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EXCELENCIA SEVERO OCHOA

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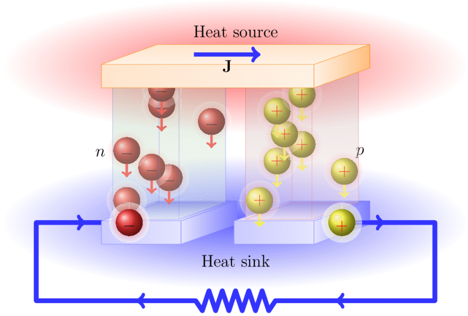
THERMAL TRANSPORT IN DISORDERED NANOSTRUCTURED MATERIALS

5th HPC Advisory Council Spain Conference & 10th RES Users 'Conference
León (Spain), September 20, 2016

Manipulating heat flow at the nanoscale

THERMOELECTRIC DEVICES

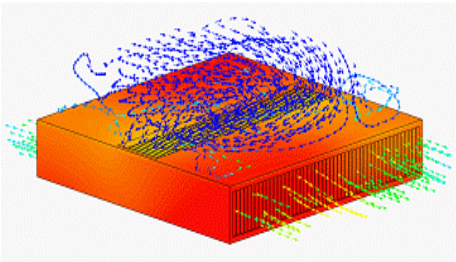
Conversion of ΔT into electricity through the Seebeck effect



$$ZT = S^2 T \frac{\sigma}{\kappa}$$

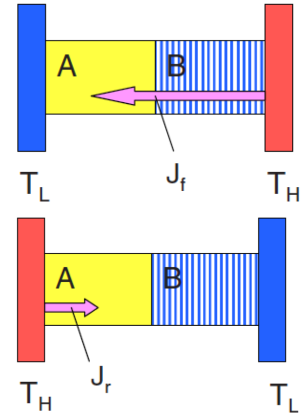
THERMAL MANAGEMENT

Heat dissipation at the nanoscale is becoming a major issue



New generation electron devices must be cooled

PHONONICS

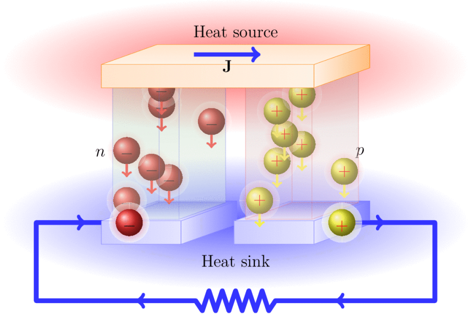


Manipulating heat flow to code and transmit information

Manipulating heat flow at the nanoscale

THERMOELECTRIC DEVICES

Conversion of ΔT into electricity through the Seebeck effect



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THERMAL MANAGEMENT

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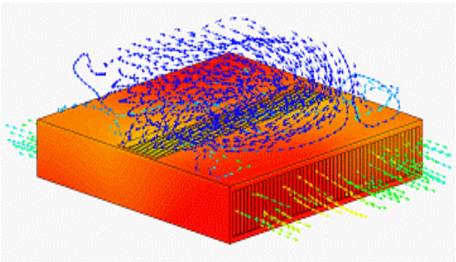

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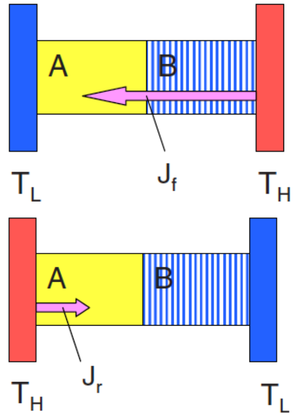


Manipulating heat flow to code and transmit information

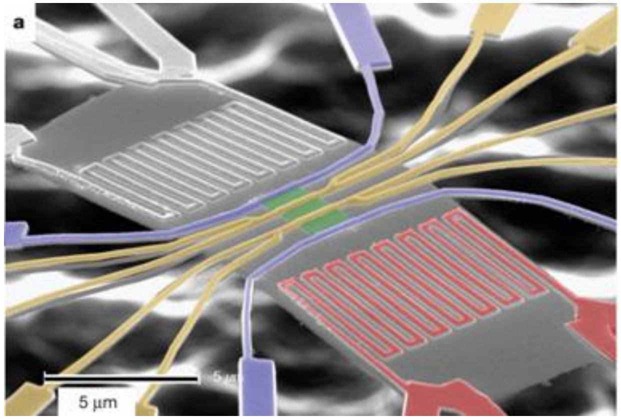
Introduction

$$ZT = S^2 T \frac{\sigma}{\kappa}$$

electrical conductivity

thermal conductivity

Thermoelectrics



Boukai *et al.*, Nature **451**, 168 (2008)

How do we increase ZT?

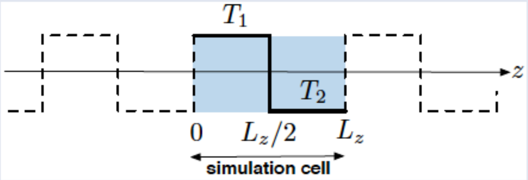
Either increasing the electrical conductivity or decreasing the thermal conductivity

❶ Molecular dynamics

- Si-Ge interactions modelled by the **Tersoff potential**
- use of **large-scale simulation cells** (up to $\mathcal{O}(10^6)$ atoms)
- LAMMPS code

