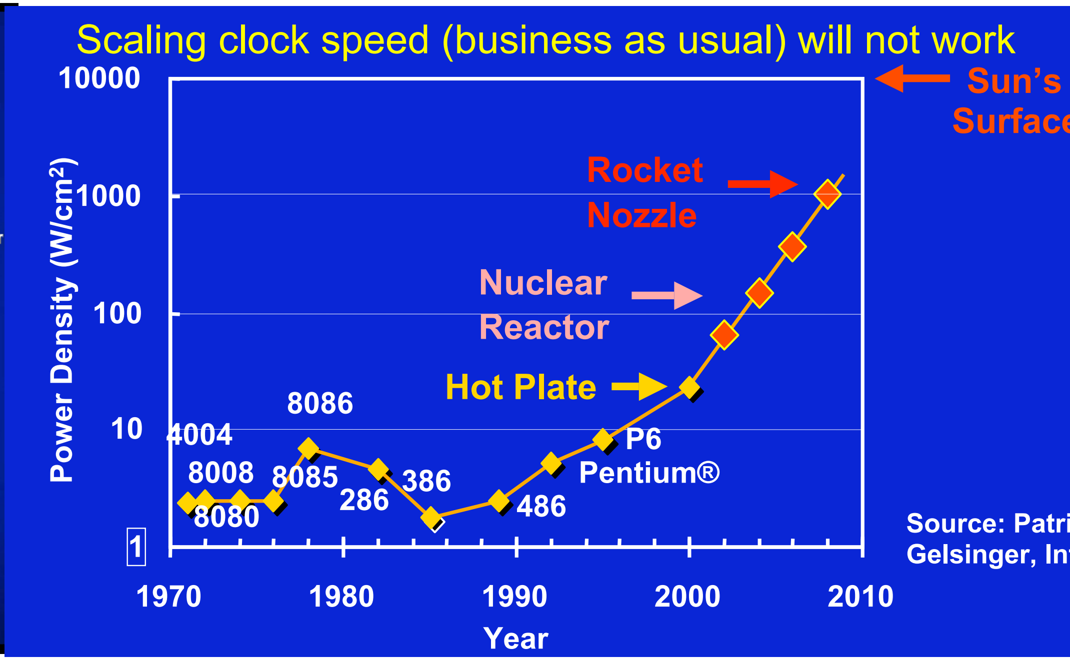


Moore's law….a NANO heat transfer problem

Power flux= Power/area

Length scale goes down, power flux goes up as L^2



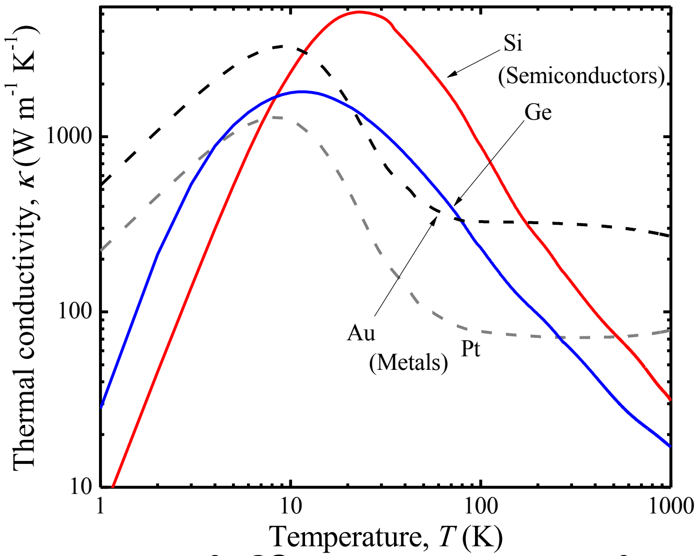


Moore, "Cramming more components onto integrated circuits," Electronics, **38**, 113 (1965)

Nanoscale heat transfer

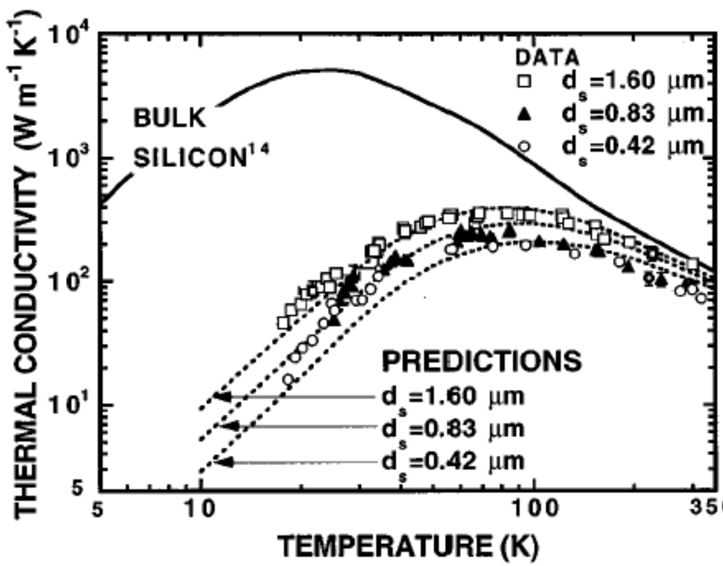
$$q = -\kappa \frac{\partial T}{\partial z}$$

This doesn't work when lengths become too short....why??? We'll find out soon!



Notice different trends between κ in metals and κ in semiconductors

Silicon thin films



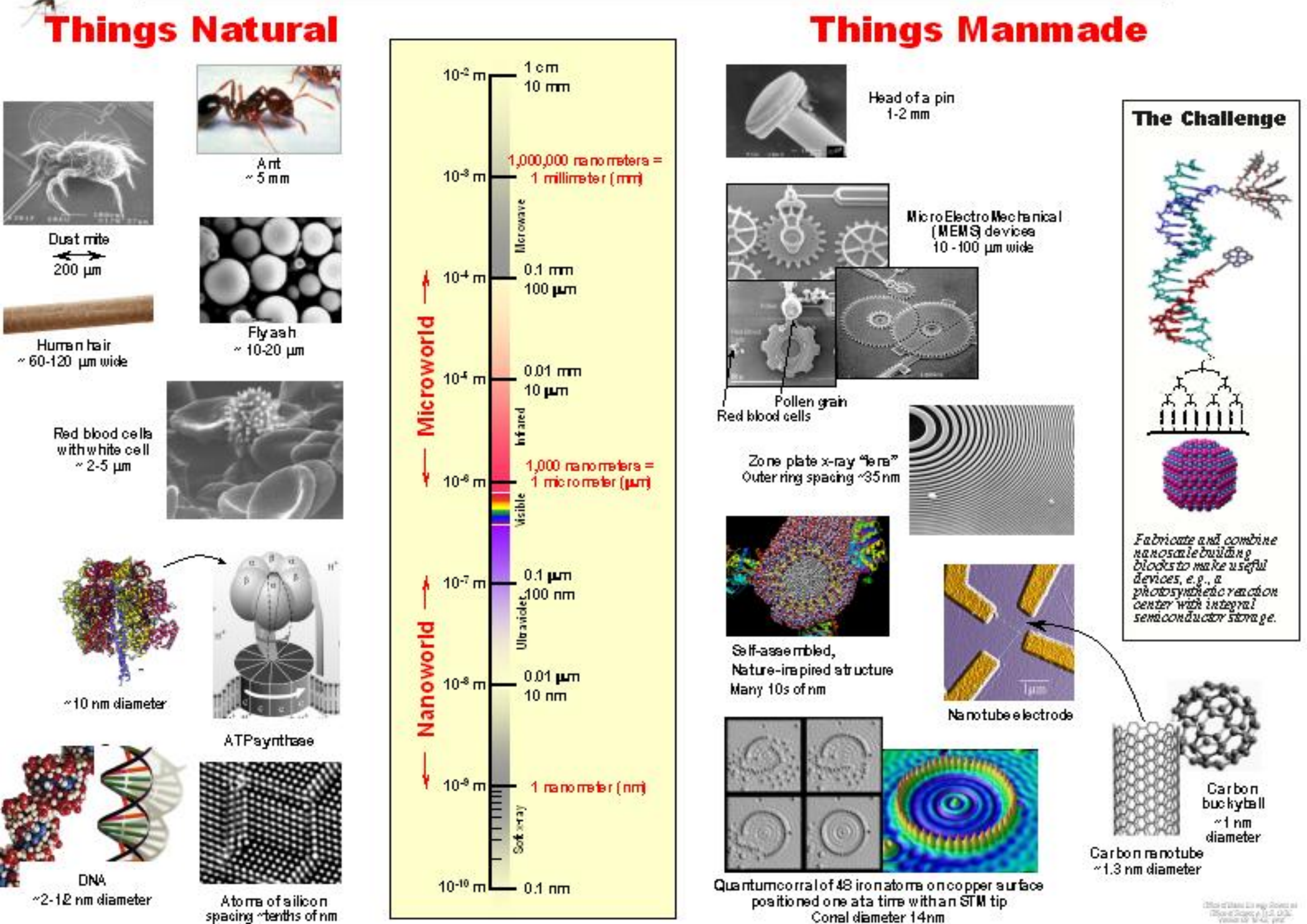
Tabulated data from: Ho, Powell, and Liley, "Thermal conductivity of the elements," Journal of Physical and Chemical Reference Data, **1**, 279 (1972).

Definition of nanotechnology

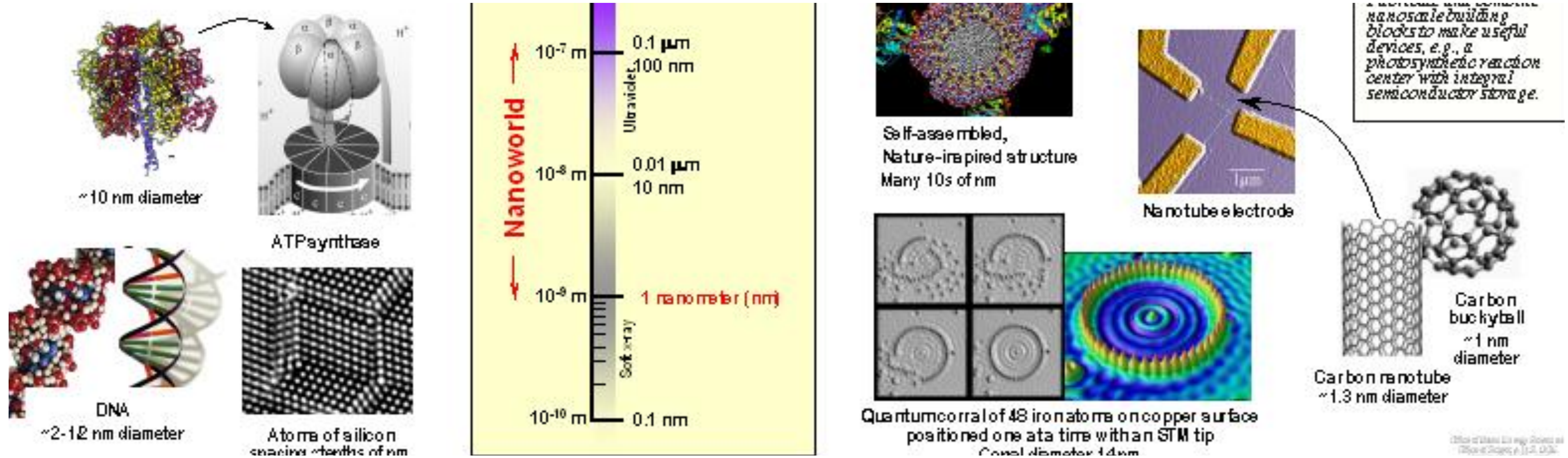
"Nanotechnology is the understanding and control of matter at dimensions of roughly **1 to 100 nanometers**, where unique phenomena enable novel applications. Encompassing nanoscale science, engineering and technology, nanotechnology involves imaging, measuring, modeling, and manipulating matter at this length scale."

-National Nanotechnology Initiative

The Scale of Things – Nanometers and More



What does this mean for heat?



NEED TO UNDERSTAND HEAT TRANSFER ON THE ATOMIC LEVEL WHERE ALL THE ACTION HAPPENS ON THE ORDER OF FEMTOSECONDS TO NANOSECONDS

How fast is a femtosecond (10^{-15} s)?

5.4 µs - Time for light to travel 1 mile in vacuum

330 ps Time it take a 3.0 GHz computer to add two integers

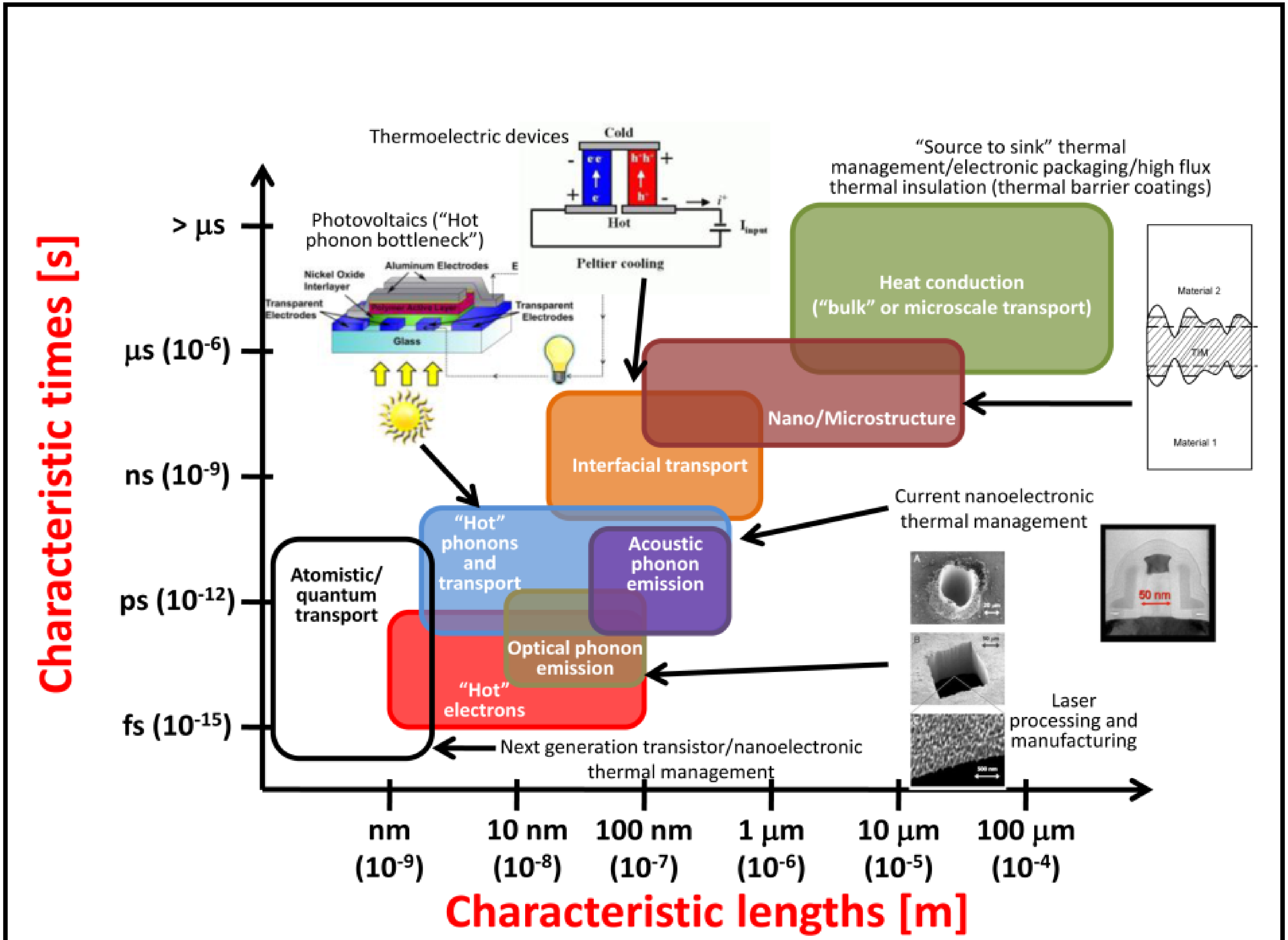
$$0.000000000000001\ s$$

1 ms - Typical duration of a camera flash

10-20 ns Time of fustion in the hyrdogen bomb

200 fs Fastest chemical reactions (pigment reaction in the eye)

