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Nanostructuration for thermoelectricity: The path to an unlimited reduction of phonon transport

Nanostructuration pour la thermoélectricité : la voie vers une diminution illimitée du transport phonique

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ABSTRACT

Improvements of the thermoelectric properties in bulk materials have very often relied on the reduction of thermal conductivity, which is mostly based on phonon propagation. Reducing further phonon transport has remained a difficult task due to the fact that current thermoelectric materials are already efficient thermal insulators, and also because of the broadness of the Planckian phonon spectrum. Nanostructuring has provided new paths for decreasing thermal conduction, especially by means of scatterers, be them nano-objects, surfaces, or interfaces. In this chapter, the physics of demonstrated nanoscale methodologies for the reduction of thermal conduction will be proposed together with illustrations from direct simulations.

RÉSUMÉ

L'amélioration des propriétés thermoélectriques des matériaux massifs est souvent liée à la réduction de leur conductivité thermique, qui est principalement basée sur la propagation des phonons. Réduire encore plus le transport des phonons reste une tâche difficile, parce que les matériaux thermoélectriques usuels sont déjà de bons isolants thermiques, mais aussi du fait de la largeur du spectre de Planck des phonons. La nano-structuration a fourni de nouveaux moyens pour décroître la conduction thermique, particulièrement par le biais de structures diffusantes, qu'elles soient des nano-objets, des surfaces ou des interfaces. Dans ce chapitre, la physique des méthodes éprouvées visant les échelles nanométriques pour réduire la conduction thermique est décrite, accompagnée d'illustrations directement tirées des simulations.

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1. Introduction

Affecting phonon transport by nanostructuring has been an increasing trend in the field of thermoelectricity during the two last decades. High electronic power factor, as in crystals, but low thermal conductivity (TC), as in a glass, [1] are required to improve the thermoelectric figure of merit, and designing crystalline systems with low thermal conductivities, especially below the amorphous limit, remains an open challenge [2]. In most of the previous attempts, reducing TC has consisted in introducing phonon scattering from nanoparticles or at surfaces and interfaces in nanostructured composites or superlattices [3,4], but only a limited range of phonon frequencies undergo scattering, typically at frequencies beyond 1–2 THz. Nevertheless, low-frequency modes also have a significant contribution to the total TC due to their long mean free paths (MFP) [5,6] and high population.

In this regard, multiscale scatterers have brought in significant progresses [7]. In silicon based materials, this approach was followed by synthesizing SiGe nano composites [8], superlattices [9], and silicon nanomeshes [10,11]. However, scattering elements such as grain boundaries, inclusions and pores have negative impacts on electronic transport, thus hampering thermoelectric performances.

A recent proposition from the acoustics community consists in implementing phonon resonant effects [12,13] for the engineering of thermal conductivity [14,15]. Due to anti-crossing effects, the interaction between resonator-based flat bands and propagating modes strongly reduce group velocities and resultant heat flux.

In this chapter, the usual, but also the more unexpected size effects on phonon heat transport will be reviewed in the second section, and several illustrations will be provided in the last part.

2. Physical mechanisms

2.1. Phonons

Phonons are quanta of vibrational waves arising in crystals due to thermal fluctuations. They can be called “sound waves” at low frequencies. They are exactly defined in the harmonic framework where interatomic forces are spring forces. In a linear chain such as the one of Fig. 1, the force between two neighbouring atoms would hence be defined by $F_{ij} = K \cdot (u_j - u_i)$ where u_i refers to the displacement of atom i and K is the force constant.

Newton’s second law provides the governing equation for the displacement u_i of the atom with mass m as:

$$m\ddot{u}_i = -K(2u_i - u_{i-1} - u_{i+1}) \tag{1}$$

and the Fourier Transform – consisting in setting $u_i = \sum_k u_k e^{j(kia-\omega t)}$ – of this equation yields the dispersion relation between wave vector k and frequency ω. This operation is of great help for decomposing the chaotic vibrational motion of the atom into well-defined normal modes as illustrated in Fig. 2.

The set of atomic displacements is now replaced by a set of eigenmodes, each one having its amplitude, polarization, wave vector, and frequency. One of the key outcomes of this transformation is that the system Hamiltonian can be equally written in terms of a sum over the atom index or over the Fourier components. Replacing the complex amplitude coordinate u_k by its expression in terms of the second quantised operators straightforwardly yields the eigenmode energy:

$$E_k = \hbar\omega\left(n_k + \frac{1}{2}\right) \tag{2}$$

in terms of the phonon energy quantum and of the number n_k of quanta in the mode. A phonon can therefore be assimilated to an energy quantum of an eigenmode.

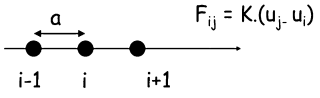

Fig. 1. Linear harmonic atomic chain. K and a refer to the force and the lattice constant, u_i to the displacement of atom i and F_{ij} to the force between atoms i and j.

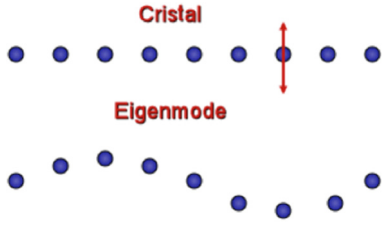

Fig. 2. Schematic of a linear crystalline chain (top) and of the typical atomic displacement field due to one eigenmode (bottom).

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