❷ Non-equilibrium simulations

- **approach-to-equilibrium-MD**
  Melis et al., EPJ-B **87, 96 (2014)**



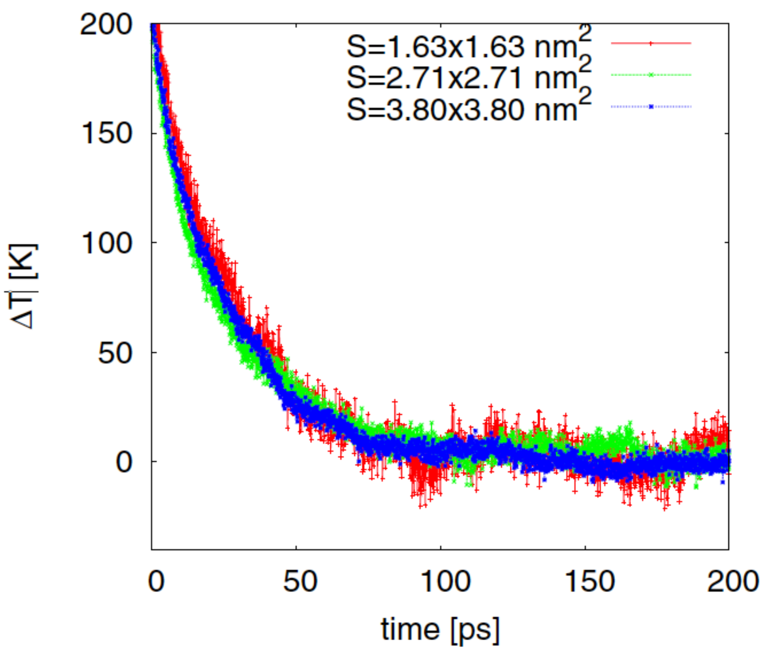
- average local temperature:
  $T_{i,ave}(t) = \frac{1}{L_z/2}\int_0^{L_z/2} T(z;t)dz$
- time-dependent temperature offset:
  $\Delta T(t) = T_{1,ave}(t) - T_{2,ave}(t)$
- fit κ on

$$\Delta T(t) = \sum_{n=1}^{\infty} C_n e^{-\alpha_n^2 \kappa t/\rho c_V}$$

$\Delta T(t)$ calculated on-the-fly in the AEMD run

FI-2014-1-0001/0003
Nanoporous silicon for thermoelectric applications

FI-2016-1-0022
Thermal transport in isotopically disordered Si NWs

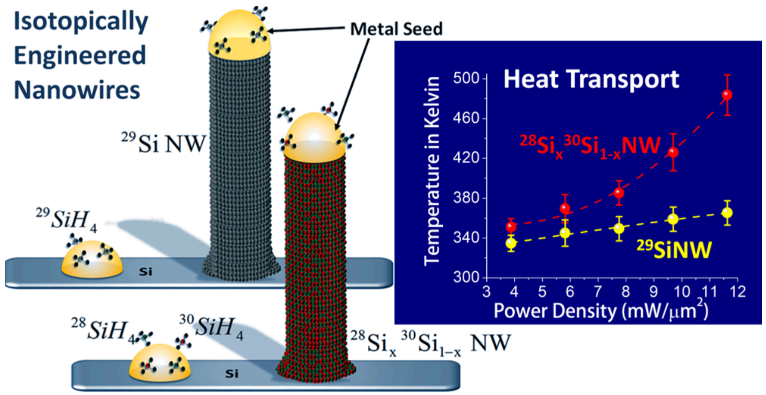


Melis *et al.*, Eur. Phys. J. B **87**, 96 (2014)

Tuning thermal transport in Si NWs by isotope engineering

Isotope engineering in Si NWs

Isotope blends represent a textbook approach to increase the ZT in a semiconductor



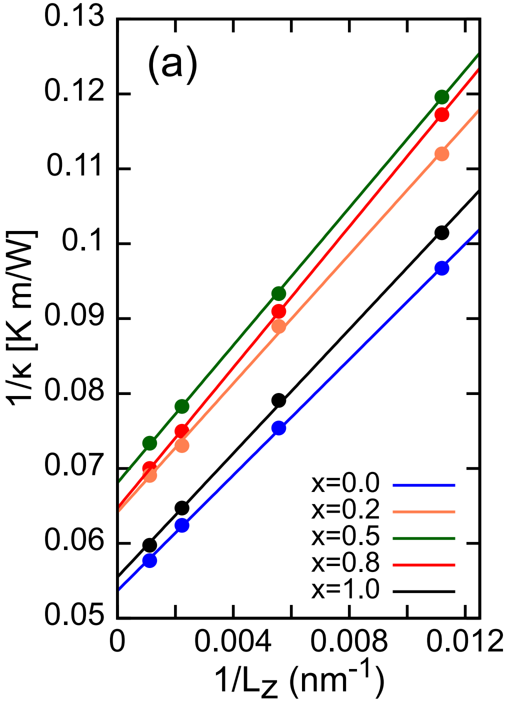
Mukherjee *et al.*, Nano Lett. **15**, 3885 (2015)

Isotopes have <u>different masses</u>, but <u>the same electron shell</u> configuration. Therefore, the electrical conductivity, σ is preserved, while —as by adding different isotopes one is adding scattering centres for the incoming phonons— κ will decrease, leading to the corresponding increase of ZT.

We study heat transport in $^{28}Si_x{}^{30}Si_{1-x}$ NWs as a function of the composition x and account for the nonuniform radial distribution observed in the experiments of Mukherjee and coworkers.