Energy/heat time and length scales



Outline

- **Thermophysics background**

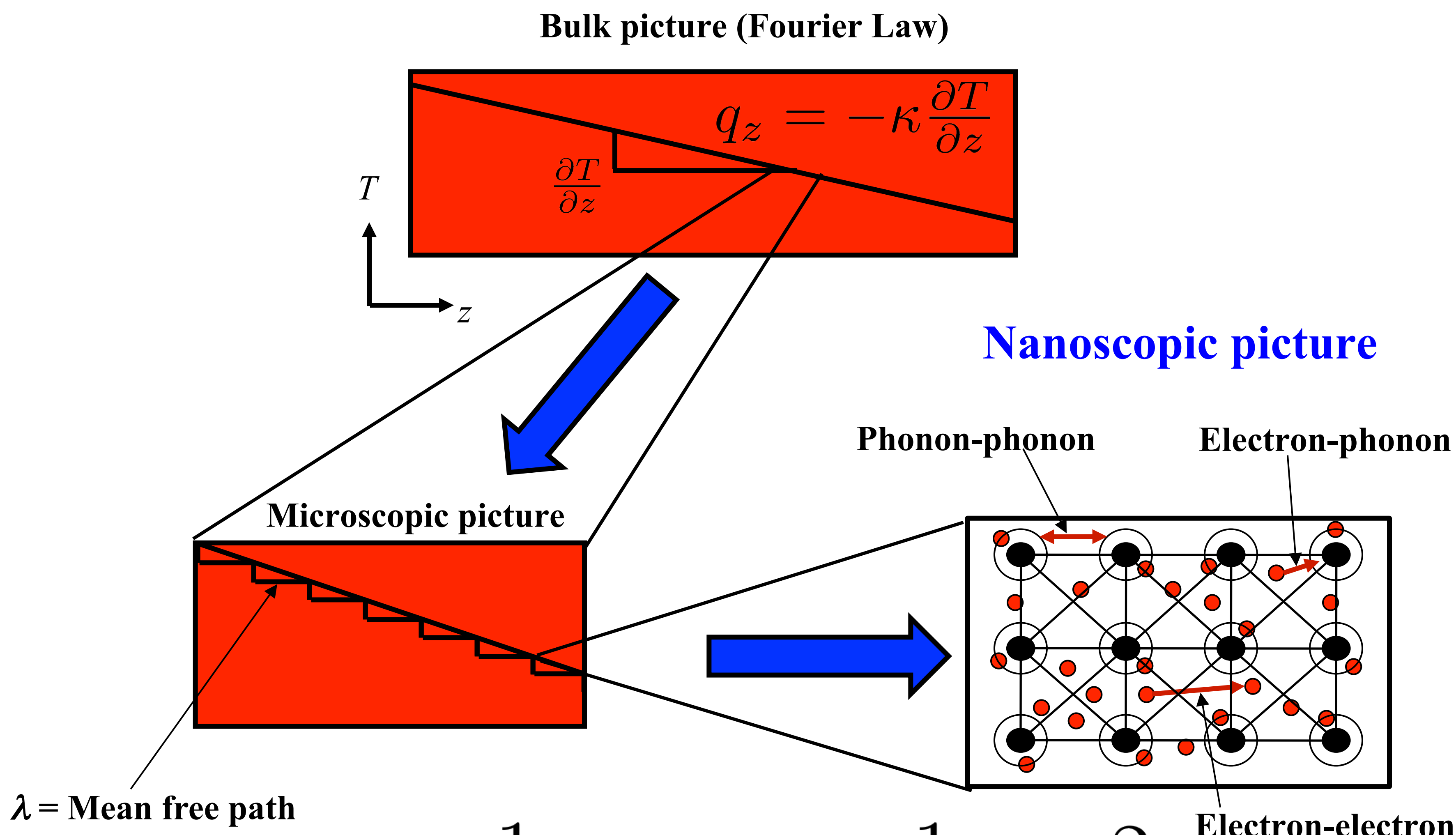
- **Measurement of electron and phonon thermal properties on the nanoscale with time domain thermoreflectance – time scales and phenomena**

- **Example 1: Amorphous metals: electron AND phonon transport**

- **Example 2: Interfaces: disorder and adhesion**

- **Example 3: Exceptionally low thermal conductivity of organic semiconducting polymers: making Einstein proud**

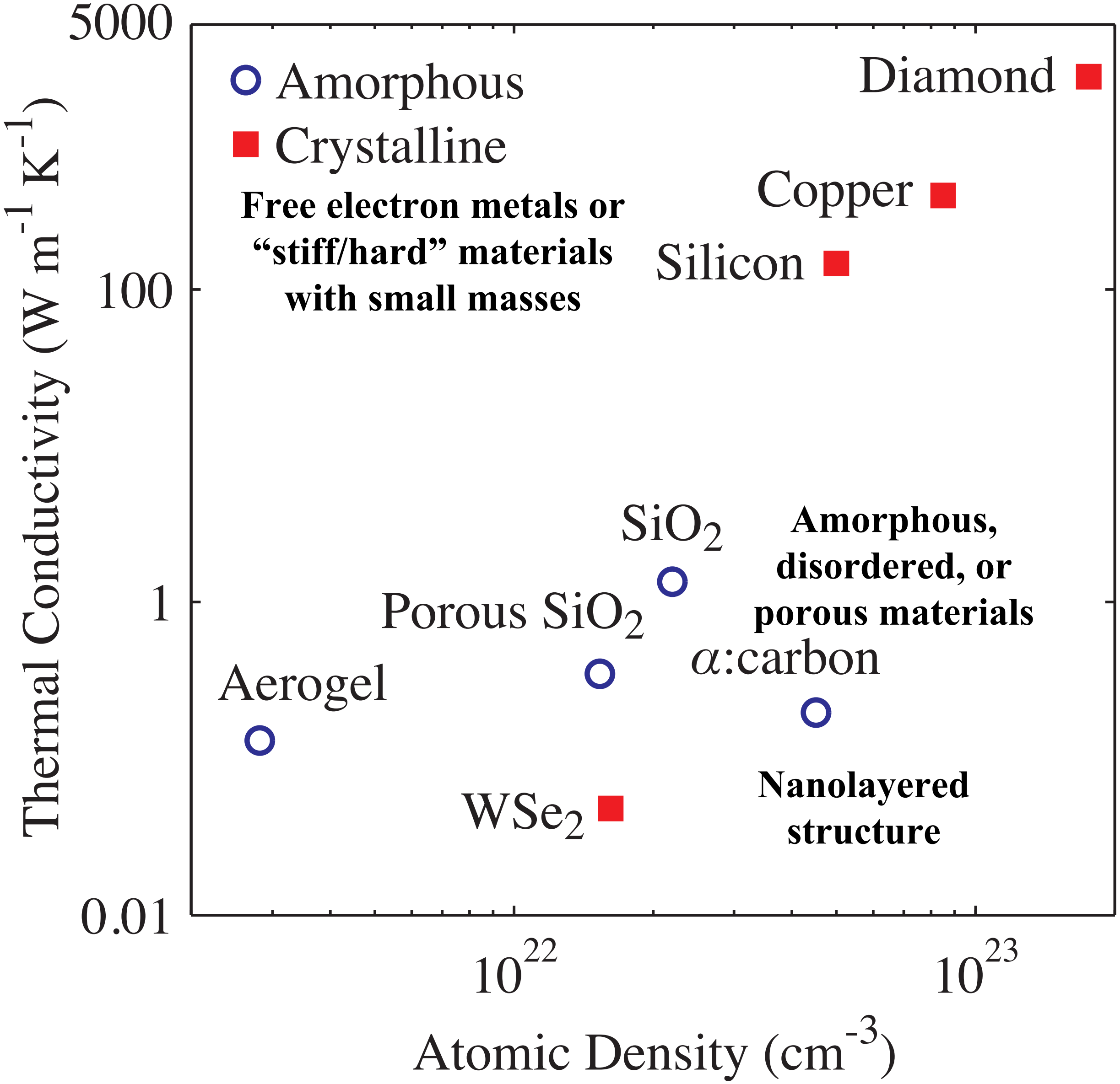
Thermophysics on the nanoscale



$$\kappa = \frac{1}{3} C v \lambda = \frac{1}{3} C v_g^2 \tau$$

Thermal conductivity of solids

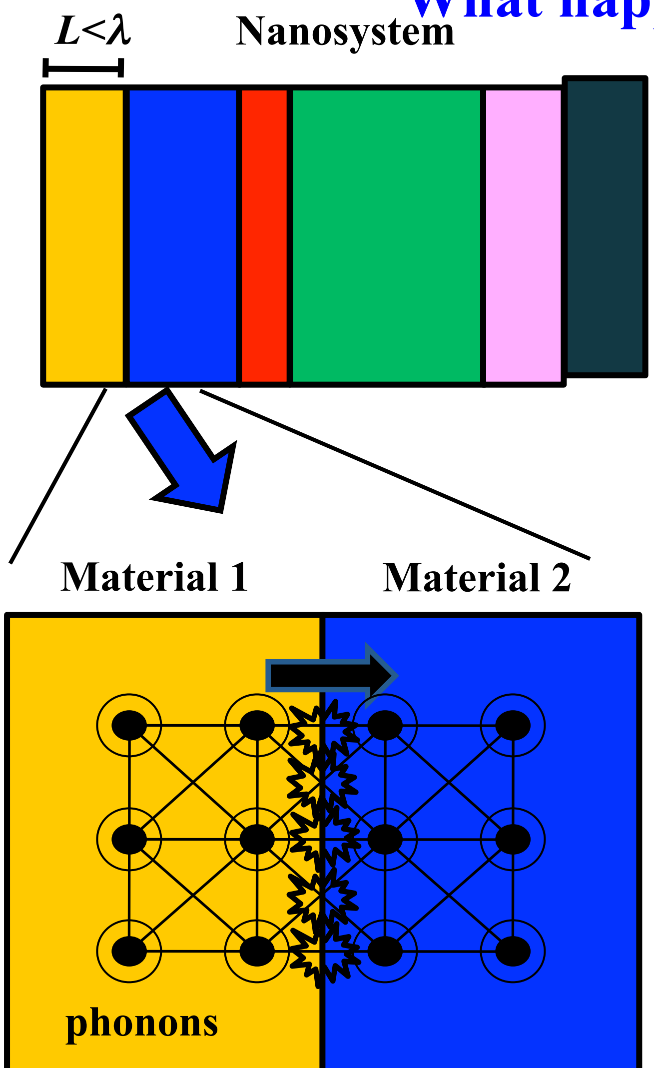
What's the nanoscopic story here???



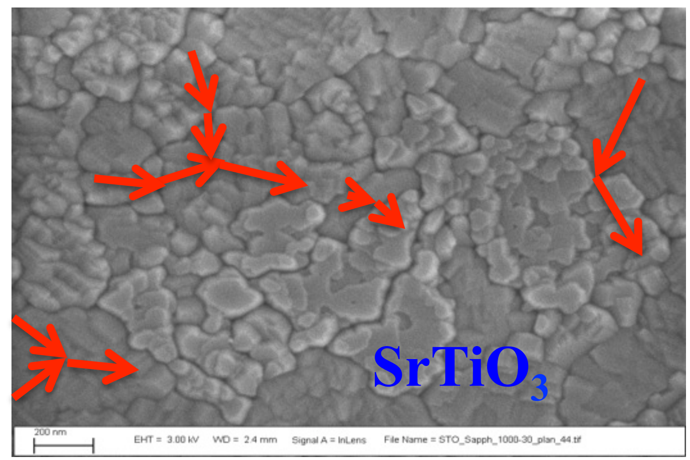
Thermophysics on the nanoscale

$$\kappa = \frac{1}{3}Cv\lambda = \frac{1}{3}Cv_g^2\tau$$

What happens if λ is on the order of L?



e.g. Nanoscale composites and thin films



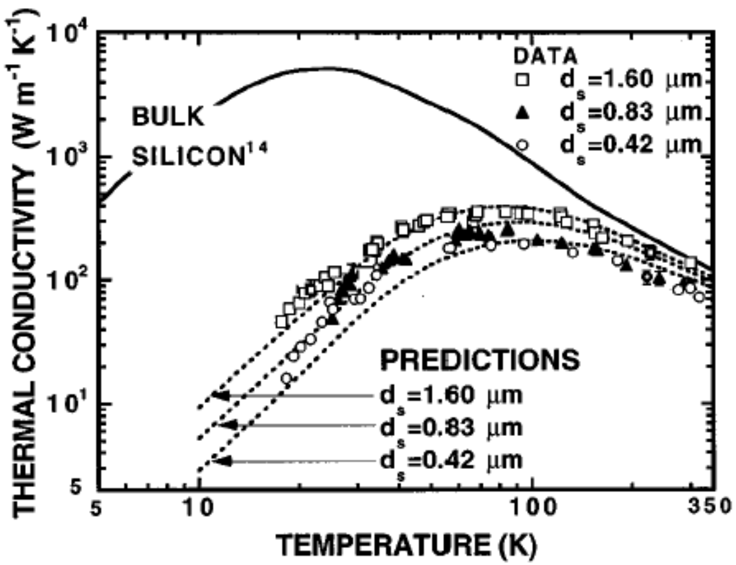
APPLIED PHYSICS LETTERS **101**, 231908 (2012)

Thermal conductivity of nano-grained $SrTiO_3$ thin films

Brian M. Foley,[1] Harlan J. Brown-Shaklee,[2] John C. Duda,[1,2] Ramez Cheaito,[1] Brady J. Gibbons,[3] Doug Medlin,[4] Jon F. Ihlefeld,[2] and Patrick E. Hopkins[1,a)]

[1]*Department of Mechanical and Aerospace Engineering, University of Virginia, Charlottesville, Virginia 22904, USA*
[2]*Sandia National Laboratories, Albuquerque, New Mexico 87185, USA*
[3]*Materials Science, School of Mechanical, Industrial, and Manufacturing Engineering, Oregon State University, Corvallis, Oregon 97331, USA*
[4]*Sandia National Laboratories, Livermore, California 94550, USA*

Effects of “nano” on thermal conductivity



Thermal conductivity of various silicon-based structures v. temperature

How far does energy move before it loses momentum?

$$\kappa = \frac{1}{3} C v \lambda = \frac{1}{3} C v_g^2 \tau$$

How much energy?

How fast does the energy move?

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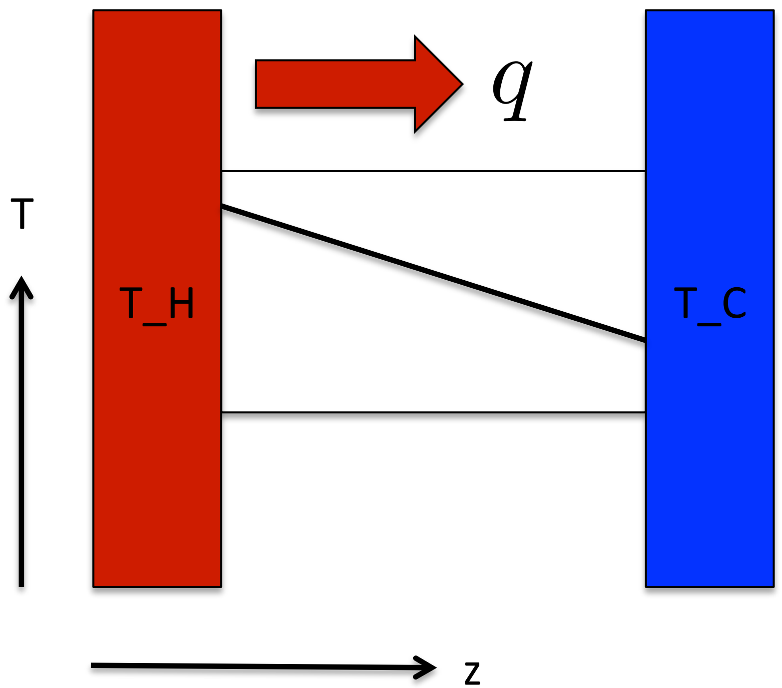
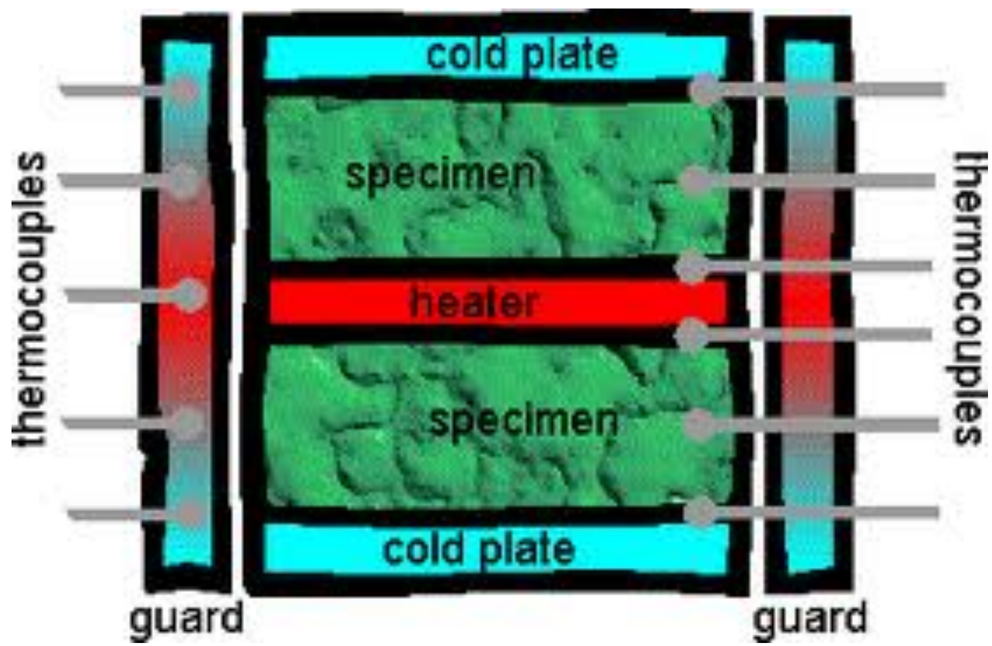
Steady state measurements

"Guarded hot plate"

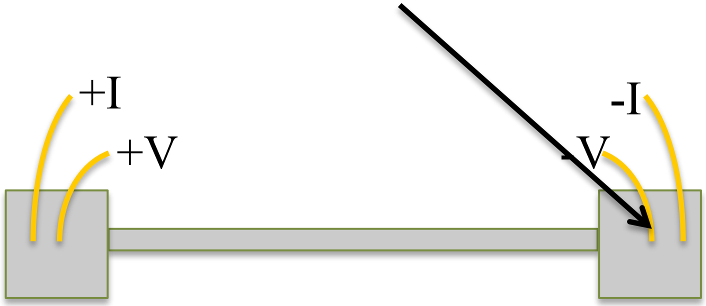
$$q = -\kappa \frac{\partial T}{\partial z}$$

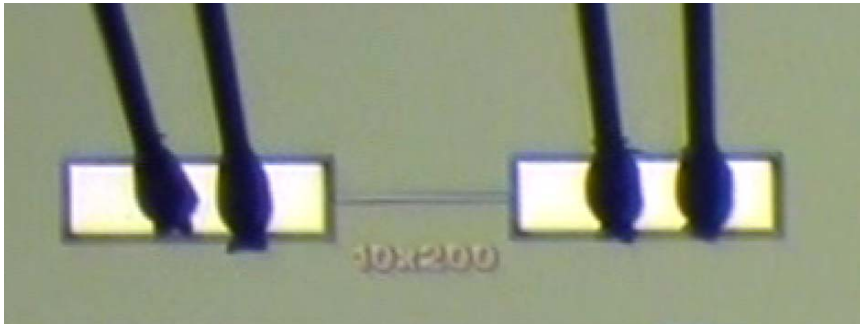




Steady state measurements - nano

Electrical/thermal contact resistances are inherently present in measurements





How do you make these contacts in a nanosystem??

