Effects of colored disorder on the heat conductivity of SiGe alloys from first principles

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Introduction

Lattice thermal conductivity is critical for the performance of silicon-based thermoelectric (TE) devices.

- Thermoelectric figure of merit

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

Thermal conductivity $\kappa = \kappa^{el} + \kappa^{l}$. For TE devices based on doped silicon, $\kappa \approx \kappa^{l}$.
The lattice thermal conductivity is estimated through the **Quasi-Harmonic Green-Kubo** formula:

$$\kappa^{l} = \frac{1}{3V}\sum_{\mu\mu'} C_{\mu\mu'}|v_{\mu\mu'}|^2 \frac{\gamma_\mu + \gamma_{\mu'}}{(\omega_\mu - \omega_{\mu'})^2 + (\gamma_\mu + \gamma_{\mu'})^2}$$

where γ_μ is the normal mode linewidth, $\langle \hat{a}^{\dagger}_{\mu}(t)\hat{a}_{\mu}\rangle \approx (n_\mu + 1)e^{i\omega_\mu t - \gamma_\mu |t|}$
Alloying with germanium **enhances** thermoelectric performance by **reducing** lattice thermal conductivity. The introduction of spatially correlated (colored) disorder [2] can further improve this effect.

Hydrodynamic extrapolation

QHGK is computationally expensive for disordered systems $\sim O(N^3)$.

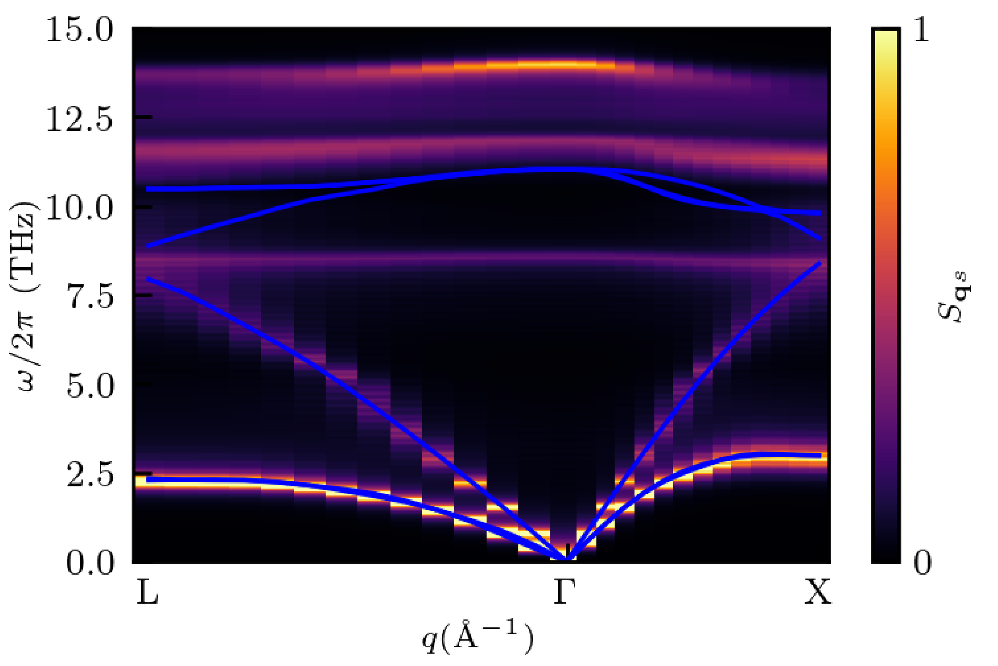
$\kappa_{\mathrm{hydro}} = \kappa_{\mathrm{P}} + \kappa_{\mathrm{D}}$

$$\kappa_{\mathrm{P}} = \frac{1}{3V}\sum_{\mathbf{q}b} C_{\mathbf{q}b}|v_{\mathbf{q}b}|^2 \frac{1}{2\Gamma_{\mathbf{q}b}}\Theta(\omega_{\mathrm{P}} - \omega_{\mathbf{q}b})$$

$$\kappa_{\mathrm{D}} = \sum_{\mu\mu'} \frac{C_{\mu\mu'}}{3V}|v_{\mu\mu'}|^2 \tau_{\mu\mu'}\Theta(\omega_\mu - \omega_{\mathrm{P}})\Theta(\omega_{\mu'} - \omega_{\mathrm{P}})$$