Isotope engineering in Si NWs

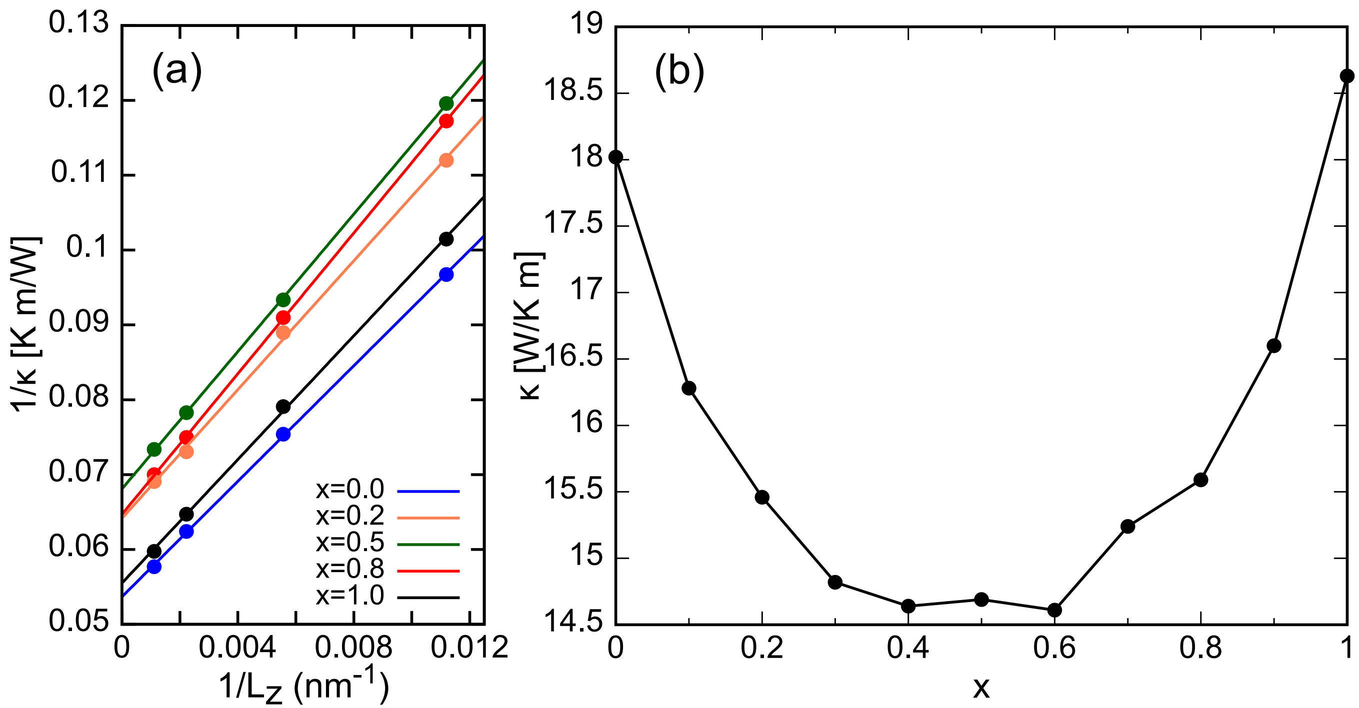
$^{28}Si_{1-x}{}^{30}Si_x$ NWs, 15 nm diameter



To get rid of finite size effect one must calculate κ for increasing cell sizes and extrapolate its value in the $\kappa^{-1}=\kappa^{-1}(L_z^{-1})$ plot for $L_z^{-1}\text{->}0$ (i.e. $L_z\text{->}\infty$)

Isotope engineering in Si NWs

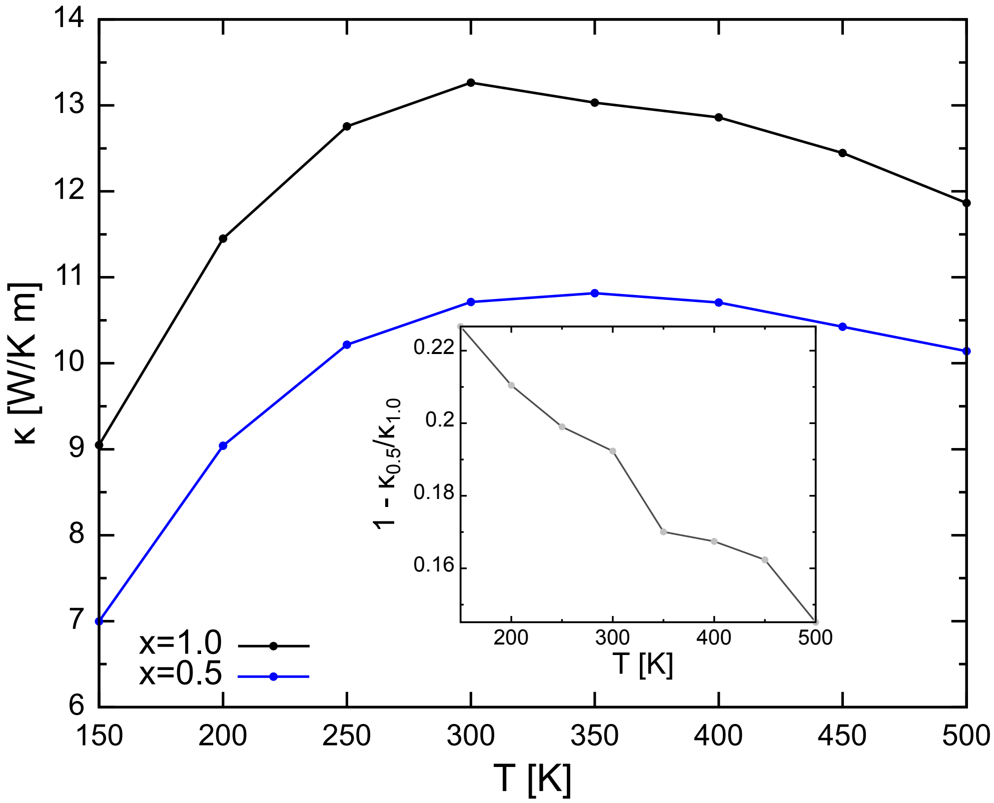
$^{28}Si_{1-x}{}^{30}Si_x$ NWs, 15 nm diameter



We obtain a *U*-shape curve similar to previously reported data of $Si_{1-x}Ge_x$ alloys ⇒ a precise control of the composition is not required to achieve the maximum reduction of κ, around 20% with respect to isotope purified NWs

Isotope engineering in Si NWs

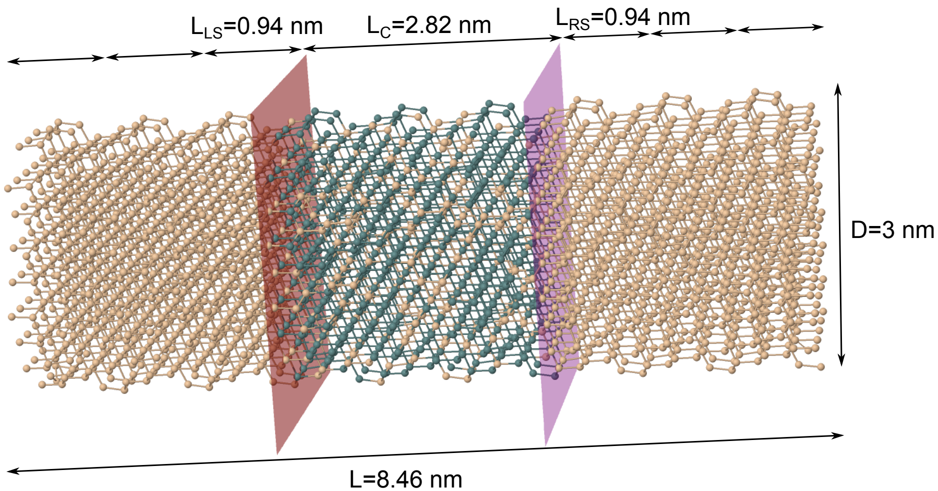
$^{28}Si_{0.5}{}^{30}Si_{0.5}$ NWs, 15 nm diameter