When would these contact resistances matter in terms of sample geometry???

P. E. Hopkins and L. M. Phinney. Thermal conductivity measurements on polycrystalline silicon micro- bridges using the 3w technique. Journal of Heat Transfer, 131:043201, 2009.

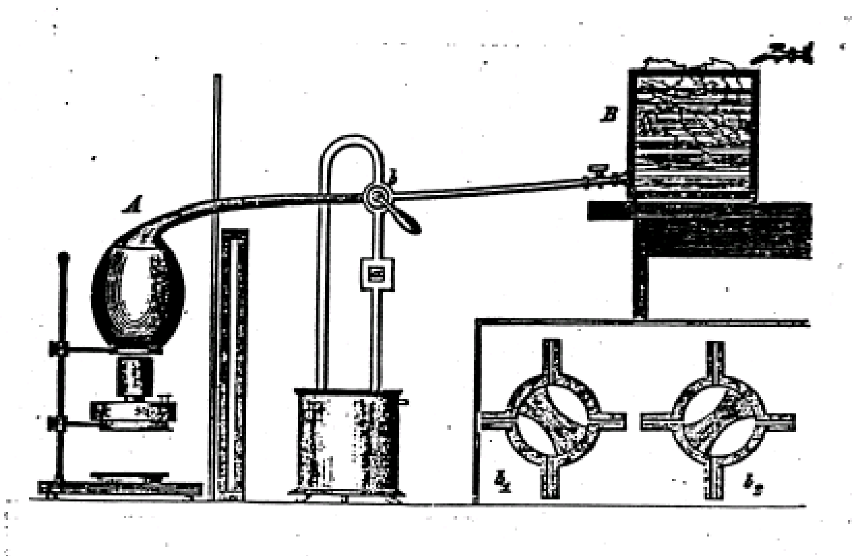
Ångström method

Used fixed temperature boundary conditions

$$T\left(x=0\right)=0^{\circ}\mathrm{C} \qquad 0<t<\Gamma/2$$

$$T\left(x=0\right)=100^{\circ}\mathrm{C} \qquad \Gamma/2<t<\Gamma$$

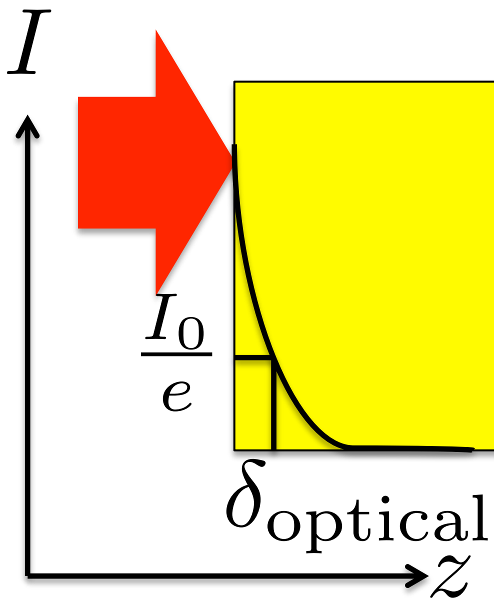
where Γ is the period of temperature oscillations produced by alternating flow of ice water and steam



Frequency dependent temperature rise leads to temperature fluctuation at end of sample with some phase lag based on RC

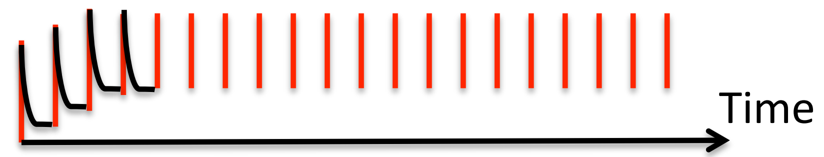
Can we do this optically???

Coat surfaces with metals to achieve near-surface absorption high *opto-spatial* resolution (i.e., surface localized heat source)

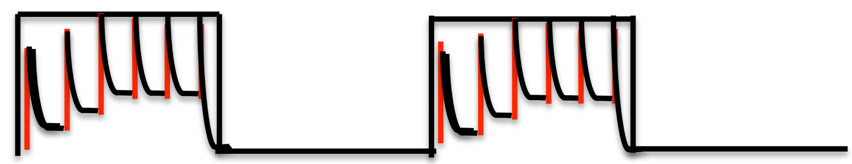


$$\delta_{\text{optical}} = \frac{\lambda}{4\pi k} \approx 10\,\text{nm}$$

Modulated heat transfer regime achieves variable *thermo-spatial* resolution (i.e., variable temperature gradient via distance)



Probe TDTR (accumulates due to 80 MHz rep. rate)

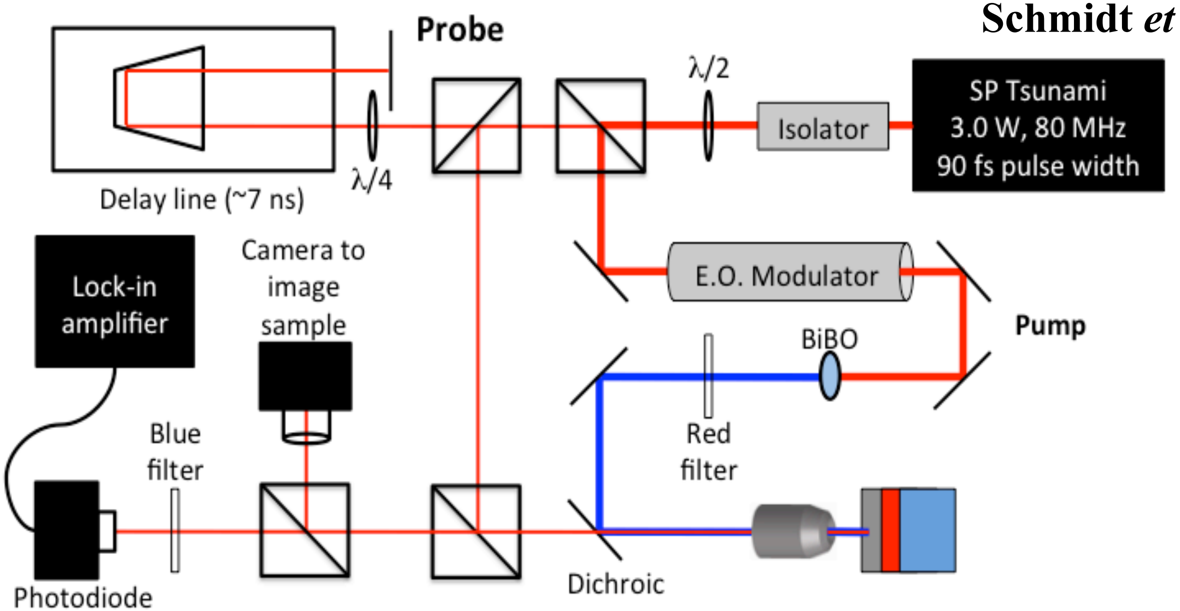


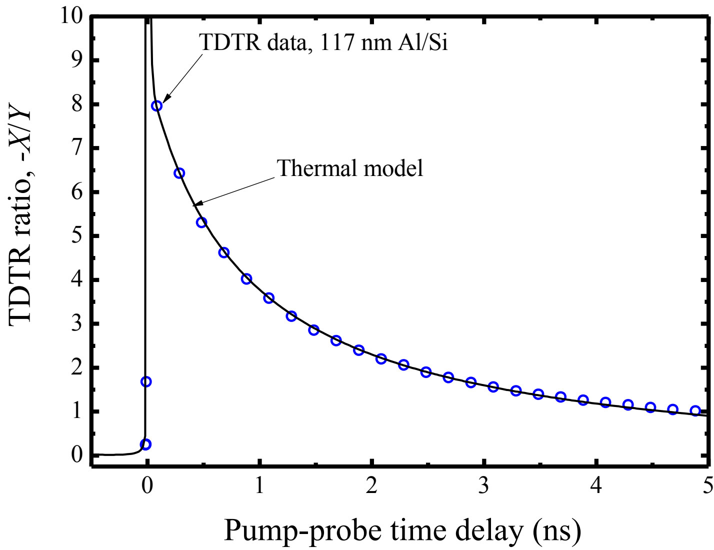
Accumulation leads to *MODULATED* heating events

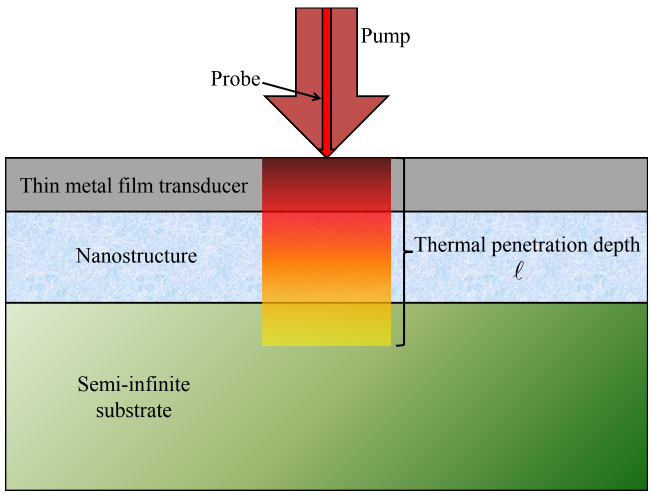
Pulses on the order of femtoseconds and pulse separation on the order of 12 ns

Time Domain ThermoReflectance (TDTR)

Hopkins *et al.*, *J. Heat Trans.* 132, 081302 (2010)
Cahill, *Rev. Sci. Instr.* 75, 5119 (2004)
Schmidt *et al.*, *Rev. Sci. Instr.* 74, 114902 (2008)



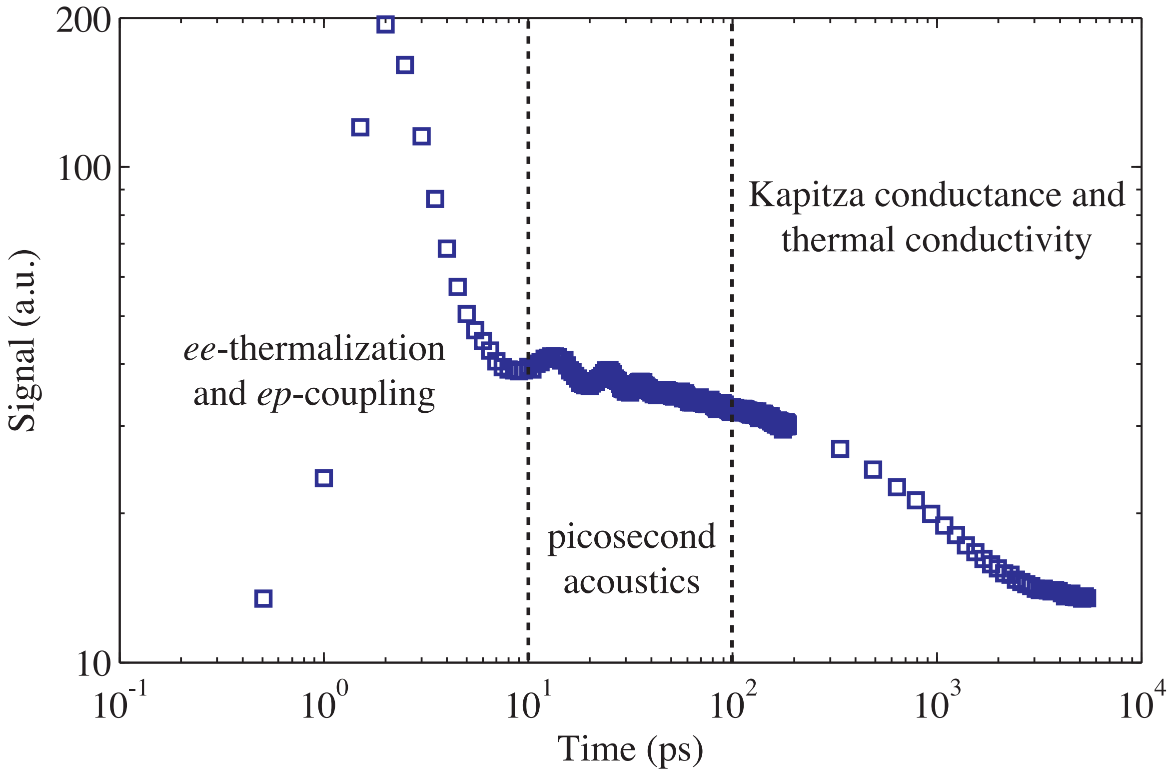




- Can measure thermal conductivity of thin films and substrates (κ) separately from thermal boundary conductance (h_K)
- Nanometer spatial resolution (~10's of nm)
- Femtosecond to nanosecond temporal resolution
- Noncontact

Temporal regimes in TDTR data

FANTASTIC temporal resolution (limited by pulse width)



Pulse absorption (~100 fs)

↓

Fermi relaxation and ballistic transport (few hundred fs)

↓

Electron-phonon coupling (a few ps)

↓

Strain propagation in film (10's of ps)

↓

Thermal diffusion (hundreds of ps to ns)

Now let's look at a few specific examples….

