Super-suppression of Long Mean-free-path Phonons in Nanoporous Silicon

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ABSTRACT

In 2020, using equilibrium molecular dynamics simulations, we identified specific nanoporous geometries that create narrow constrictions in the passage of phonons, leading to anticorrelated heat fluctuations [1]. These geometries were found to lower phonon transport to levels below the characteristic scattering length defined by the pore spacing, leading to a decrease in thermal conductivity by as much as 80% beyond what Matthiessen's rule would predict. Adjusting the size and arrangement of the pores offers control over phonon transport in these materials. In more recent work, we probed the nature of this phonon "super-suppression" with wavepacket molecular dynamics simulations [2], analyzed resonances in the power spectrum of the heat current autocorrelation function (HCACF), and developed an equilibrium ray tracing Monte Carlo model to help explain the observed anticorrelations in the heat flux of the porous geometries [3]. This model allowed us to detect the distinctive signatures that different types of correlated scattering leave in the HCACF, thereby clarifying the conditions required for diffusely scattered phonons to cancel their heat flow. With this model, we identified a region of experimentally accessible geometries likely to exhibit super-suppressed phonon transport.

MOTIVATION

Thermoelectric applications require materials to be thermally insulating and electrically conducting. In typical semiconductor materials, the majority of the heat is carried by long mean free-path phonons, which generally correspond to long wavelengths. Nanostructuring offers a route for minimizing thermal conductivity, and incorporating nanopores is a frequent nanostructuring technique. Nanoscale pores have been shown to significantly reduce phonon thermal transport in materials, often causing only minimal degradation to electron transport, which is ideal for thermoelectric applications. A comprehensive molecular dynamics study examining the role of geometry, such as pore size, shape, and distribution, in nanoporous silicon [4], led to the discovery of the examined unusual porous geometries with exceptionally low thermal conductivities.

METHODS

This study utilized molecular dynamics, non-equilibrium Green's function, and ray tracing Monte Carlo simulations. Thermal transport was evaluated within equilibrium molecular dynamics (MD) using the Green-Kubo method, and non-equilibrium MD wave packets generated from atom displacement and velocity profiles based on plane waves. The ray-tracing scheme was developed to simulate the trajectories of phonons undergoing diffuse elastic backscattering and compute their HCACF.

REFERENCES

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[3] P. A. Greaney, S. A. Hosseini, L. de Sousa Oliveira, A. Davies, and N. Neophytou, *Super-suppression of long wavelength phonons in constricted nanoporous geometries*, Nanomaterials 14.9 (2024): 795.

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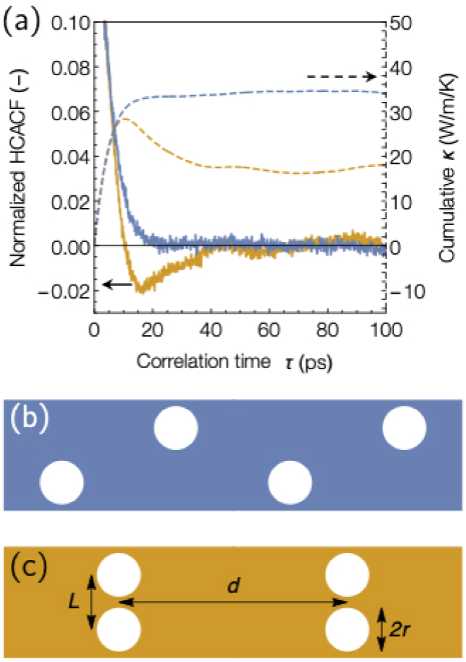

Fig. 1. Plot (a) shows the HCACF (solid lines, left-hand axis) and HCACF integral (dashed lines, right-hand axis) with the color-coding corresponding to the two porous geometry arrangements shown in (b) and (c). Both geometries have identical porosity, but the pores are offset in the blue geometry and stacked in the orange geometry. Figure adapted from [2].