At **high temperature** isotopes are somewhat **less efficient** to reduce the thermal conductivity

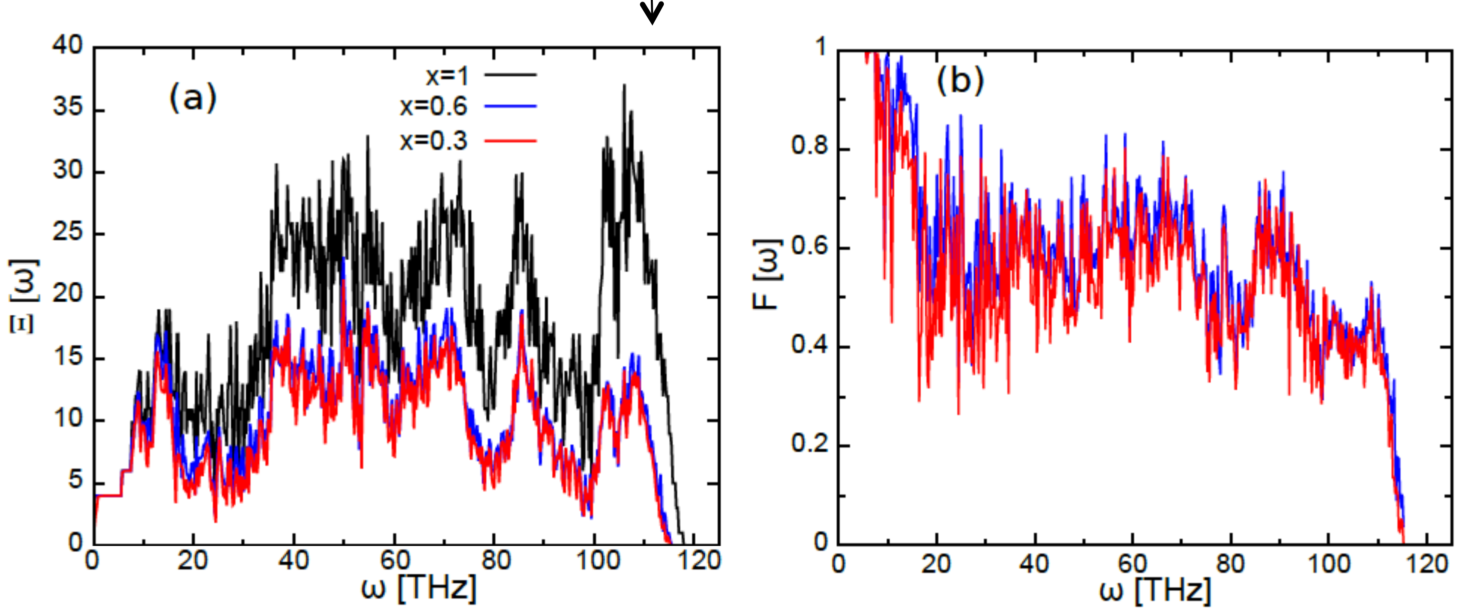
This observation suggests that it's worth while giving a look at the (very) low temperature regime, but there MD results are not reliable because of quantum effects

Isotope engineering in Si NWs



We tackle the low temperature limit within **nonequilibrium Green's functions**

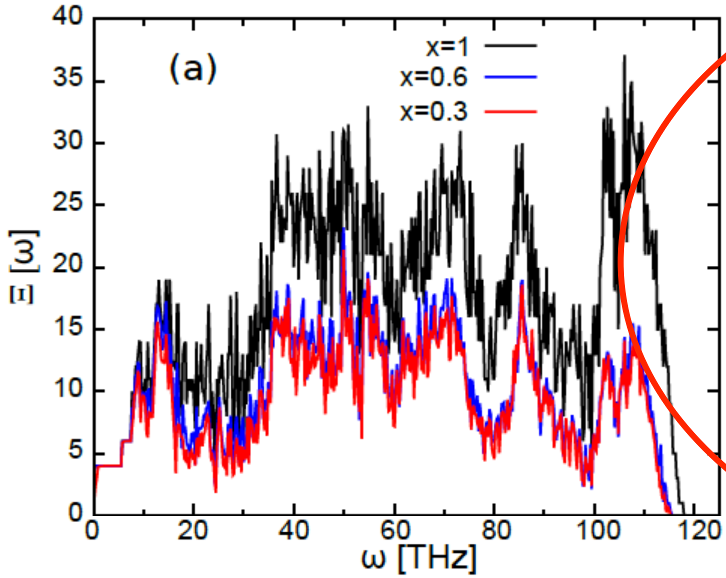
The conductance in harmonic approximation is calculated as the <u>transmission probability</u> of scattering states