Electron thermalization and scattering (100's of fs to a few ps)

Journal of Heat Transfer

APRIL 2011, Vol. 133 / **044505-1**

Re-examining Electron-Fermi Relaxation in Gold Films With a Nonlinear Thermoreflectance Model

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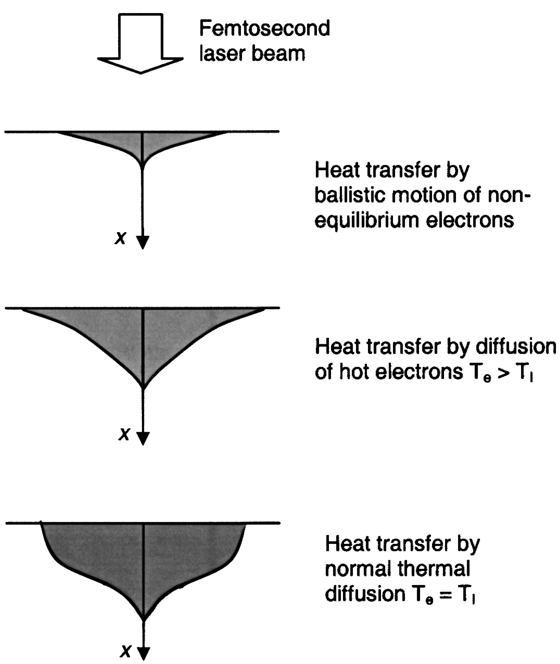
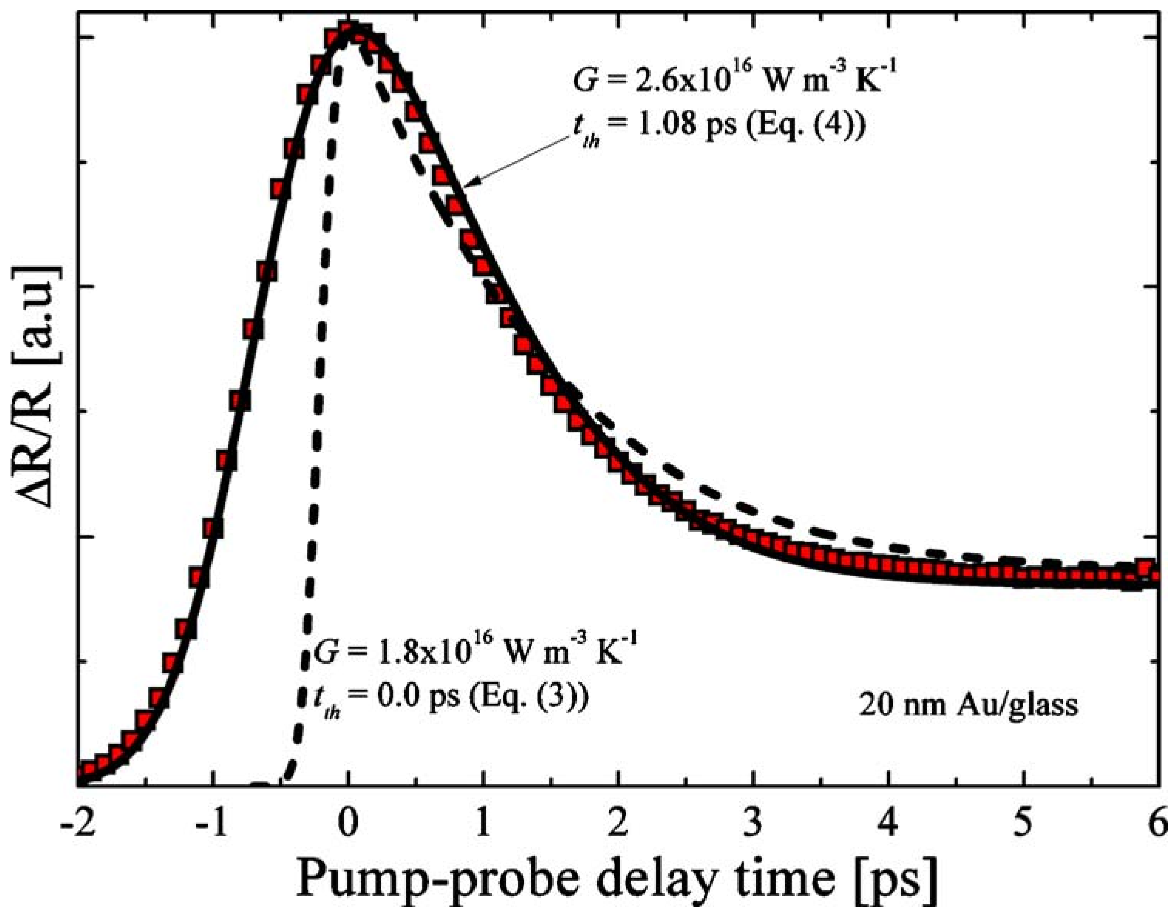
Leslie M. Phinney

Justin R. Serrano

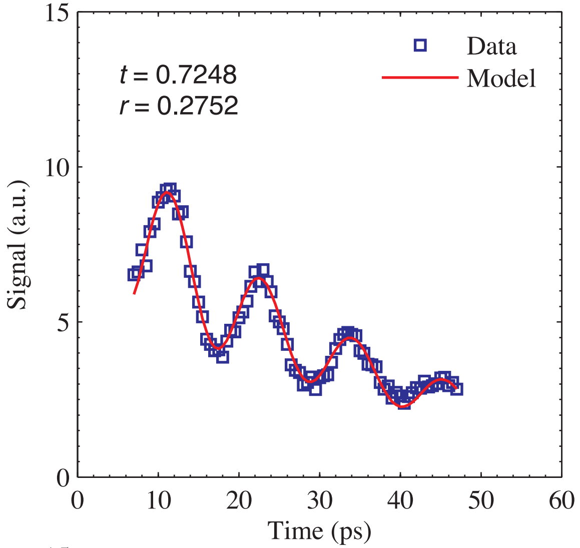
Sandia National Laboratories,
Albuquerque, NM 87185

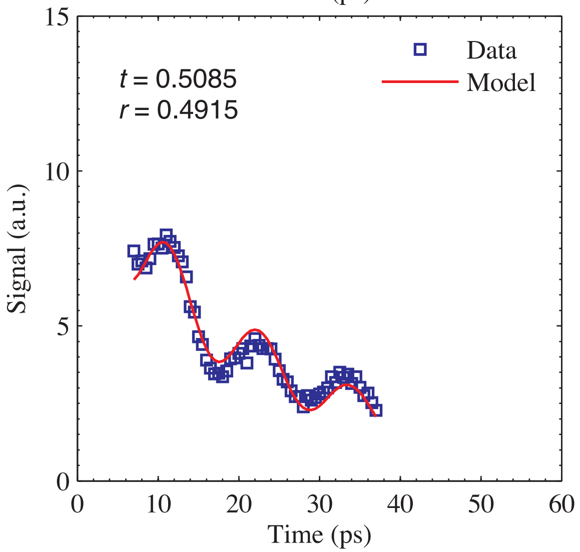


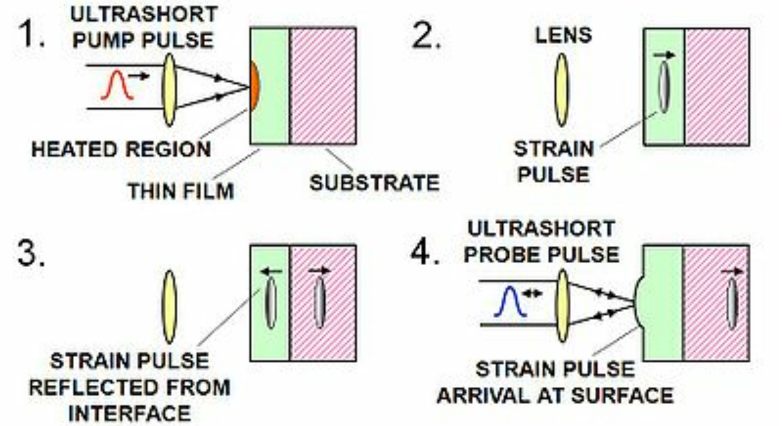


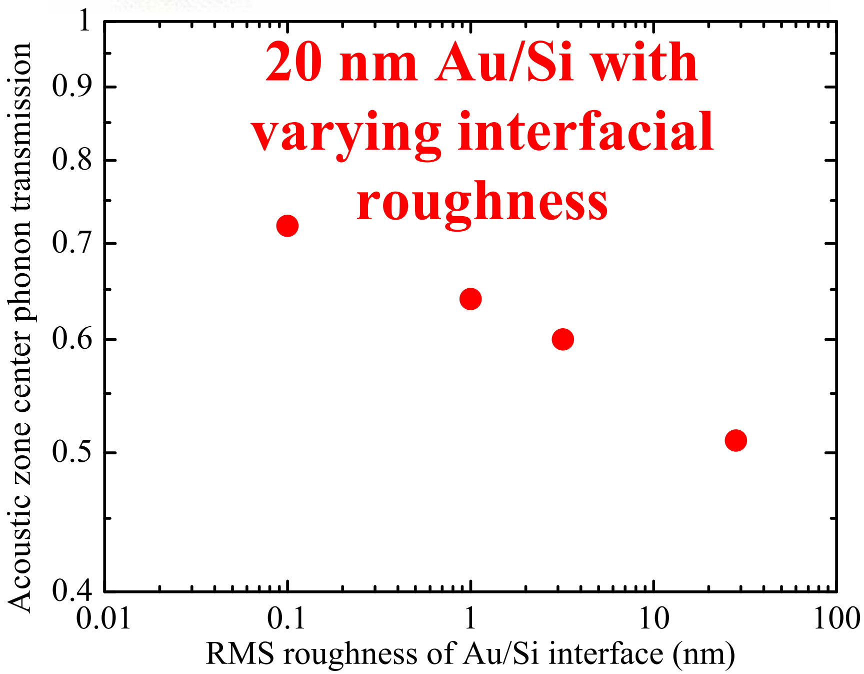
Phonon transmission (10's of ps)

"Echoes" related to strain wave partially reflecting at film/substrate interface. Can determine interfacial transmission of zone center modes via *picosecond ultrasonics*







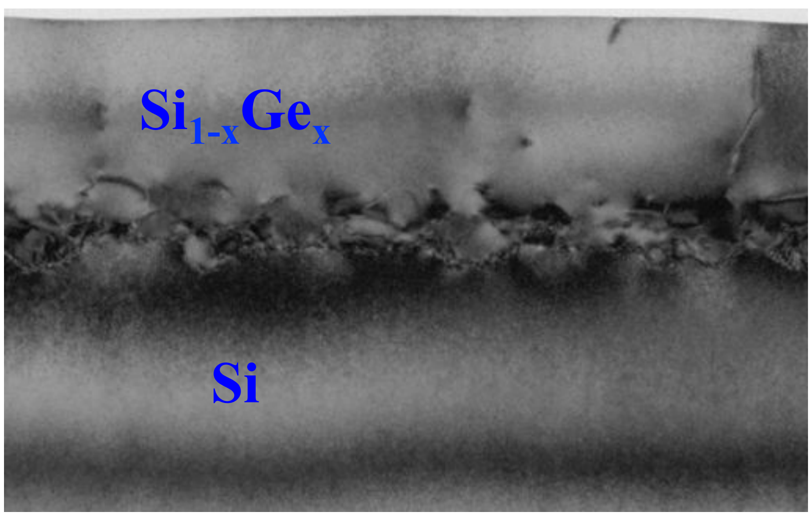


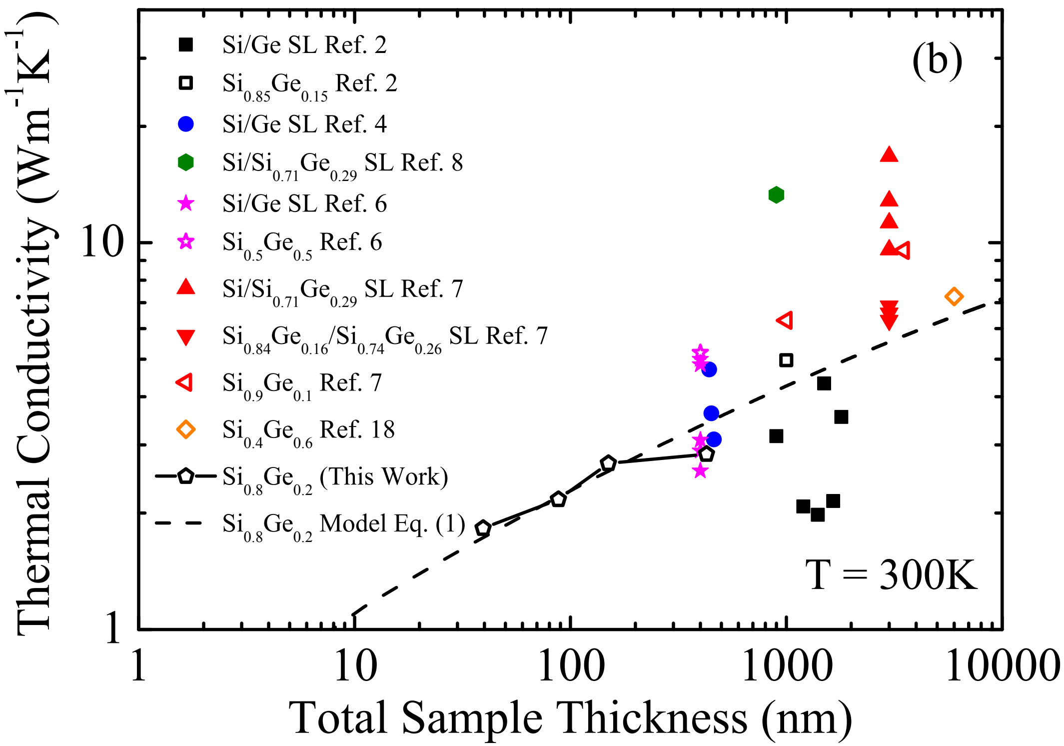
Thermal conductivity of thin films (100's of ps – ns)

PRL **109,** 195901 (2012) PHYSICAL REVIEW LETTERS week ending 9 NOVEMBER 2012

Experimental Investigation of Size Effects on the Thermal Conductivity of Silicon-Germanium Alloy Thin Films

Ramez Cheaito,[1] John C. Duda,[1,2] Thomas E. Beechem,[2] Khalid Hattar,[2] Jon F. Ihlefeld,[2] Douglas L. Medlin,[3] Mark A. Rodriguez,[2] Michael J. Campion,[2,4] Edward S. Piekos,[2] and Patrick E. Hopkins[1,*]



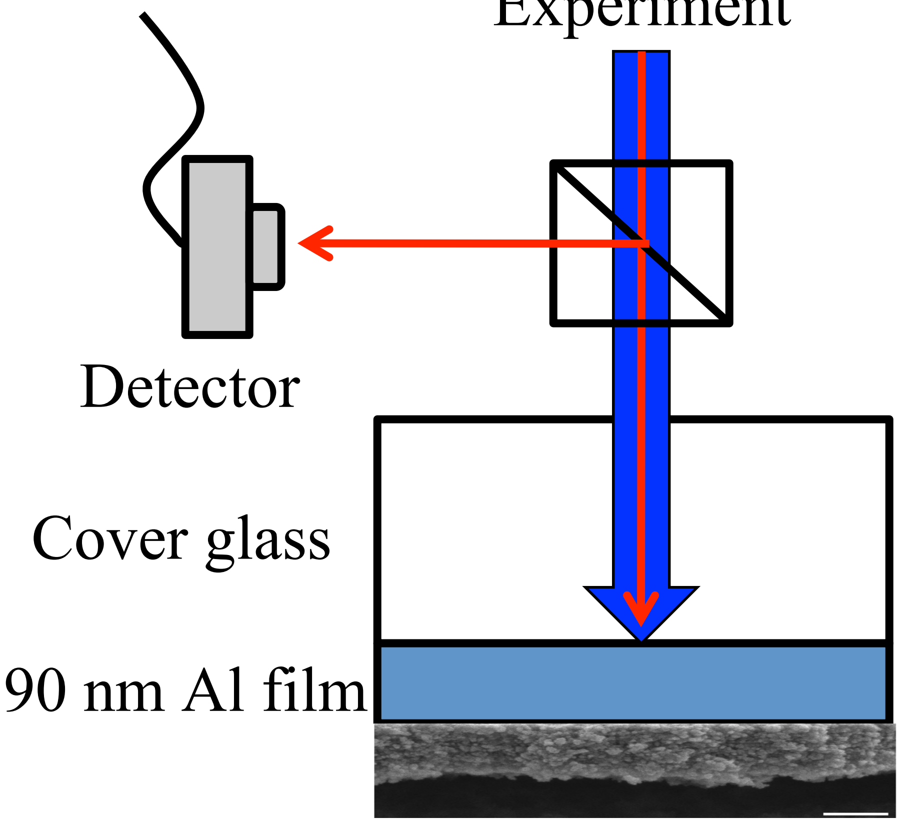


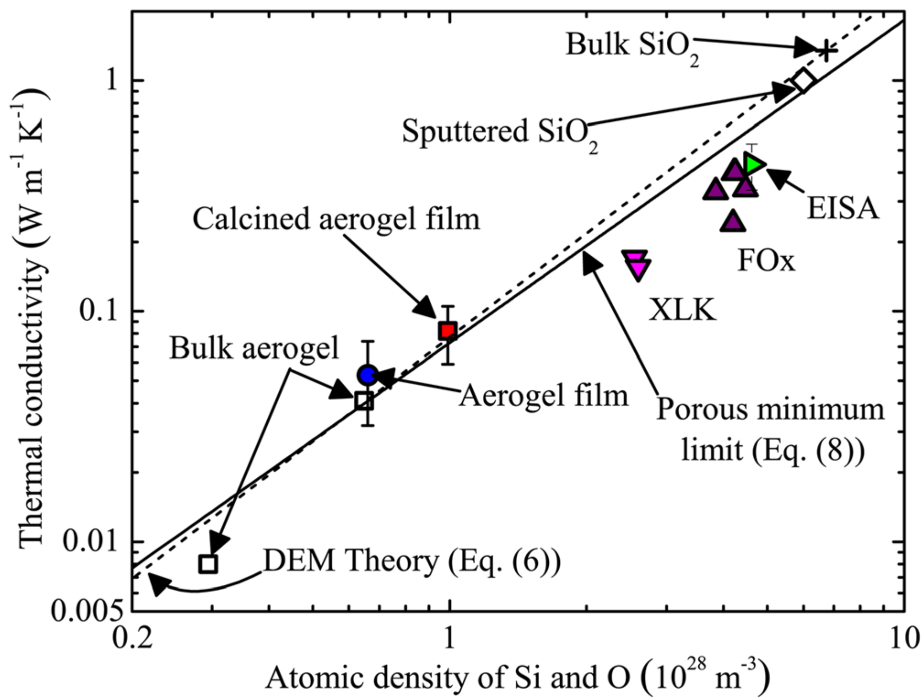
Highly porous/nonconformal films (*e.g.*, aerogels)