κ_{D} is computed on small samples, $N \lesssim 10^4$.
κ_{P} is modeled effectively using the Vibrational Dynamical Structure Factor [3,4].

$$S_{\mathbf{q}b}(\omega) = \sum_\mu \frac{1}{\pi}\frac{\gamma_\mu}{\gamma_\mu^2 + (\omega - \omega_\mu)^2}|\langle \mu|\mathbf{q}b\rangle|^2 \approx \frac{A_{\mathbf{q}b}}{\pi}\frac{\Gamma_{\mathbf{q}b}}{(\omega - \omega_{\mathbf{q}b})^2 + \Gamma^2_{\mathbf{q}b}},$$



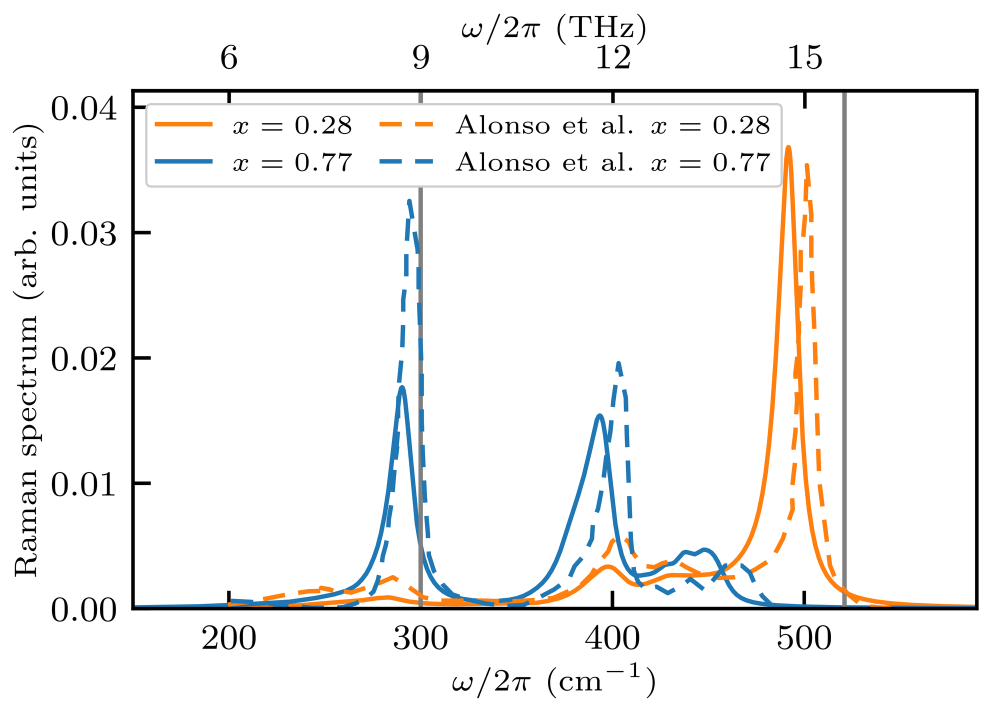
Computationally inexpensive $\sim O(N)$.
Affordable size $N > 10^5$.

First-principles interatomic force constants

Density Functional Theory electronic virtual crystal approximation

$$\tilde{D}^{c}_{IJ}(x) = \frac{1}{\sqrt{M_I M_J}}\frac{\partial^2 U_x}{\partial R_I \partial R_J},$$

$U_x = (1-x)U_{\mathrm{Si}} + xU_{\mathrm{Ge}}$
Material characterization with Raman spectroscopy