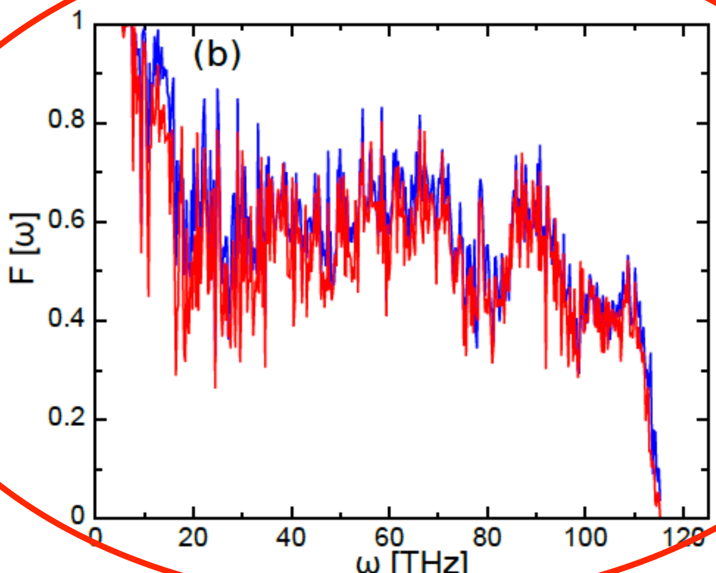


Isotope engineering in Si NWs

A substitutional isotope defect does not distort the host lattice, thus scattering mostly comes from short wavelength phonons

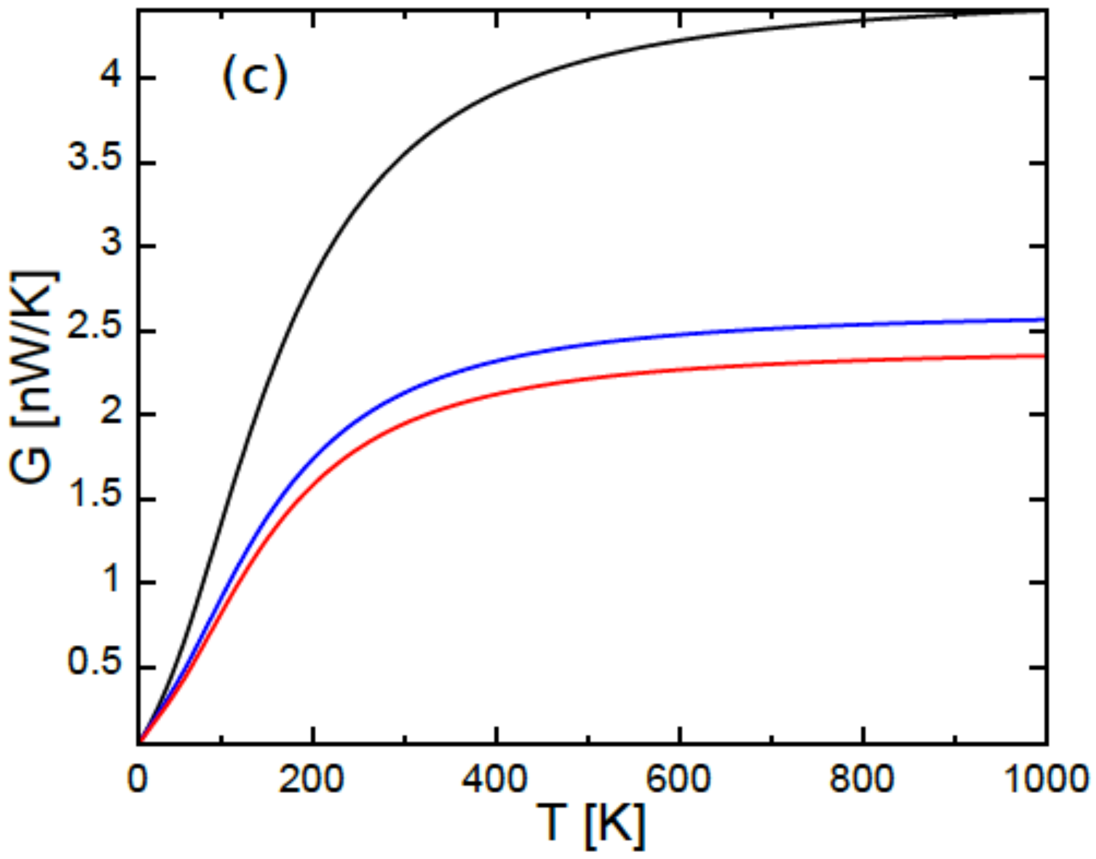
These results suggest that isotope engineering can be used to implement a **phonon low-pass filter** that mostly suppress midrange and high phonon frequencies



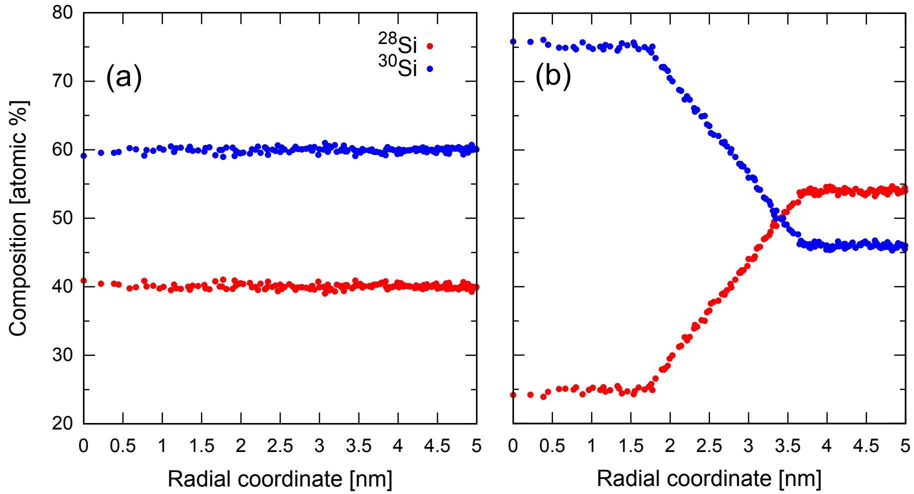


Isotope engineering in Si NWs

As hinted by the high temperature MD results, in the very low temperature regime, **reductions of κ of up to the 50% can be achieved**