JOURNAL OF APPLIED PHYSICS **111**, 113532 (2012)

Minimum thermal conductivity considerations in aerogel thin films

Patrick E. Hopkins,[1,a)] Bryan Kaehr,[2,3] Edward S. Piekos,[2] Darren Dunphy,[3] and C. Jeffrey Brinker[2,3]
[1]*Department of Mechanical and Aerospace Engineering, University of Virginia, Charlottesville, Virginia 22904, USA*
[2]*Sandia National Laboratories, Albuquerque, New Mexico 87123, USA*
[3]*Department of Chemical and Nuclear Engineering, University of New Mexico, Albuquerque, New Mexico 87106, USA*





Porous or nonconformal films

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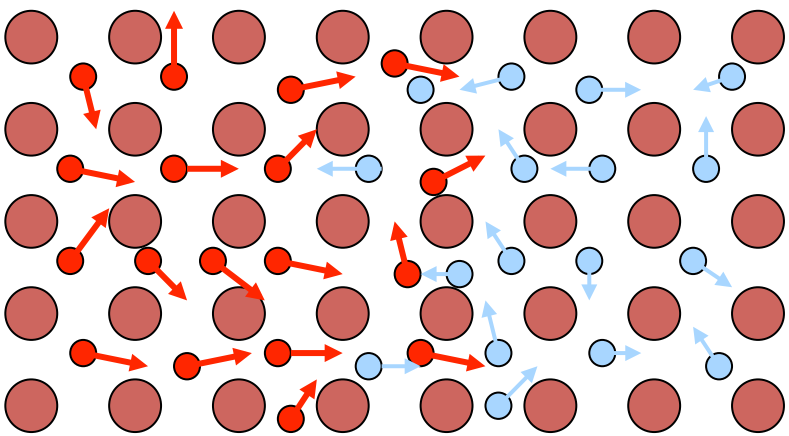
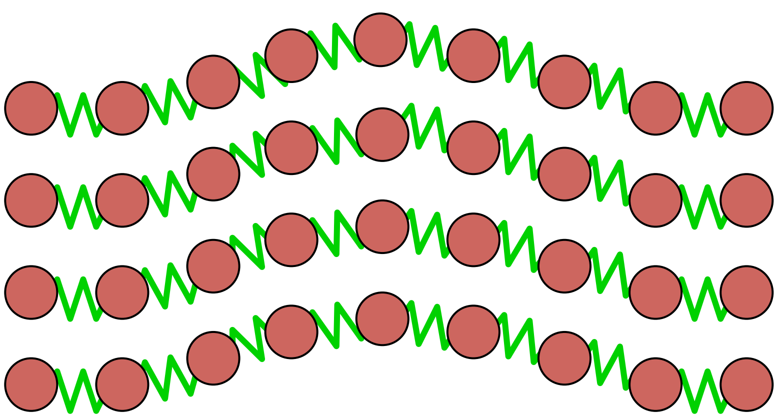
Heat transfer in metal vs non-metals

$$\kappa = \frac{1}{3} C v \lambda = \frac{1}{3} C v_g^2 \tau$$

Diffusion of "hot" electrons

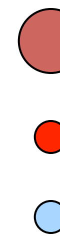




Phonon propagation

Metals:

Free electrons are the dominant energy carriers in metals, velocity ~10^6 m/s



Electron carrier density:

in metals ~10^{23} cm^{-3}

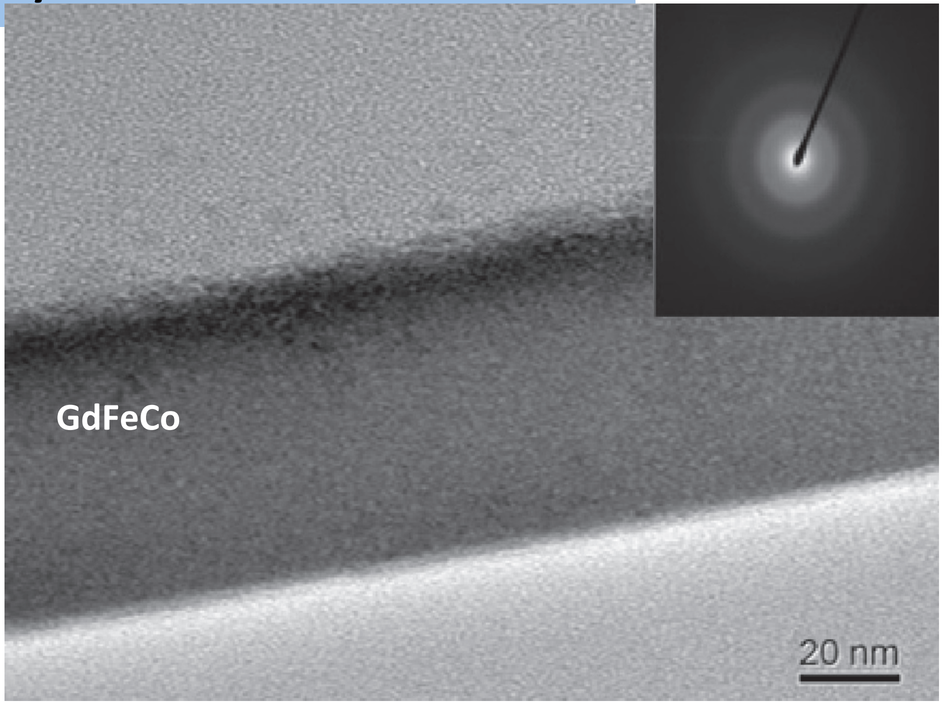
in semiconductors ~10^{18} cm^{-3}

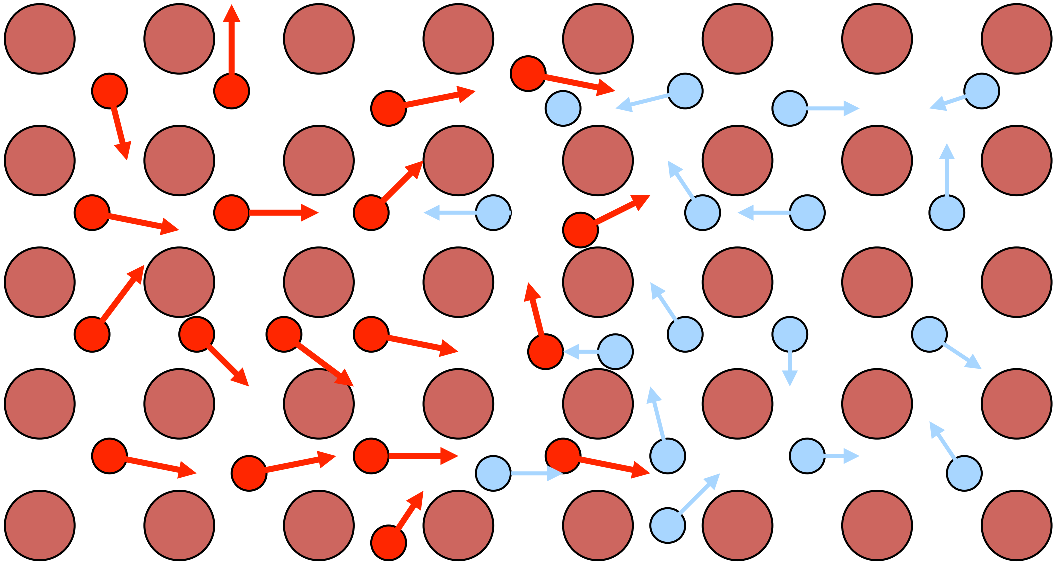
Semiconductors:

Phonons (lattice vibrations) are the dominant energy carriers in semiconductors, velocity ~10^3 m/s

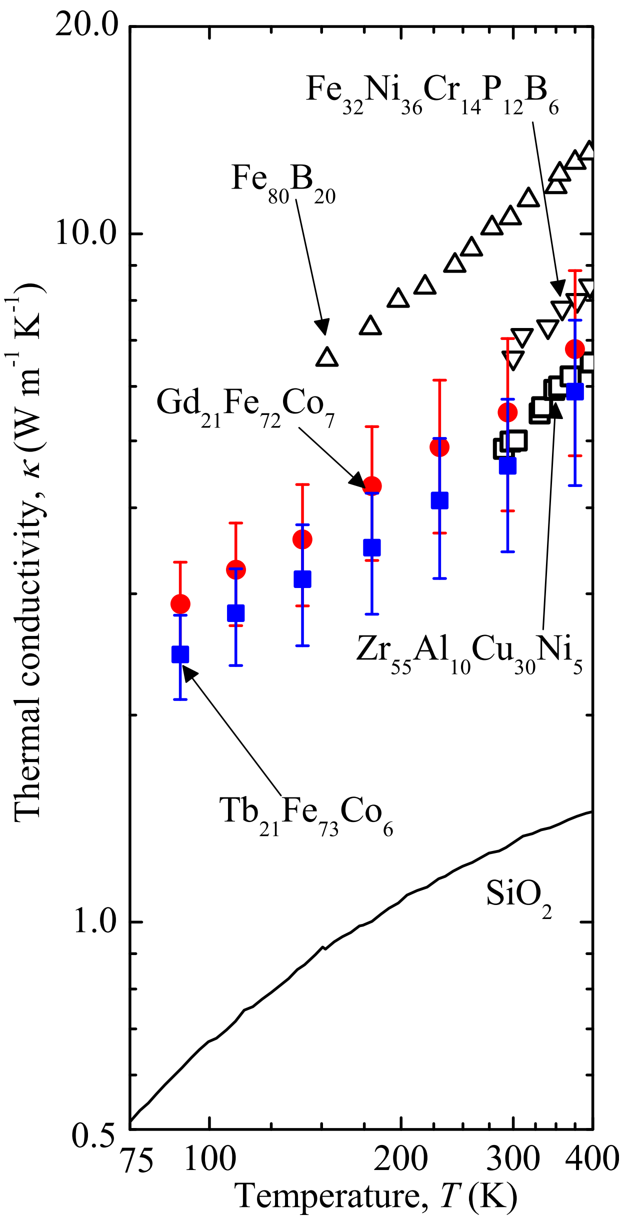
What happens if λ becomes very small in a metal?

Amorphous means no atomic order. Electrons scatter A LOT!!!!

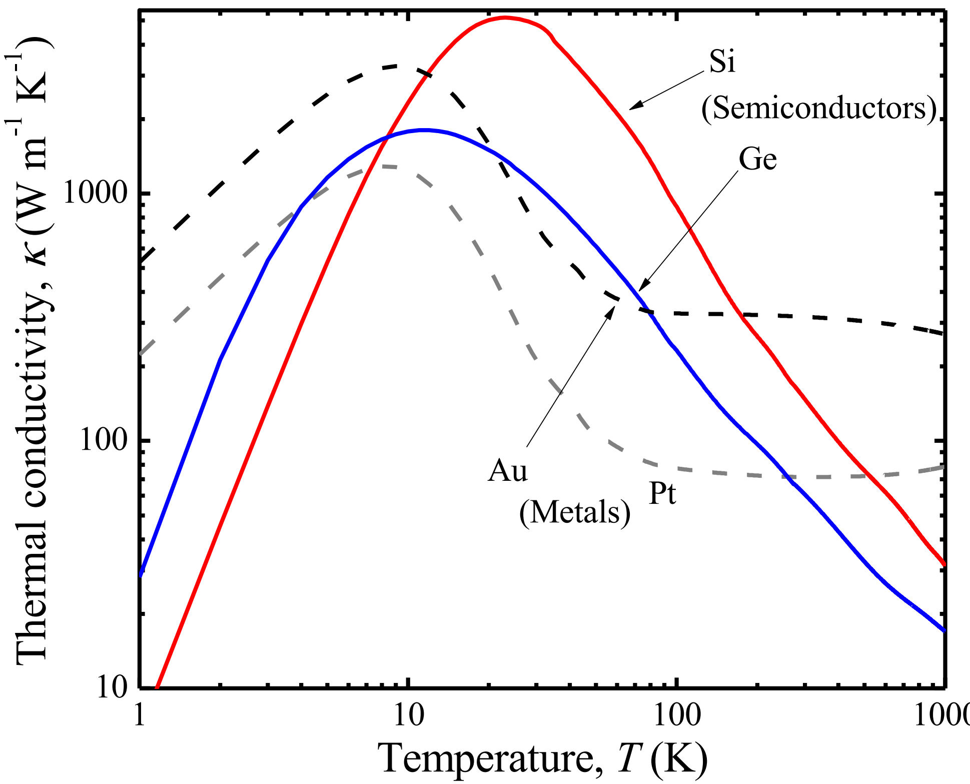




Thermal conductivity of amorphous metals

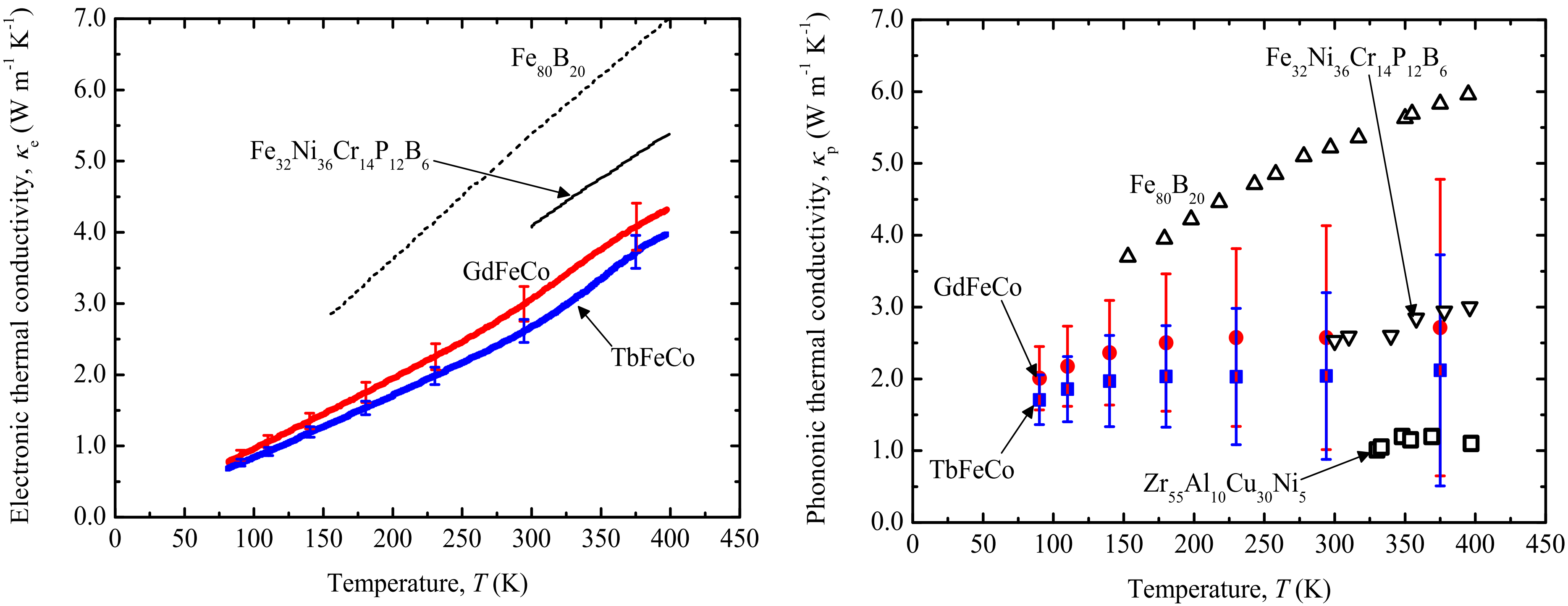


Compare to crystalline



BREAKDOWN…

Phonons contribute as much or more than electrons in amorphous metals



JOURNAL OF APPLIED PHYSICS **111**, 103533 (2012)

Contributions of electron and phonon transport to the thermal conductivity of GdFeCo and TbFeCo amorphous rare-earth transition-metal alloys

Patrick E. Hopkins,[1,a)] Manli Ding,[2] and Joseph Poon[2]
[1]*Department of Mechanical and Aerospace Engineering, University of Virginia, Charlottesville, Virginia 22904, USA*
[2]*Department of Physics, University of Virginia, Charlottesville, Virginia 22904, USA*

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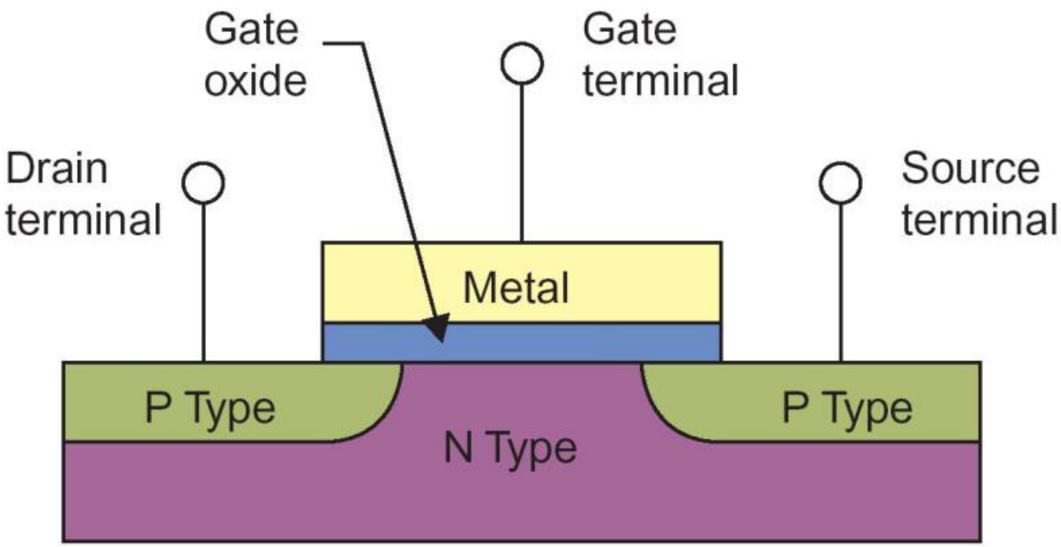
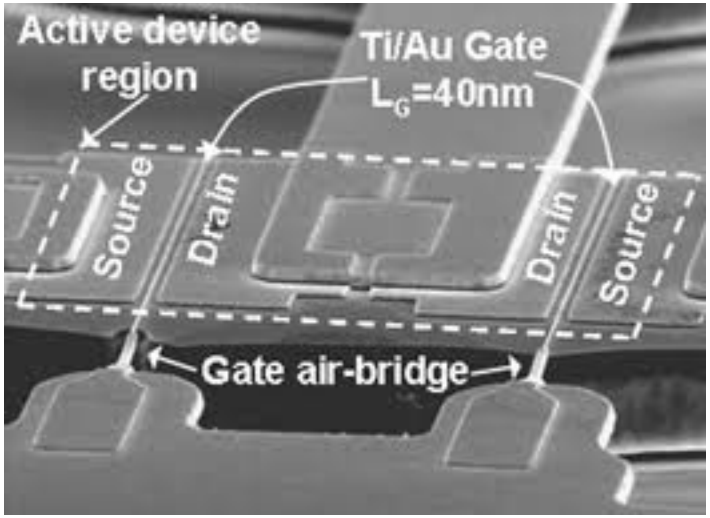
Nanodevices – interface problems

Electronic devices have length scales less than the thermal mean free paths. The various interfaces must be understood to mitigate the heat load.

