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** the 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 $\sim O(N^3)$.

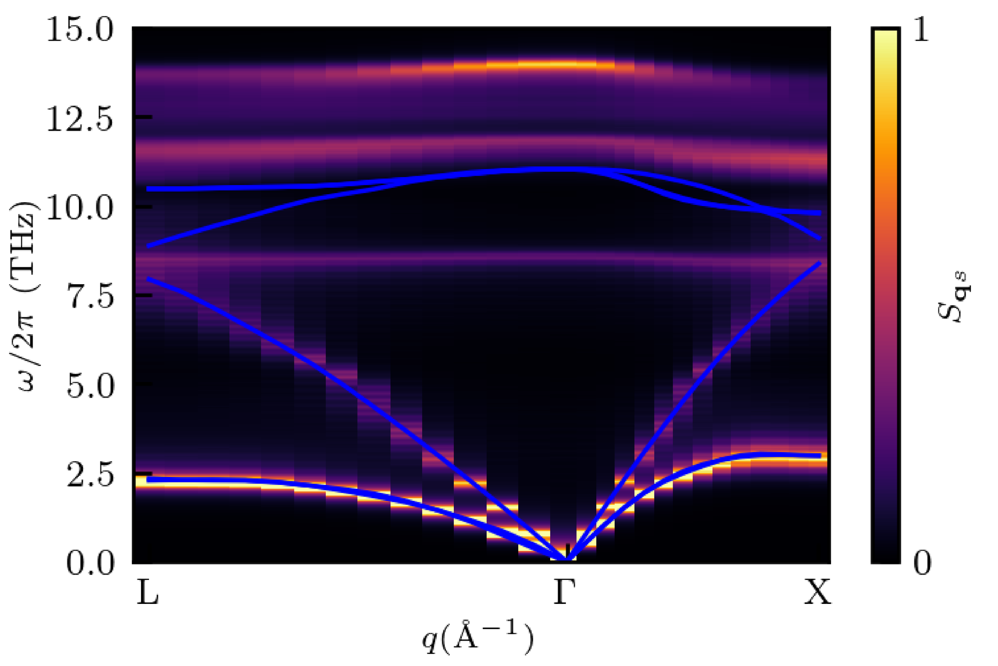
$$\kappa_{\rm hydro} = \kappa_{\rm P} + \kappa_{\rm D}$$

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

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

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

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



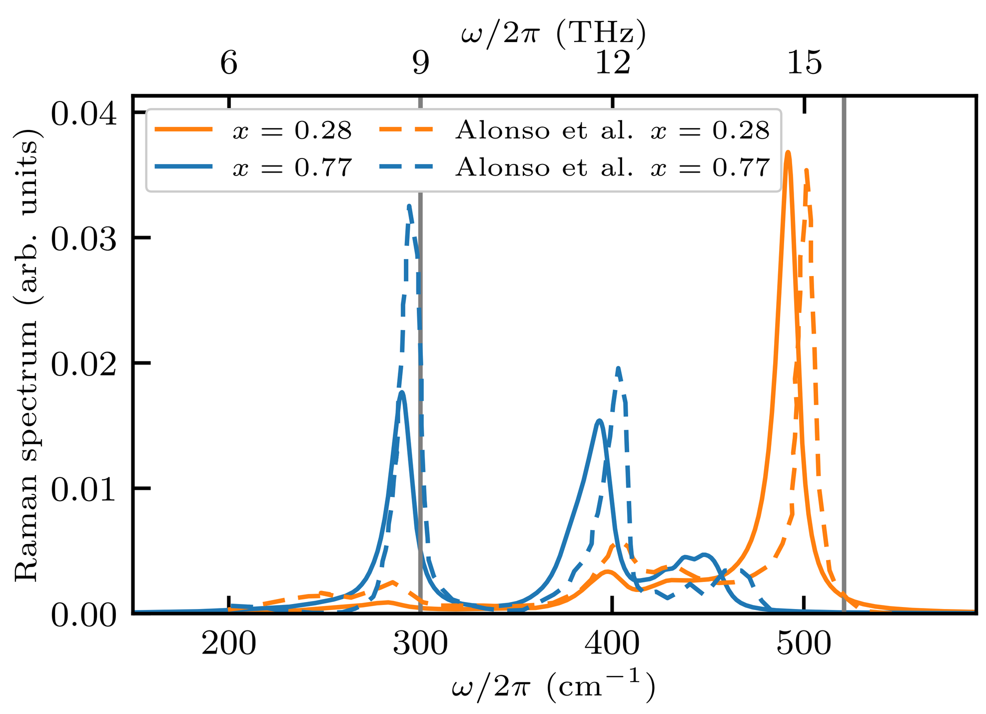
Computationally inexpensive $\sim O(N)$.
Affordable size $N > 10^5$.