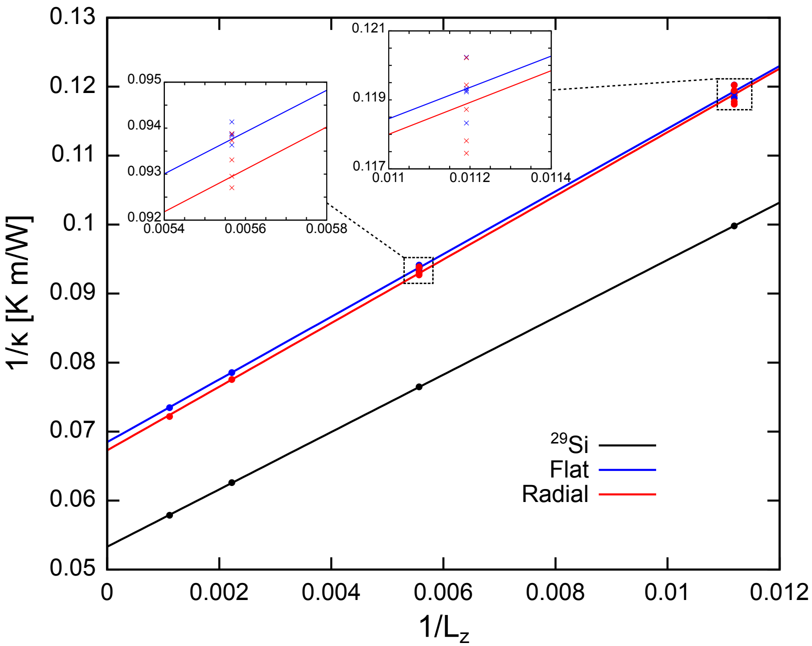


Isotope engineering in Si NWs



Finally, we compared different radial profiles for a $^{28}Si_{0.4}{}^{30}Si_{0.6}$ NW: (left) A uniform distribution and (right) Accumulation of heavy isotopes in the wire core as observed experimentally

We did **not** detect a sizeable difference between the two cases



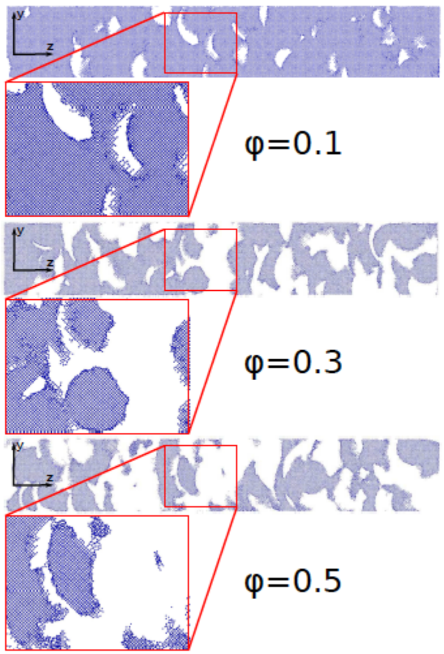
This results is not unexpected. The non-uniform radial profile studied can be seen as a coaxial structure with a $^{28}Si_{0.25}{}^{30}Si_{0.75}$ core and a $^{28}Si_{0.55}{}^{30}Si_{0.45}$ shell and we have shown that a $^{28}Si_x{}^{30}Si_{1-x}$ NWs with x=0.25 and x = 0.55 have roughly the same κ

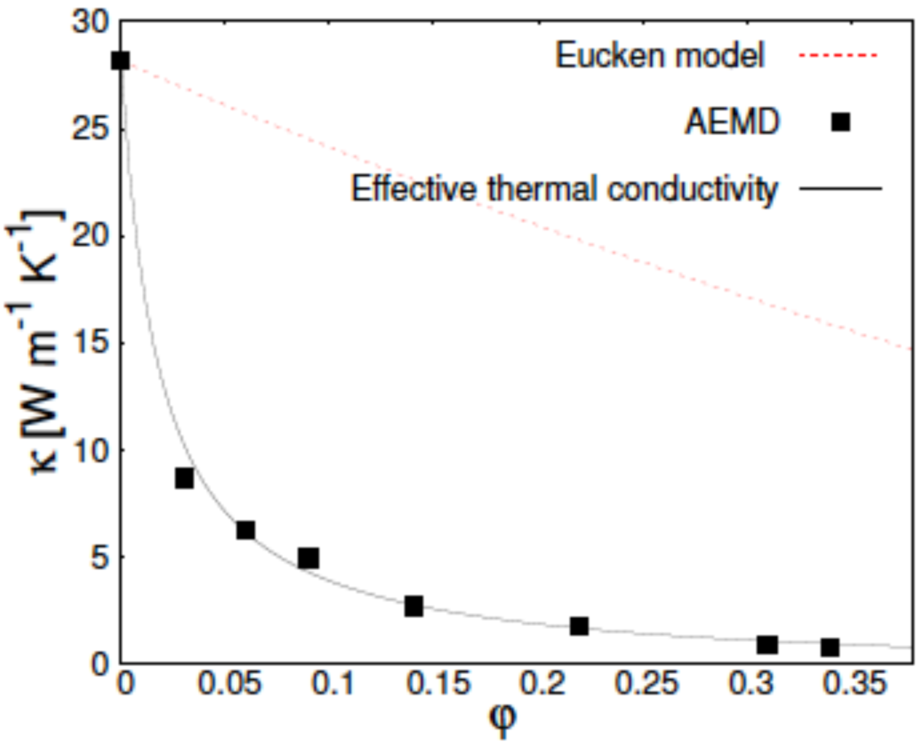
Thermal transport in porous Si NWs

Porous Si NWs

It has been shown that the thermal conductivity can be reduced by

(i) nanopores in a bulk material
(ii) surface scattering in nanowires





R. Dettori , C. Melis, X. Cartoixà , R. Rurali and L. Colombo, Phys. Rev. B **91,** 054305 (2015)

It has been shown that the thermal conductivity can be reduced by

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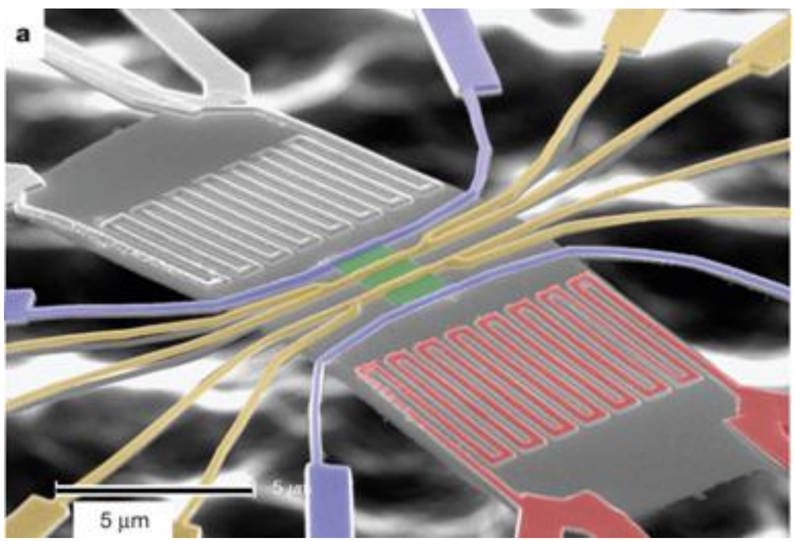