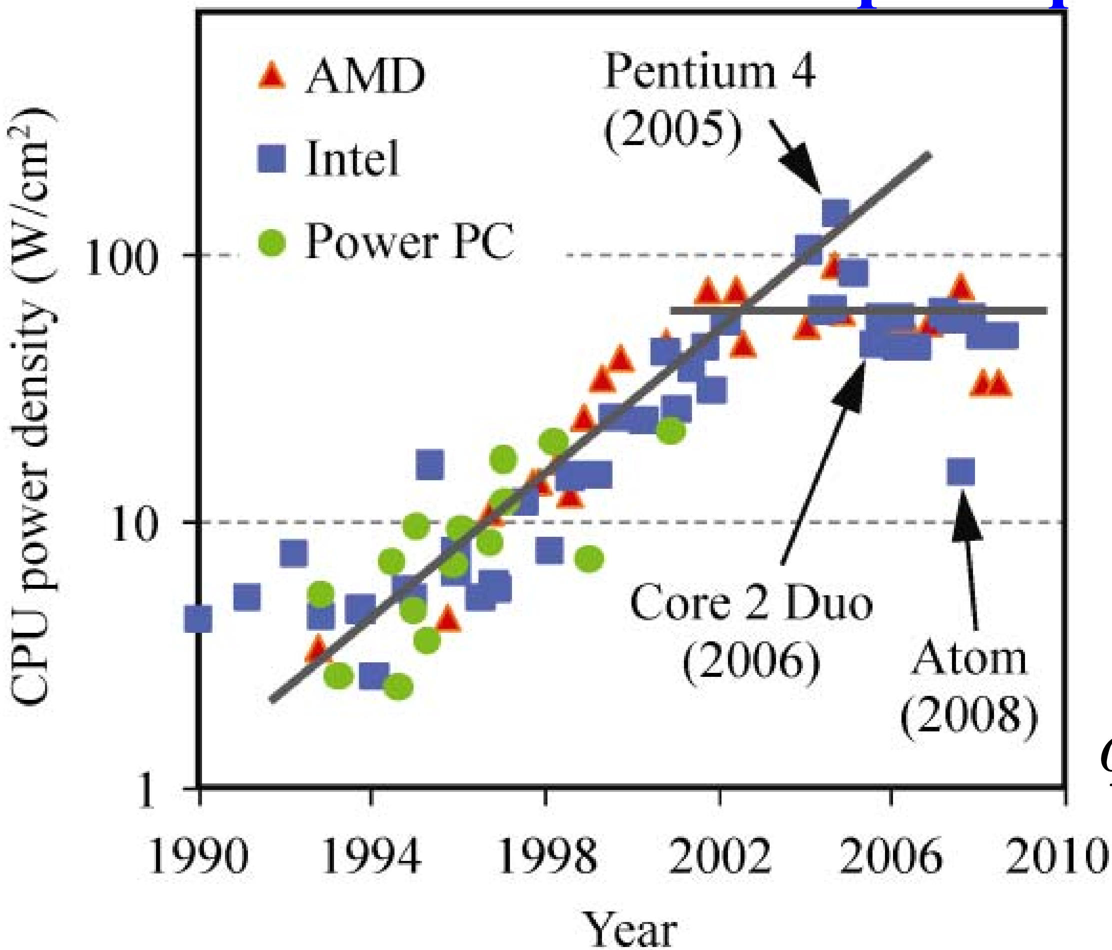




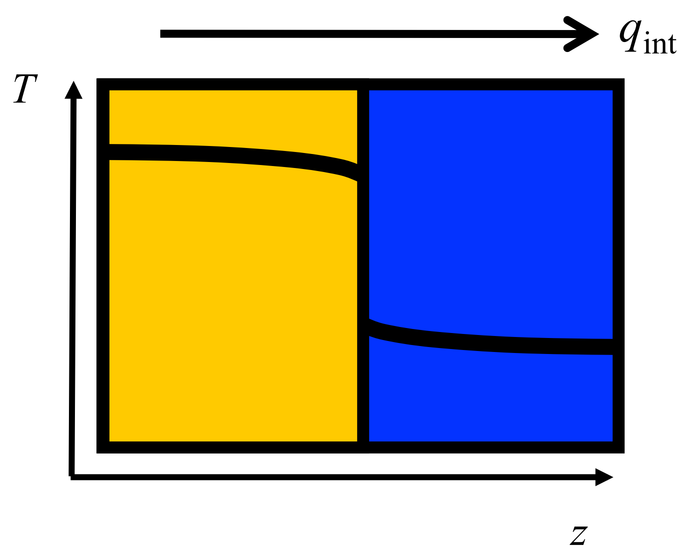
Silicon mean free paths at room temperature ~50 – 500 nm (it's a spectrum like photons)

Nanodevices – interface problems

Silicon device interfaces cause overheating
Sacrifice computer performance

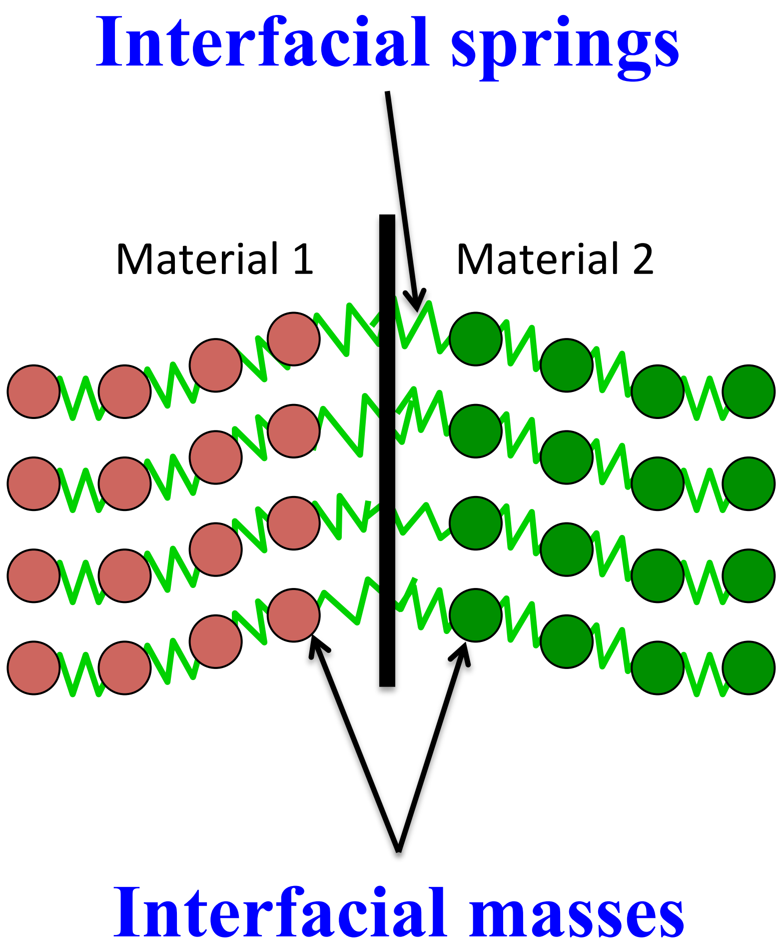


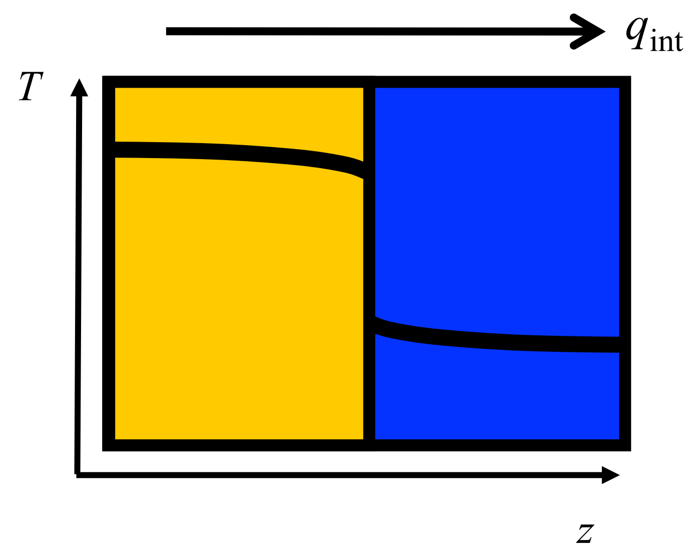
***Nano. Res.* 3, 147 (2010)**



$$q_{\mathrm{int}} = h_{\mathrm{K}} \Delta T = \frac{1}{R_{\mathrm{K}}} \Delta T$$

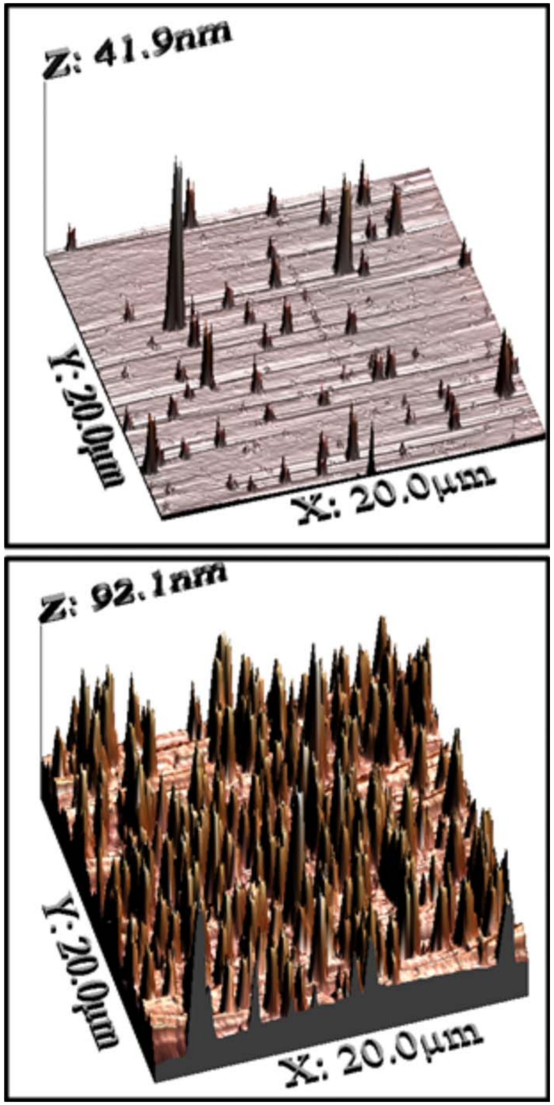
Let's just consider a mass spring problem!



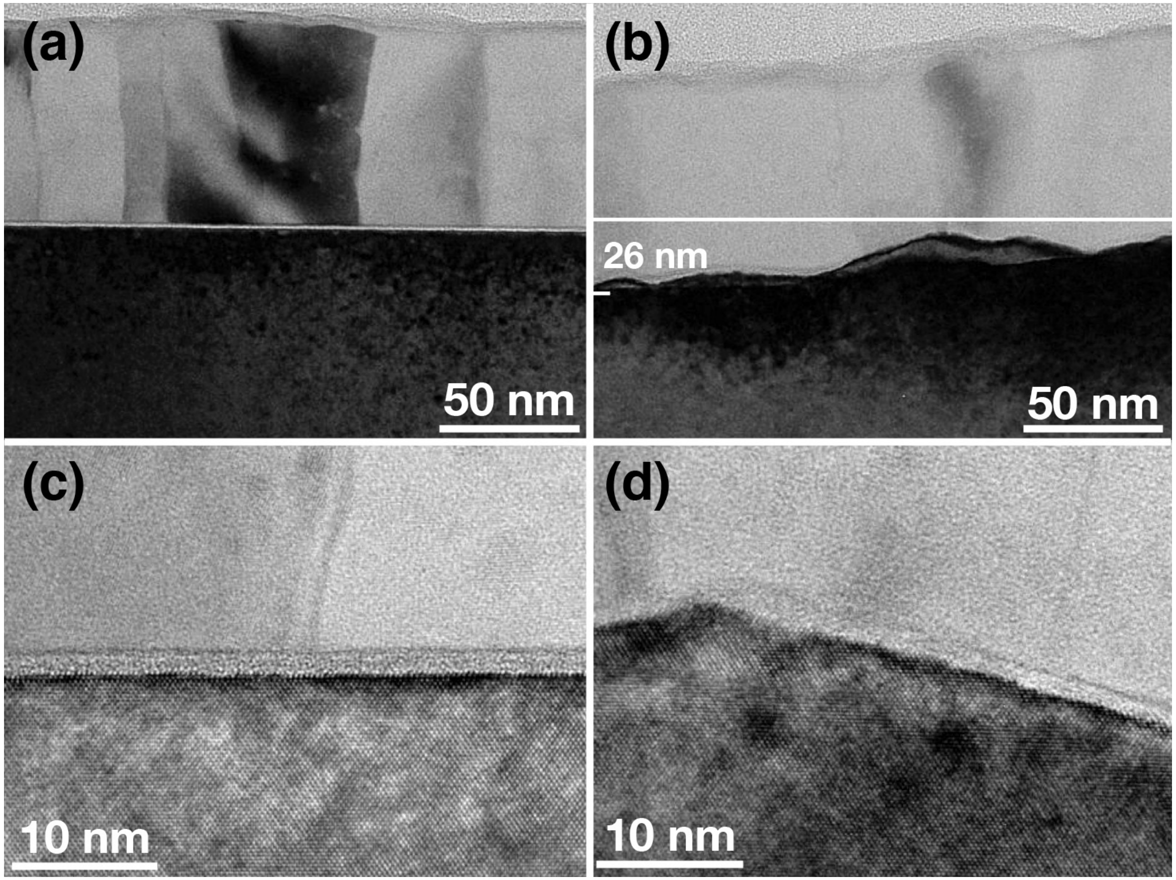


$$q_{\mathrm{int}} = h_{\mathrm{K}} \Delta T = \frac{1}{R_{\mathrm{K}}} \Delta T$$