Spatially correlated alloy

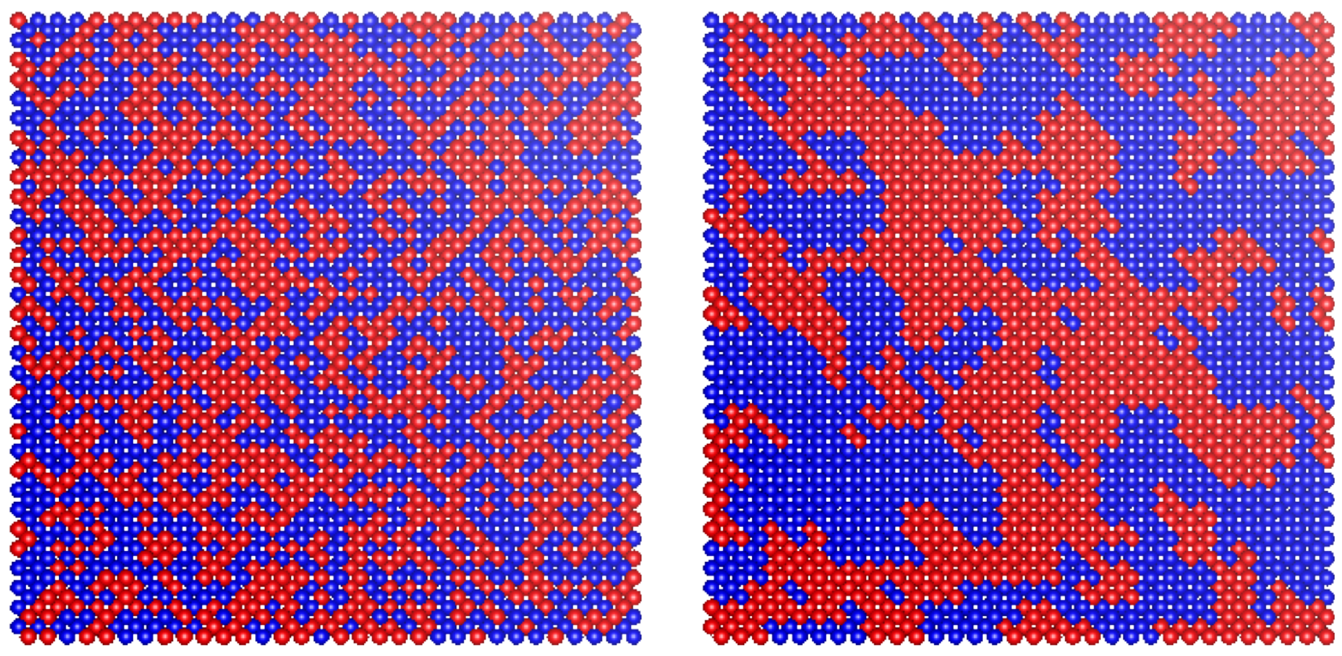
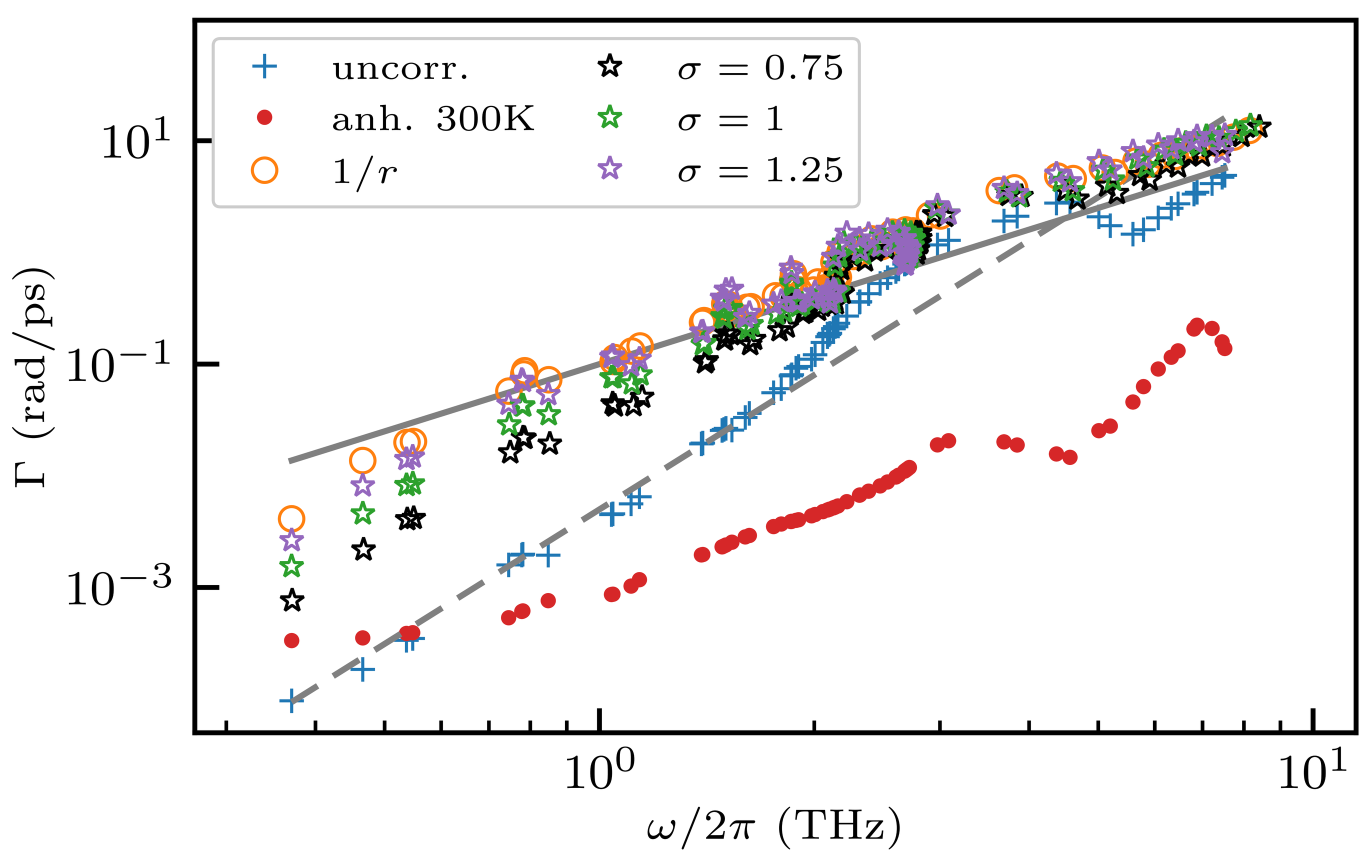