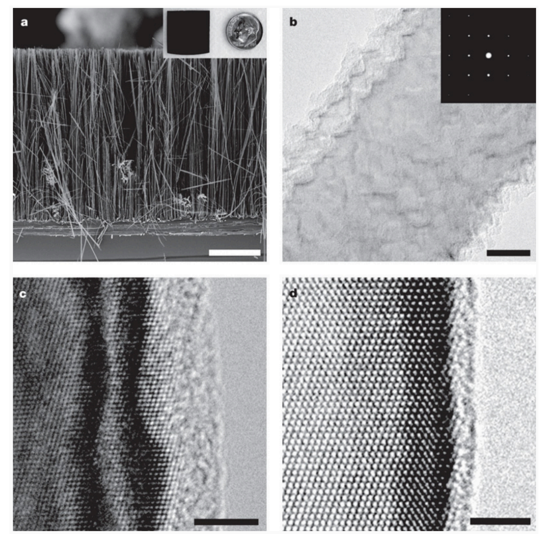

Hochbaum *et al.*, Nature **451**, 163 (2008)

Boukai *et al.*, Nature **451**, 168 (2008)

Porous Si NWs

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(i) nanopores in a bulk material
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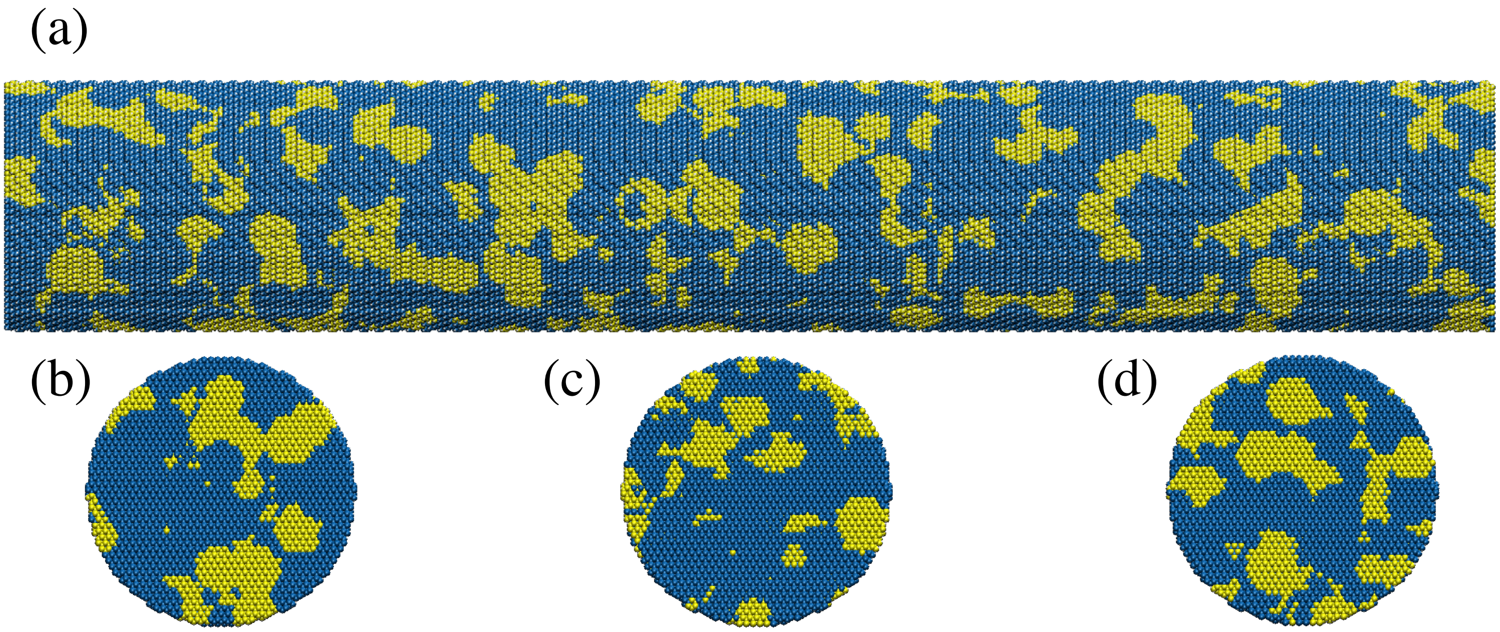
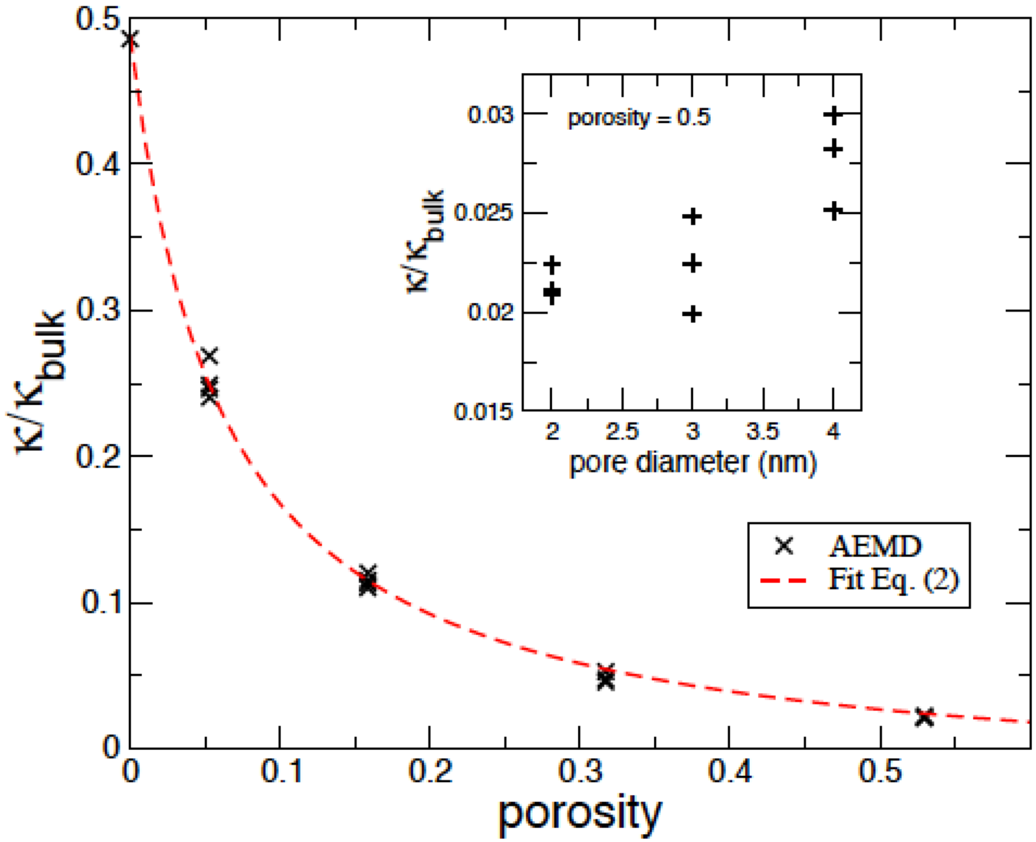
Why not bringing these two features together: **porous Si nanowires**