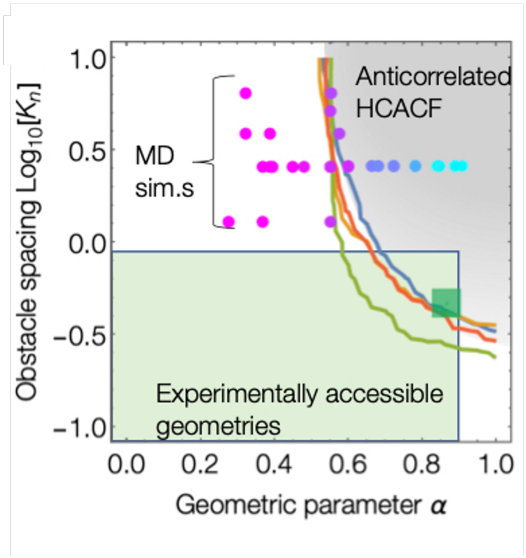

Fig. 2. The green-shaded region indicates geometries that can be experimentally accessed through fabrication methods. The green square represents pores with a 65 nm radius, arranged in a rectangular grid with long and short spacings of 400 nm and 150 nm, respectively, suggesting that the anticorrelation regime should be experimentally achievable. The circular points correspond to the geometries used in the molecular dynamics simulations conducted in this study. Figure adapted from [2].

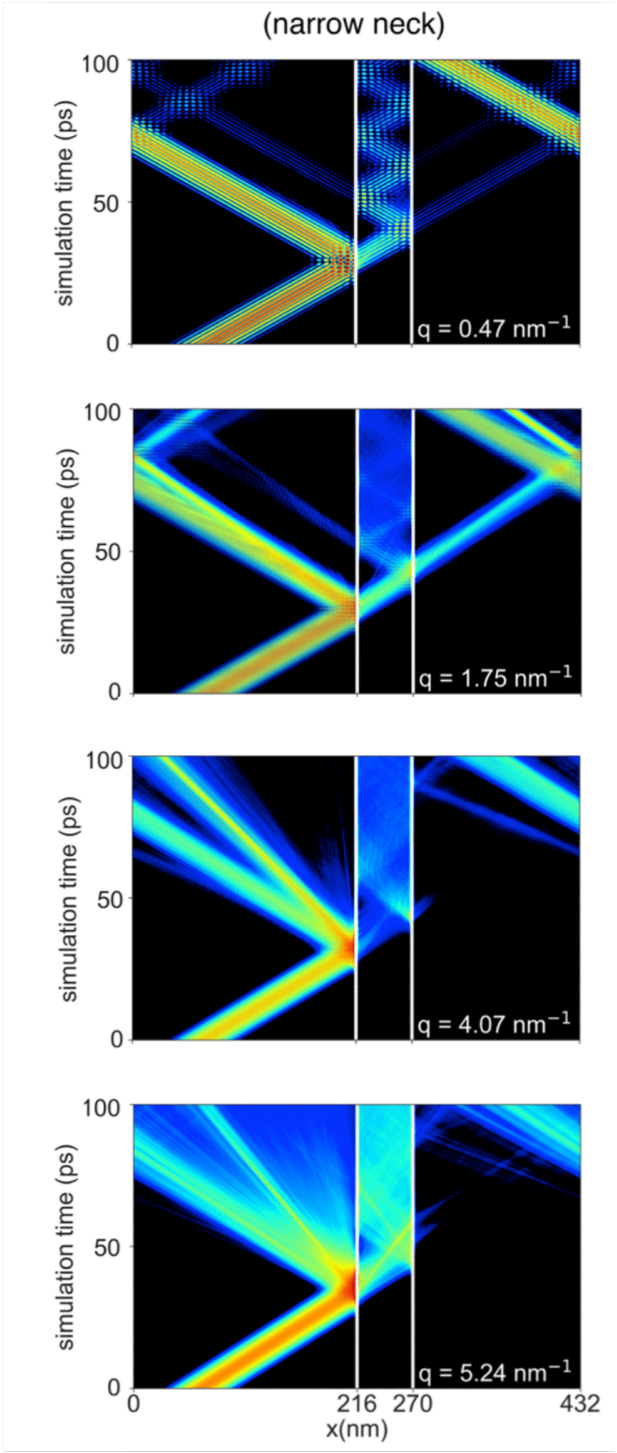

Fig. 3. A heatmap illustrating the time evolution of the wavepacket kinetic energies in the nanoporous geometry, displaying anticorrelated effects. The pore radius is 2 nm, with a neck size of 1.4 nm. White lines mark the pore locations along the transport direction. Each plot represents a wavepacket of a transverse acoustic mode centered at the specified wavevector. The distance between the pores is 54 nm. The wavepacket amplitudes are adjusted to maintain a temperature of 5 K in all simulations. Figure adapted from [2] and [3].