Figure: Left panel: uncorrelated. Right panel: spatially correlated (Gaussian).

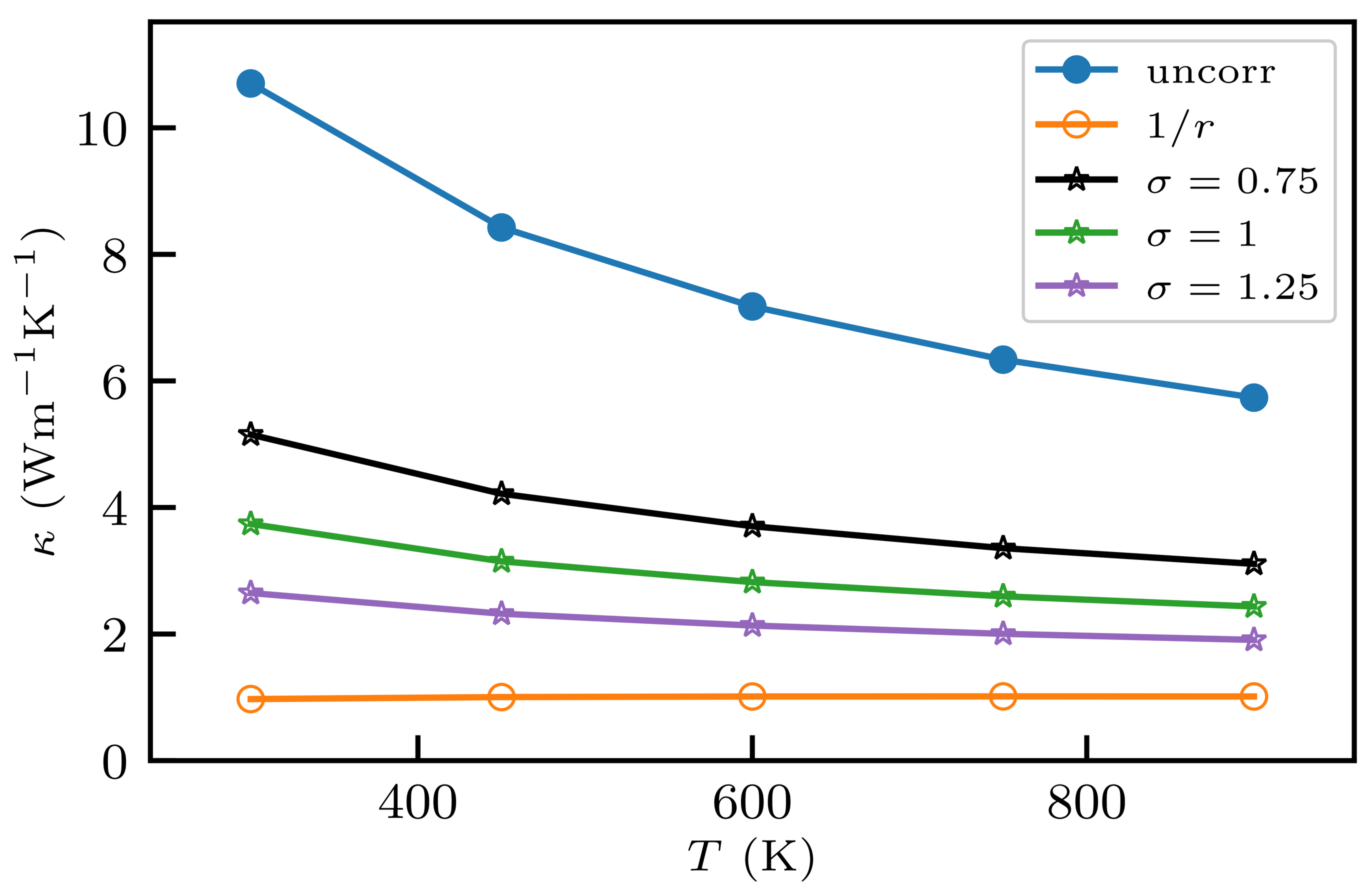
$C(\mathbf{r}) \propto \frac{1}{N}\sum_{I,J=1}^{N} \delta M(\mathbf{R}_J)\delta M(\mathbf{R}_I)\delta(\mathbf{r} - \mathbf{R}_{IJ})$