Porous Si NWs



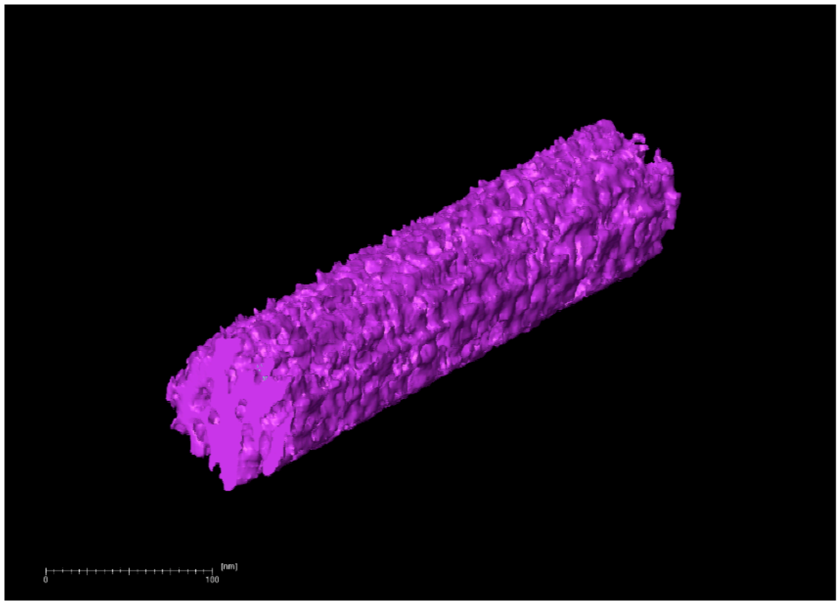
15 nm diameter SiNWs; pores of 3 nm

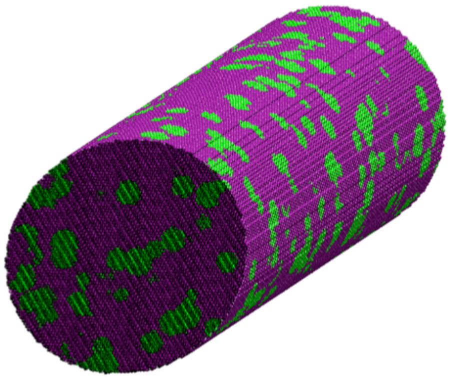
- Boundary scattering alone accounts for a reduction of a factor of two for the pristine (ϕ=0) NW with respect to bulk
- A rather low porosity ϕ=0.3 results in an additional reduction of one order of magnitude (κ/κ_{bulk}~0.05)
- We set up a predictive model, which provides an excellent agreement with the MD results

$$\frac{\kappa}{\kappa_{\text{bulk}}} = \frac{1-\varphi}{1+\frac{\varphi}{2}+\frac{3\varphi}{2d_p}\Lambda_{\text{bulk}}+\frac{\beta}{d_{\text{NW}}}\Lambda_{\text{bulk}}}$$

Porous Si NWs

pSi NWs electrical conductivity is, at least in principle, tunable by gas doping, thus their ZT could be not-so-bad…





Talos200X STEM tomography at 200kV			
Image size:	2kx2k	Frame time:	22 s
Tilt range:	-67° — 78°	Tilt step:	1°

Talos200X STEM tomography at 200kV			
Image size:	708x2048x495	Binning:	1
Method:	SIRT		

Acknowledgements

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Want to know more???

rrurali@icmab.es

SOME READING…:

These works

- M. Royo and R. Rurali, Phys. Chem. Chem. Phys. (2016), doi:10.1039/C6CP04581B
- X. Cartoixà. R. Dettori, C. Melis, L. Colombo, and R. Rurali, Appl. Phys. Lett. **109**, 013107 (2016)

Review papers on NWs

- R. Rurali, Rev. Mod. Phys. **82**, 427 (2010)
- M. Amato, M. Palummo, R. Rurali, and S. Ossicini, Chem. Rev. **114**, 1371 (2014)
- M. Amato and R. Rurali, Progr. Surf. Sci. **91**, 1 (2016)

Thank you for your attention!

Whenever anyone says, 'theoretically' they really mean, 'not really'
Dave Parnas