First-principles interatomic force constants

Density Functional Theory electronic virtual crystal approximation

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

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



Spatially correlated alloy

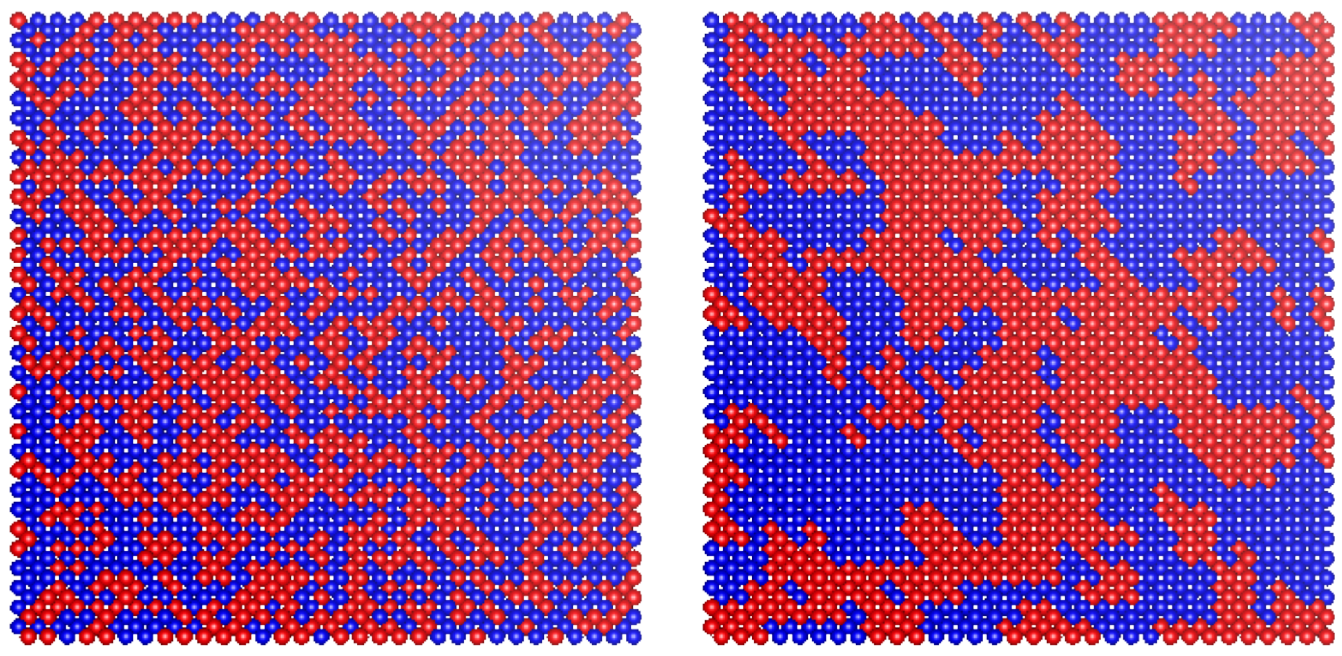
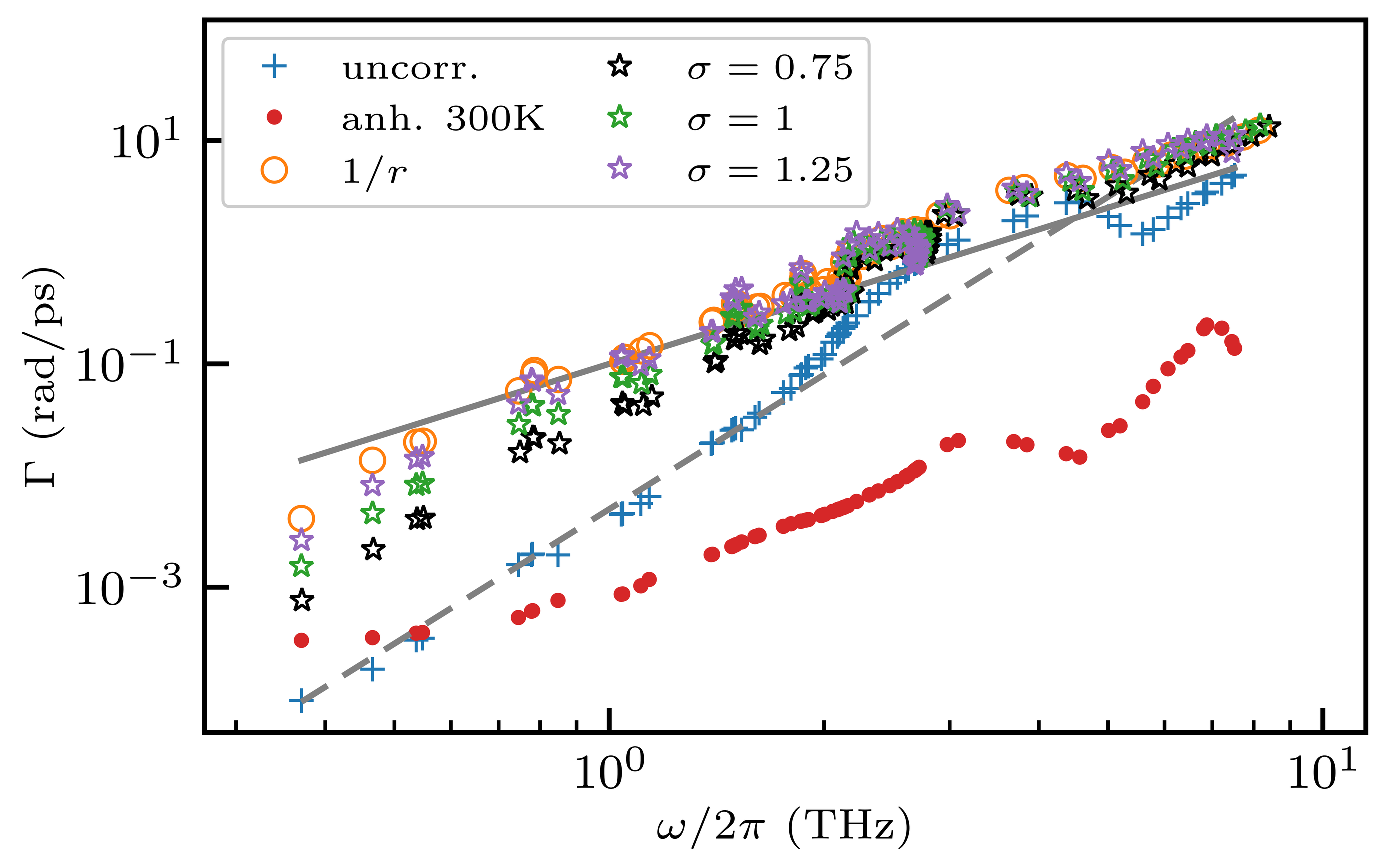