Let's mess up some simple interfaces – Al/Si

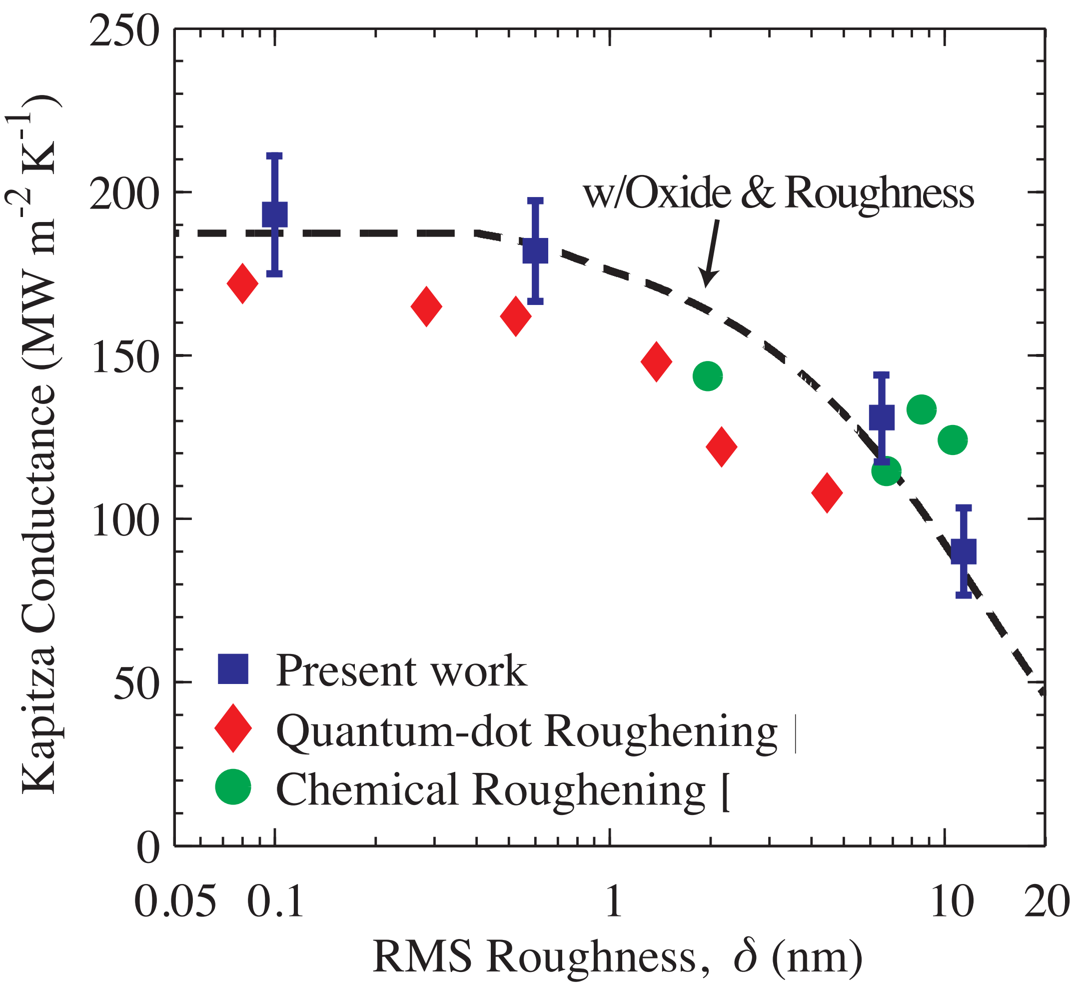


TMAH processed to change surface roughness

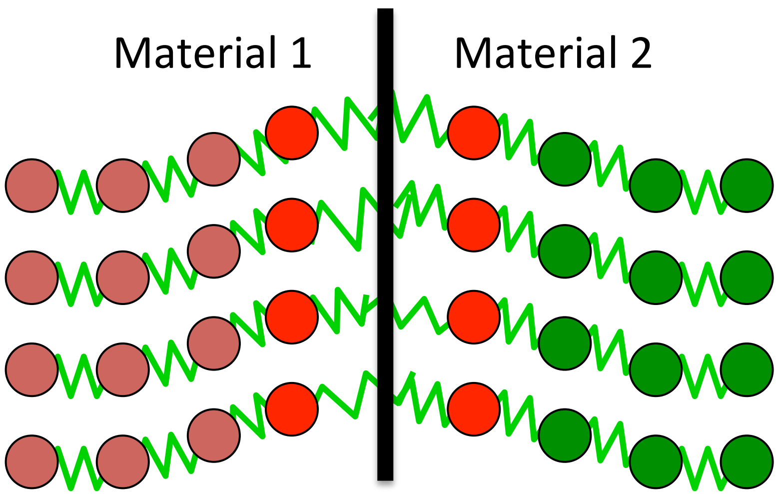


Hopkins *et al*., *Phys. Rev. B*. 82, 085307 (2010)
Duda and Hopkins, *Appl. Phys. Lett*. 100, 111602 (2012)

Roughness as a "knob" for thermal control



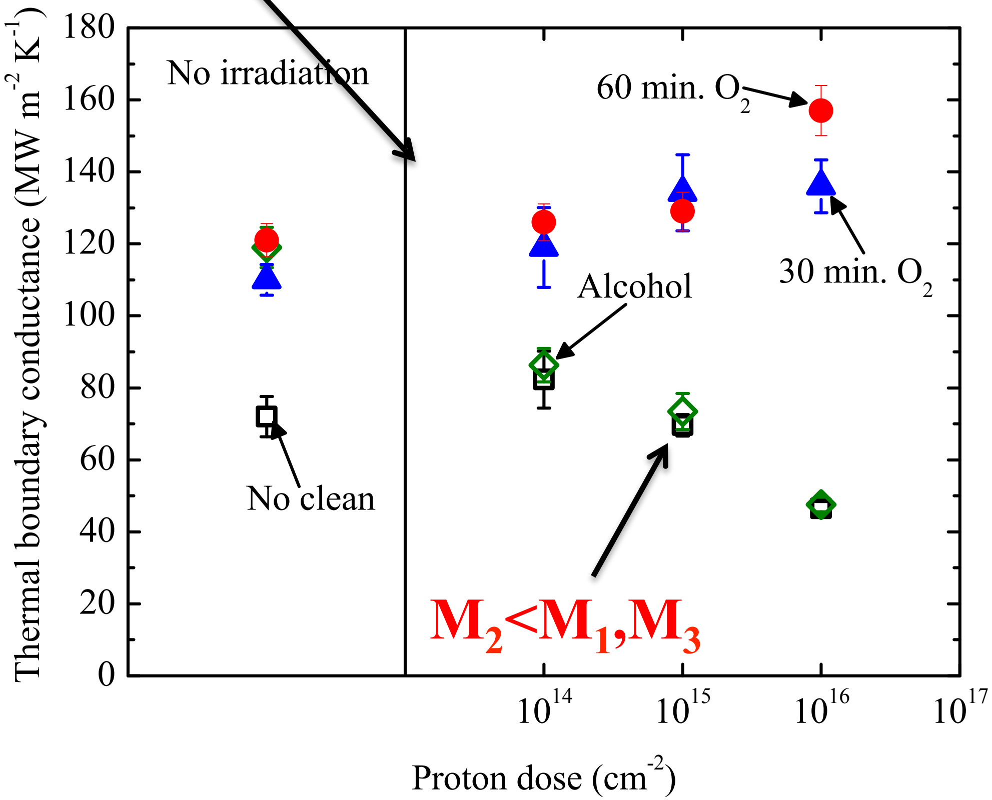
Change the arrangement of masses around the interface (disorder)



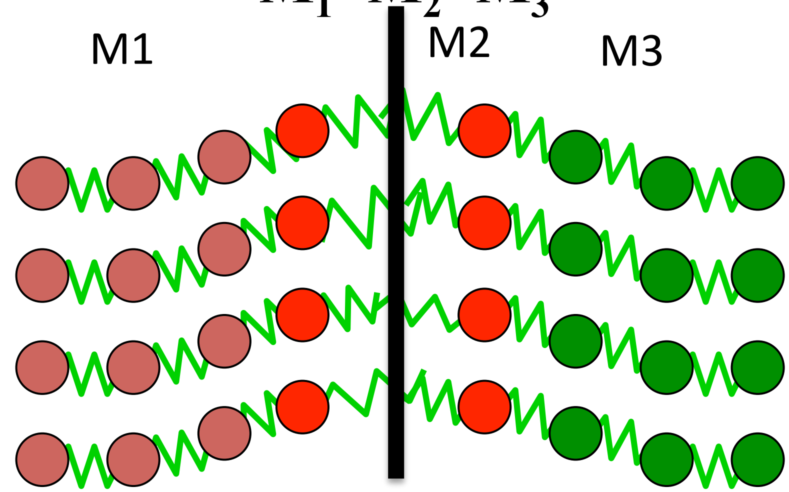
Duda and Hopkins, *Appl. Phys. Lett*. 100, 111602 (2012)

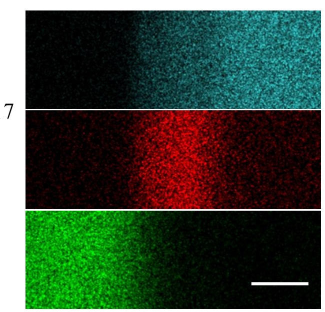
Can mass disorder *increase* TBC?

$M_1<M_2<M_3$



TBC can increase if $M_1<M_2<M_3$

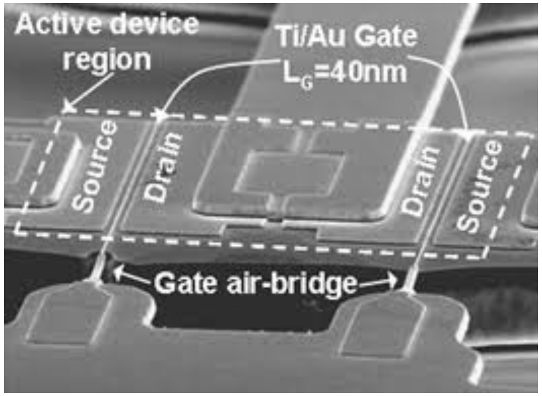




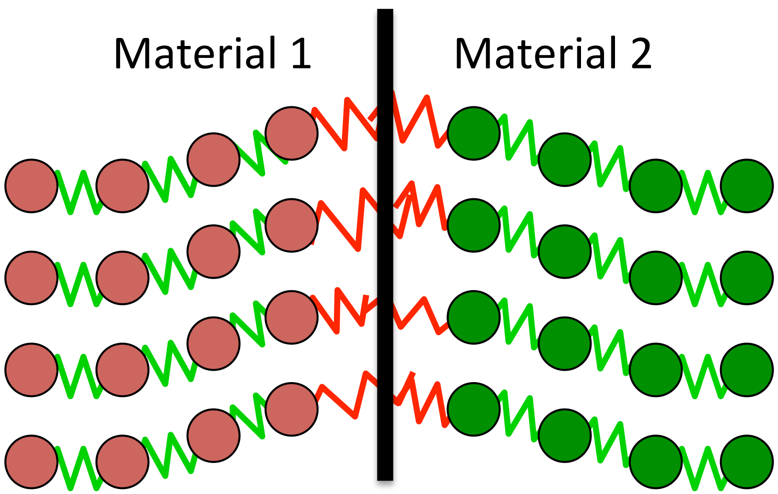
An interfacial mixing region creates an "impedance bridge" (Polanco and Ghosh, ECE)

Caroline Gorham *et al.*, to be presented next week at MRS

What about device contacts? Au/Si

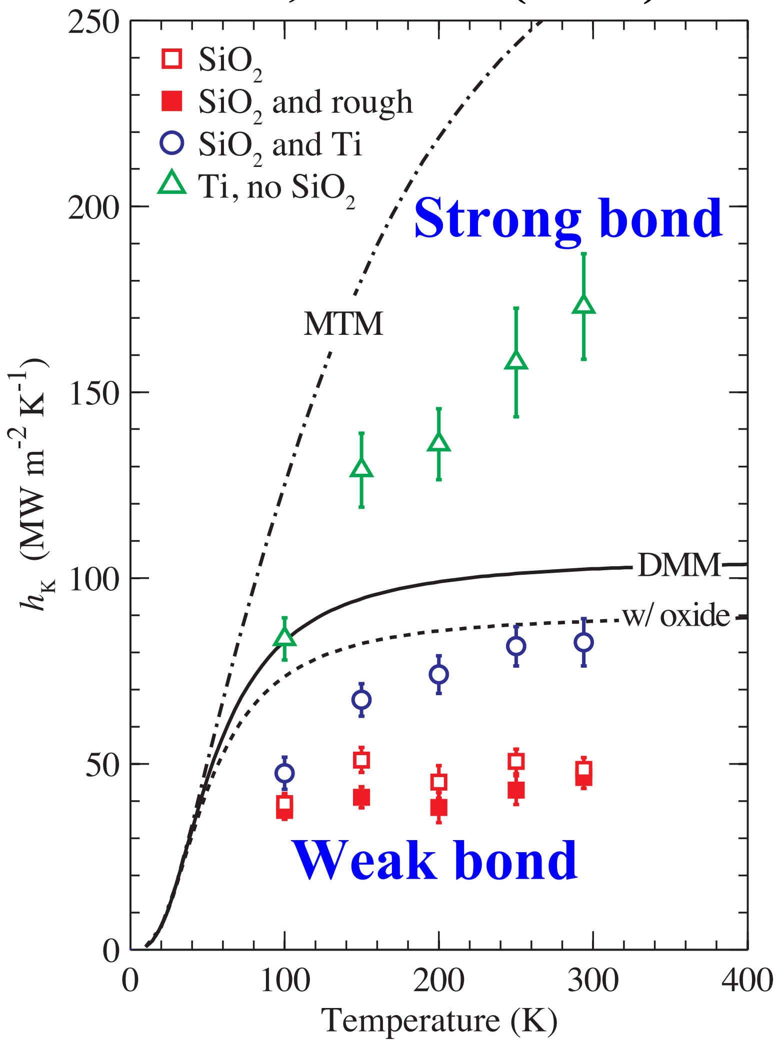


However, bonding plays a HUGE ROLE at the Au/Si interface



Change the springs around the interface (disorder)

Duda *et al. Appl. Phys. Lett.* 102, 081902 (2013)

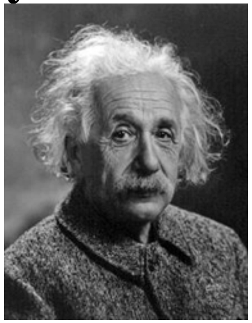


Outline

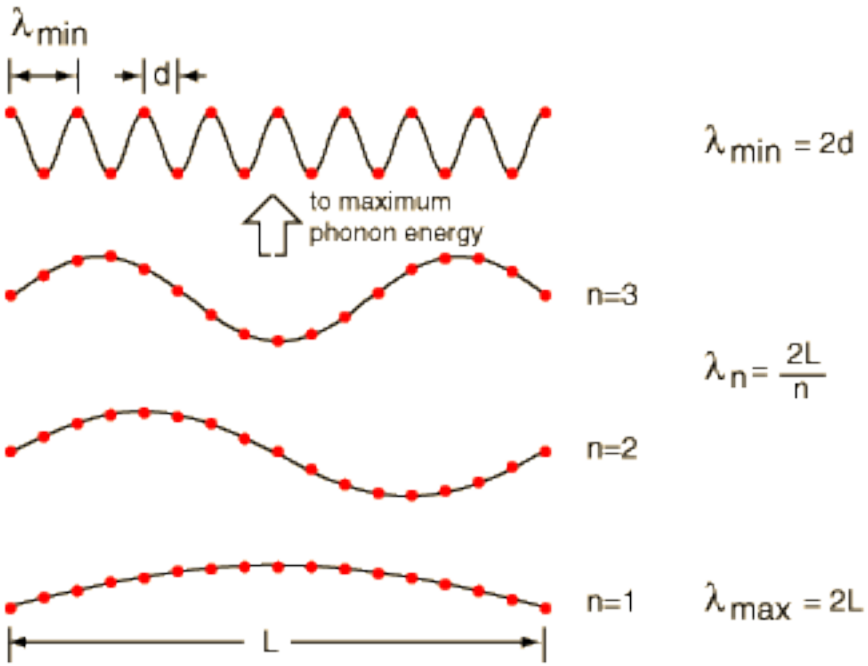
- **Thermophysics background**
- **Measurement of electron and phonon thermal properties on the nanoscale with time domain thermoreflectance – time scales and phenomena**
- **Example 1: Amorphous metals: electron AND phonon transport**
- **Example 2: Interfaces: disorder and adhesion**
- **Example 3: Exceptionally low thermal conductivity of organic semiconducting polymers: making Einstein proud**

"The Einstein oscillator"

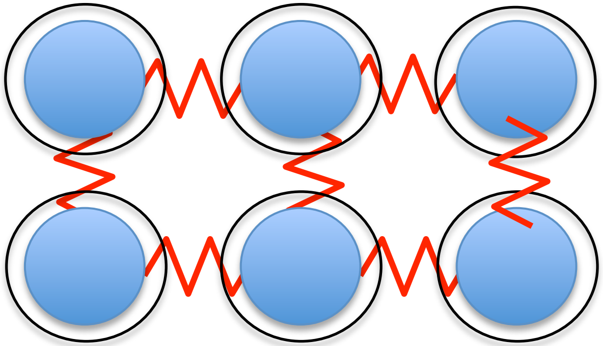
Vibrations of atoms are not coupled, they are independent with random phases



The phonon picture (coupled oscillators): several different wavelength in a lattice (many energies)