Enhanced sound attenuation and thermal conductivity reduction

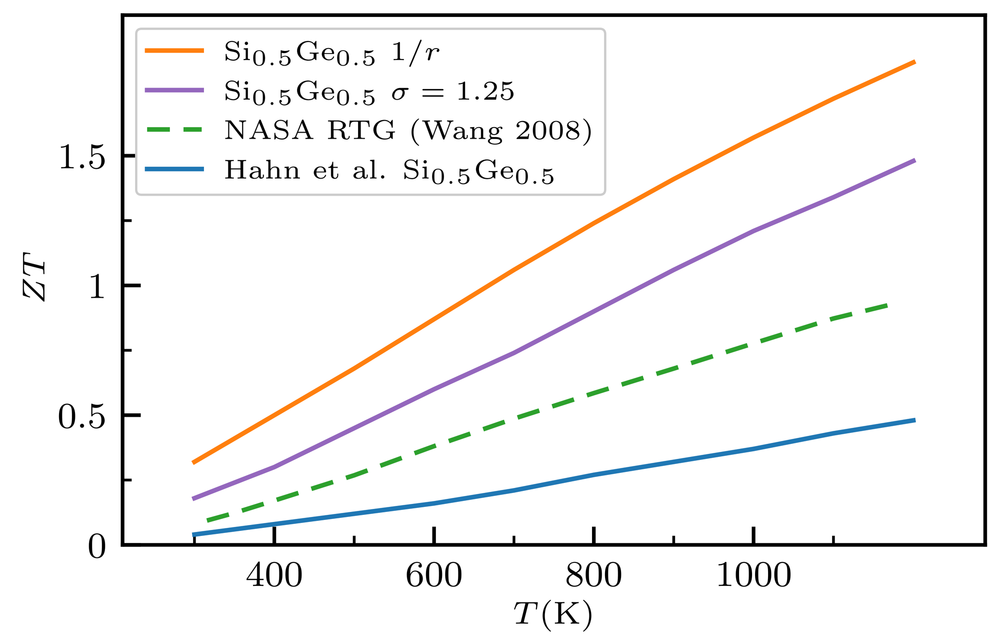


Frequency shift of the $\omega^4 \rightarrow \omega^2$ crossover. Overall, the sound attenuation due to colored disorder is **larger**.

$\Downarrow$



Thermoelectric figure of merit



ZT enhancement

- $\approx$ 4-fold with respect to white disorder
- $\approx$ 1.5 with respect to NASA RTG.

Conclusions

- Combining the QHGK formula with hydrodynamic extrapolation offers a robust workflow for calculating the thermal conductivity of disordered systems and nanostructures.
- Spatially correlated disorder induces a crossover in sound attenuation, validating predictions for glasses and deepening insights into vibrational dynamics.
- Spatially correlated SiGe alloys could surpass state-of-the-art thermoelectric devices, advancing TE applications.

References

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Acknowledgments

Partial support by MaX Centre of Excellence for supercomputing applications (grant number 101093374), Italian MUR (grant number 2022W2BPCK), and Italian National Centre for HPC, Big Data, and Quantum Computing (grant number CN00000013).

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