Figure: Left panel: uncorrelated. Right panel: spatially correlated (Gaussian).

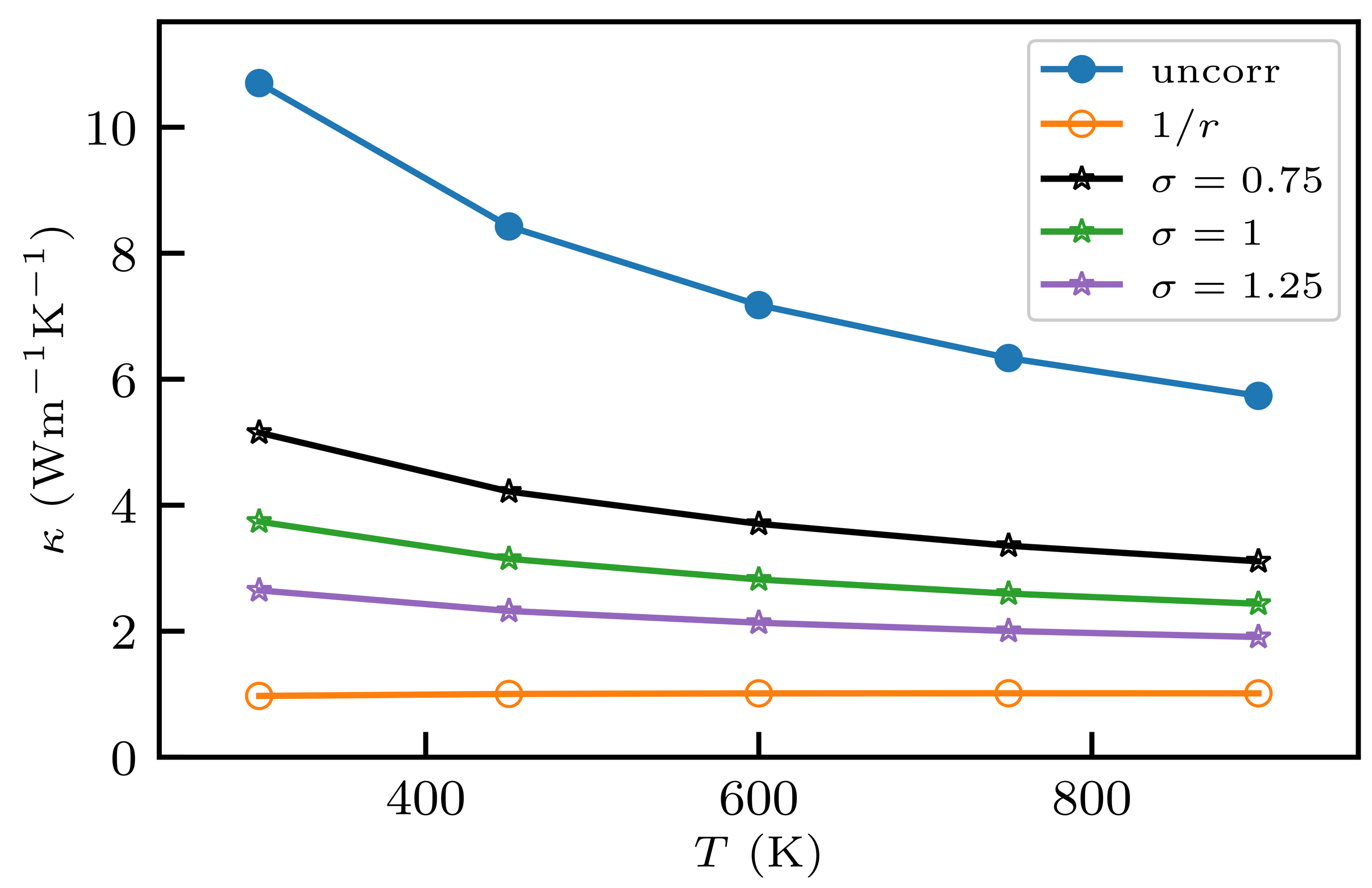
$$C(\mathbf{r}) \propto \frac{1}{N}\sum_{I,J=1}^{N} \delta M(\mathbf{R}_J)\delta M(\mathbf{R}_I)\delta(\mathbf{r} - \mathbf{R}_{IJ})$$

Enhanced sound attenuation and thermal conductivity reduction

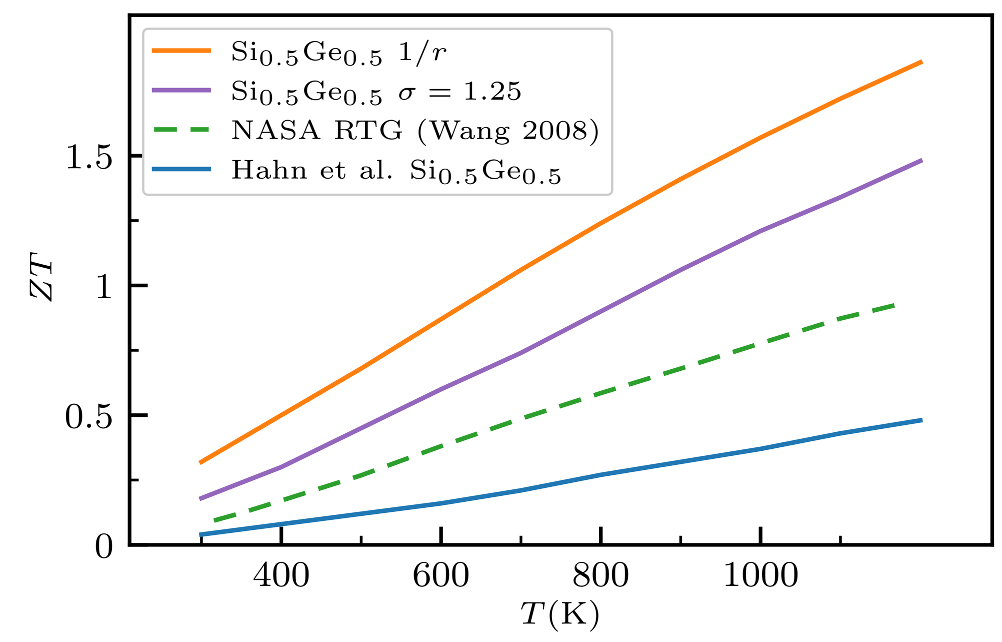


Frequency shift of the $\omega^4 \rightarrow \omega^2$ crossover. Overall, the sound attenuation due to colored disorder is **larger**.

$\Downarrow$



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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