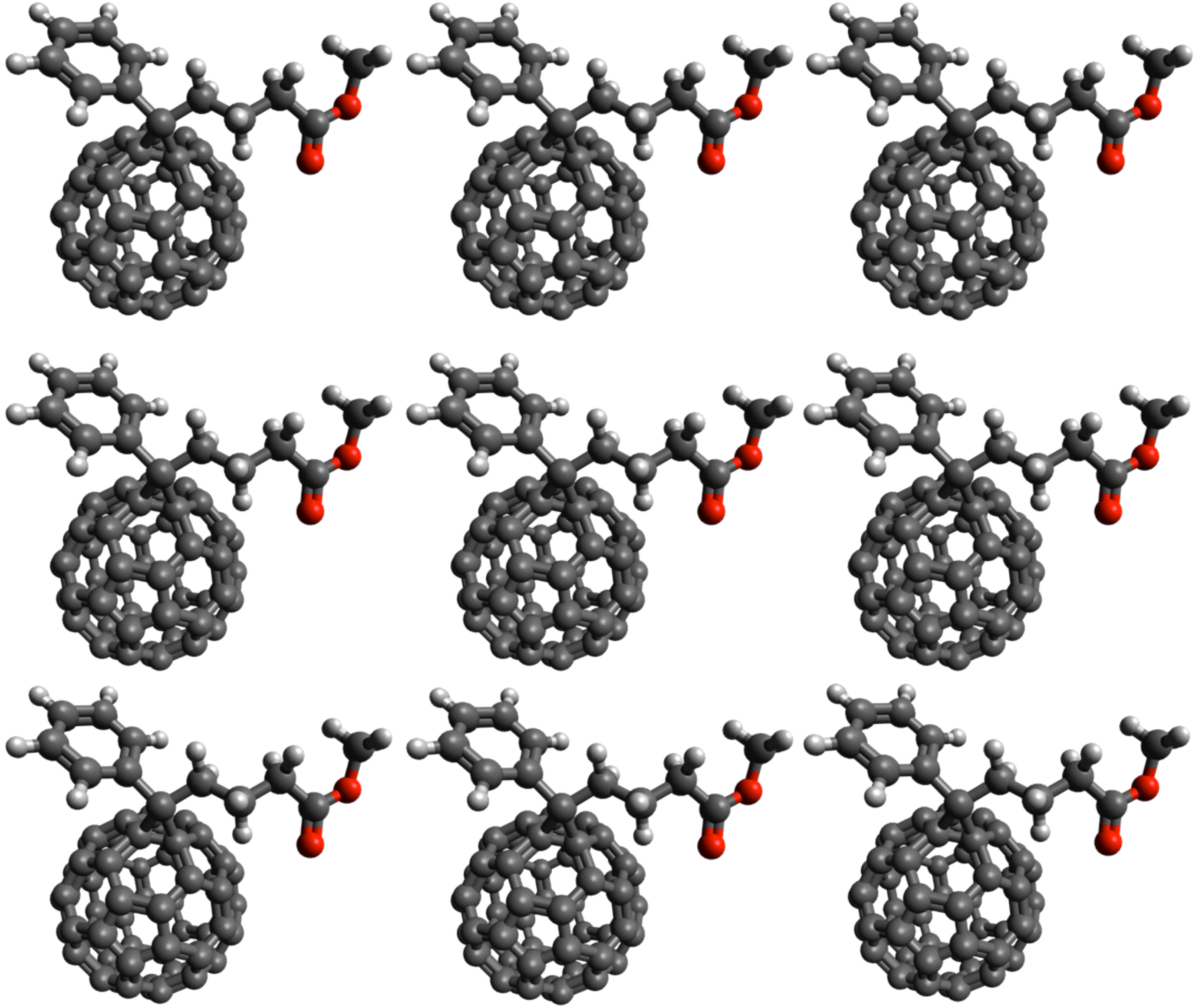
Single frequency of vibration of atom and energy "hops" from one site to another



"Springs" are very very weak

Weakly interacting buckyballs

[6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM) – an Einstein oscillator



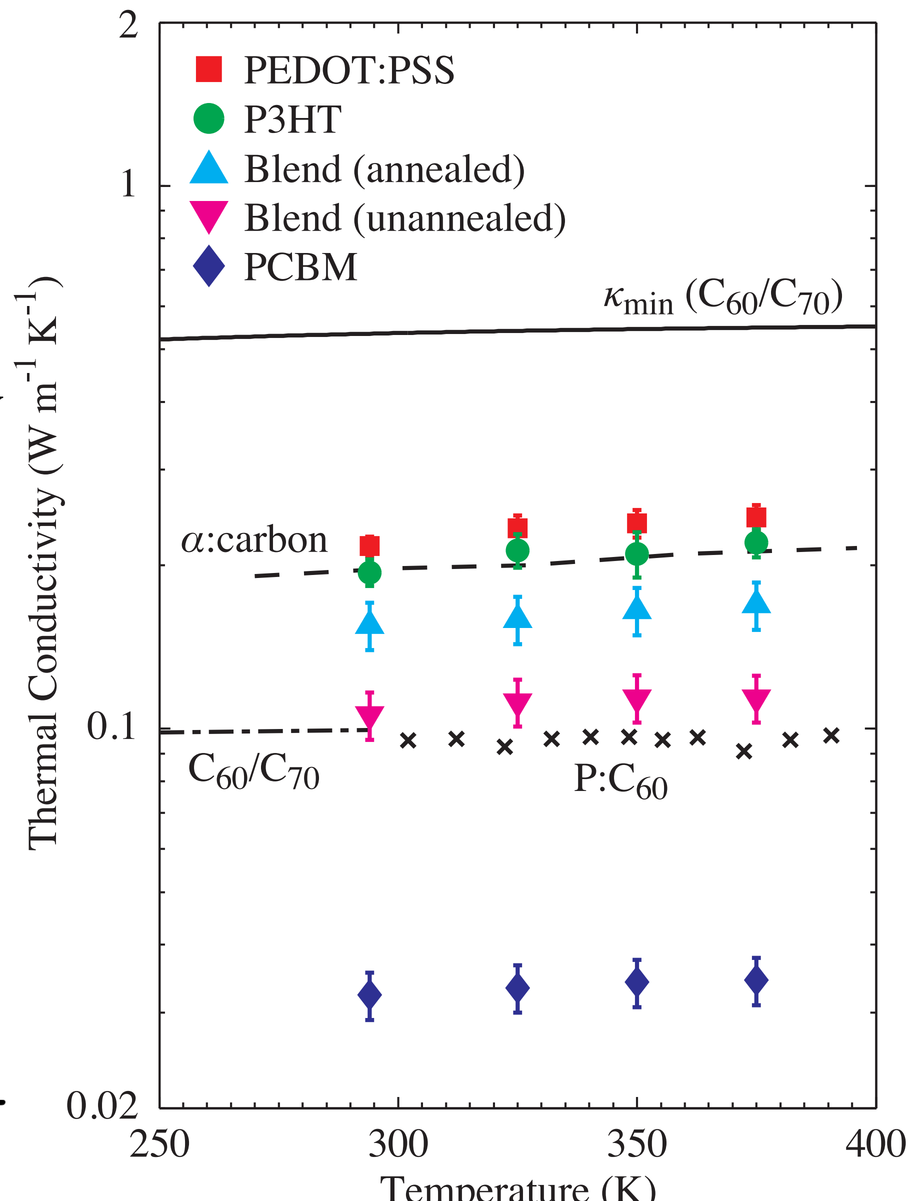
Thermal conductivity of thin film polymers

- **Annealing increases blend thermal conductivity by ~40%**

- **PCBM thermal conductivity 0.032 W m^{-1} K^{-1}**

- **Nearly 1.5 orders of magnitude less than theoretical minimum limit to thermal conductivity**

$$\kappa = \frac{1}{3} C v \lambda = \frac{1}{3} C v_g^2 \tau$$



Lowest thermal conductivity of ANY dense solid

PRL **110,** 015902 (2013) PHYSICAL REVIEW LETTERS week ending 4 JANUARY 2013

Exceptionally Low Thermal Conductivities of Films of the Fullerene Derivative PCBM

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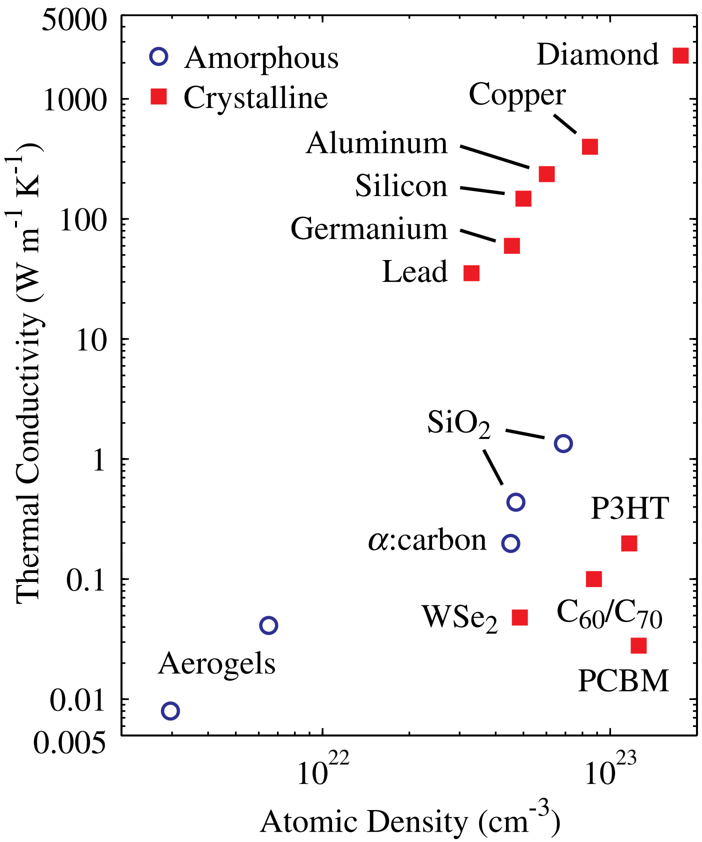
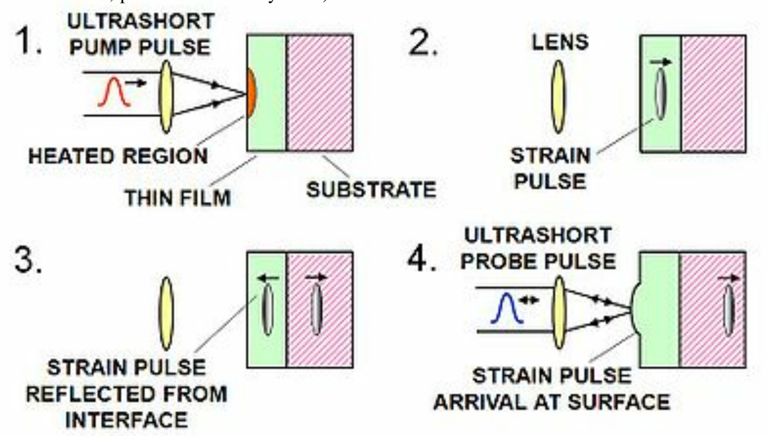
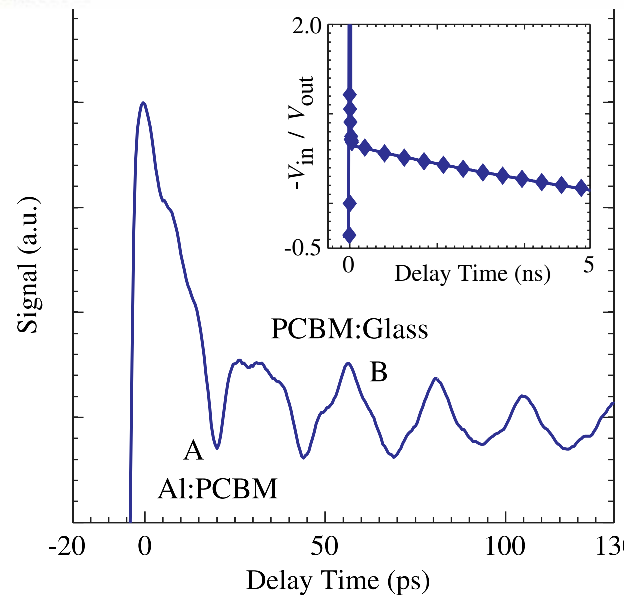
(Received 25 May 2012; revised manuscript received 30 October 2012; published 2 January 2013)



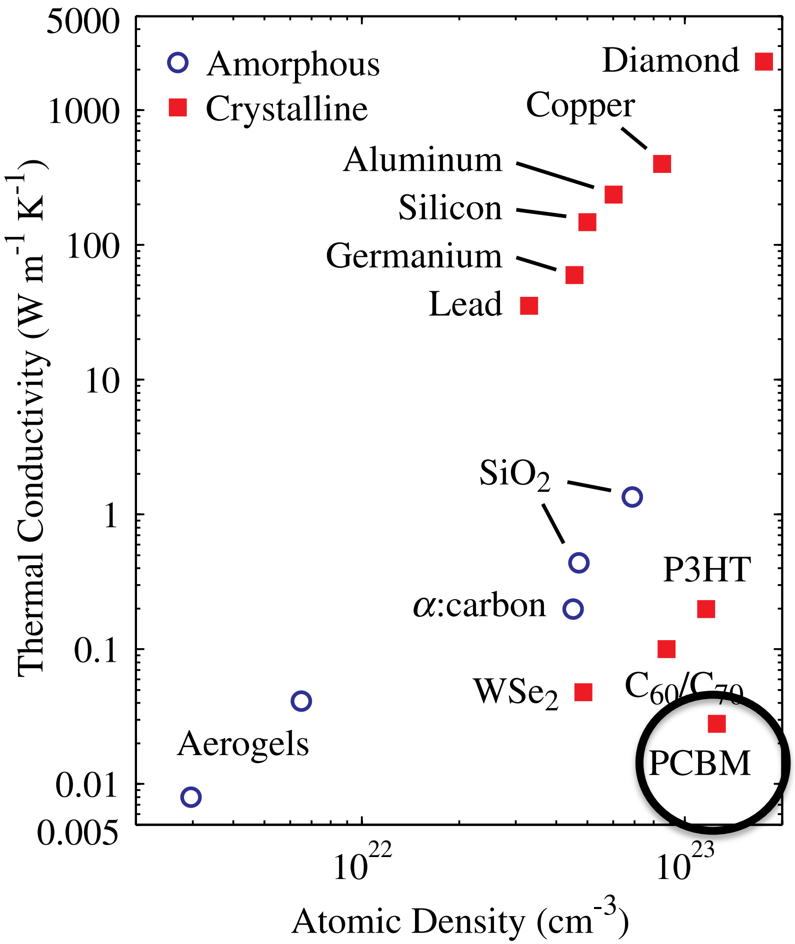
$$\kappa = \frac{1}{3} C v \lambda = \frac{1}{3} C v_g^2 \tau$$

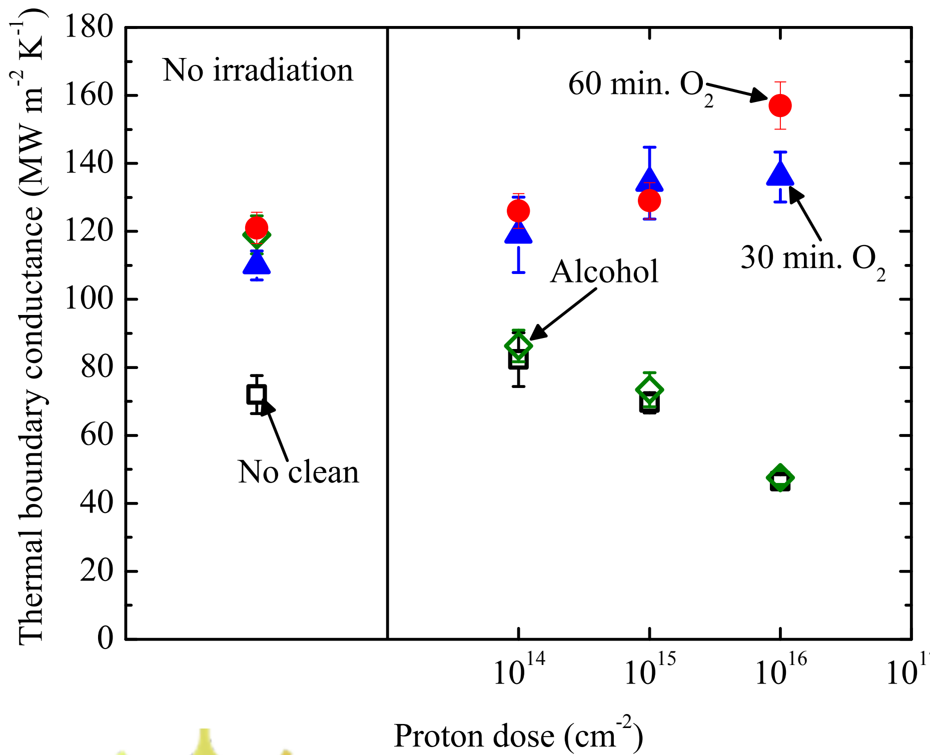




Summary – phopkins@virginia.edu & patrickehopkins.com

Nanostructuring can lead to remarkable thermal transport properties and some control of heat transfer





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