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# Heat transport in disordered network forming materials: size effects and existence of propagative modes

Thuy-Quynh Duong<sup>a</sup>, Carlo Massobrio<sup>b</sup>, Mauro Boero<sup>b</sup>, Guido Ori<sup>b</sup>, Evelyne Martin<sup>a</sup>

<sup>a</sup>*Univ. Lille, CNRS, Centrale Lille, ISEN, Univ. Valenciennes, UMR 8520 - IEMN, F-59000 Lille, France*

<sup>b</sup>*Université de Strasbourg, CNRS, Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504, Strasbourg F-67034, France*

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## Abstract

We show that in nanoscale disordered networks the thermal conductivity reduces with respect to the bulk value in a way remindful of the analogous behavior in nanocrystalline systems. Our rationale is based on the analogy with nanostructured crystalline silicon and is substantiated by results obtained (experimentally, analytically and by atomic scale modelling) on crystalline Si, amorphous Si, glassy SiO<sub>2</sub> and glassy GeTe<sub>4</sub>. We point out the implication of such findings on the potential performances of nanoscale heat devices.

*Keywords:* Thermal conductivity, Disordered materials, Nanoscale effects

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Thermal transport by conduction in non-metallic materials is due to heat carriers that either propagate with a wave vector (propagons) or that are extended but have no wave vector (diffusons) [1]. Propagons are sensitive to size reduction, diffusons are not. In crystals, the role of propagons is played by  
5 phonons travelling undisturbed without undergoing collisions (i.e. ballistically) on a mean free path (MFP) until they experience a scattering (diffusive) event. In a bulk crystalline system, diffusive events are unavoidable regardless of the extent of the largest MFP. This picture changes drastically when a material has nanoscale dimensions, as in a film or a wire for example, these changes being

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*Email address:* `evelyne.martin@univ-lille.fr` (Evelyne Martin)

10 reflected by a reduction of the thermal conductivity with respect to the infinite bulk counterpart [2, 3]. When considering a disordered material with no intrinsic long range order, one might wonder whether any dependence on the system size could be encountered, since in principle the length of the MFP for propagons is expected to vanish within a disordered topology.

15 In this paper we show that the reduction of thermal conductivity in nanosystems occurs regardless of their topological order. Such a universal feature is indicative of propagative modes corresponding to MFPs of different extension. This finding allows bridging the gap between fundamental understanding and practical applications of heat transport, toward the design of nanomaterials for  
20 thermoelectrics and memories.

As a tool of investigation, we study the thermal conductivity accumulation function  $\kappa(L)$  which identifies the thermal conductivity due to heats carriers having MFPs less than  $L$ . The accumulation function can be obtained within different methodologies. The first one (method *a*) is the broadband frequency  
25 domain thermorefectance experiment (BB-FDTR) [4]. This pump-probe set up allows measuring the thermal conductivity as a function of the signal frequency, which is ultimately related to a length equal to a maximum MFP. On the theoretical side (method *b*), we can resort to atomic scale modeling as implemented in the approach-to-equilibrium molecular dynamics (AEMD) [5, 6, 7]. In this  
30 method, the thermal conductivity depends on the length of the simulation cell  $L$  provided  $L$  is smaller than the maximum MFP. Therefore, the observation that the thermal conductivity depends on  $L$  (i.e. on size effects) is common to both experiments and modelling. This can be rationalized in terms of behavior of heat carriers: those with MFP smaller than  $L$  experience scattering events,  
35 while the transport is ballistic for heat carriers with a higher MFP. When increasing  $L$ , the contribution of heat carriers of larger MFP increases until the bulk thermal conductivity is reached for  $L$  larger than the maximum MFP. On the analytical side (method *c*), the evolution from a mixed ballistic-diffusive to a purely diffusive (scattering) regime has been described analytically by Alvarez

40 and Jou [8] who obtained the following relationship:

$$\kappa_{AJ}(L) = \kappa_{\text{bulk}} \frac{L^2}{2\pi^2 l^2} \left[ \sqrt{1 + 4 \left( \frac{\pi l}{L} \right)^2} - 1 \right], \quad (1)$$

where  $\kappa_{\text{bulk}}$  is the bulk thermal conductivity and  $l$  is a parameter with the dimension of a length.

In the case of nano-crystalline silicon, methods *a)*, *b)* (with the AEMD simulations performed via the interatomic potential developed by Tersoff [9]) and *c)* agree on the length dependence of the thermal conductivity (Fig. 1). The

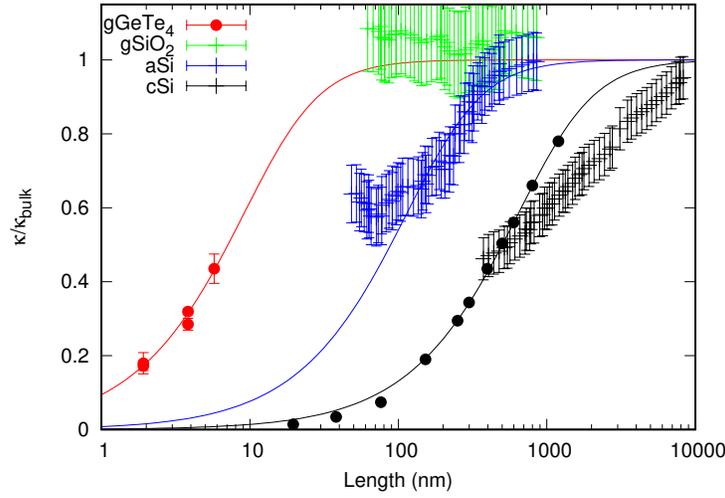


Figure 1: Variation of the thermal conductivity  $\kappa$  (normalized to the bulk value  $\kappa_{\text{bulk}}$ ) with length in crystalline silicon (cSi), amorphous silicon (aSi), silica glass (gSiO<sub>2</sub>) and glassy GeTe<sub>4</sub> (gGeTe<sub>4</sub>). Crosses are the experimental results by BB-FDTR [4]. Dots are the calculations by AEMD [6, 10]. Lines correspond to the law expressed by Eq. (1) [8] adjusted to experiments (aSi) or calculations (cSi and gGeTe<sub>4</sub>).

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variation of the thermal conductivity was investigated up to 1.2  $\mu\text{m}$  by AEMD. The thermal conductivity follows Eq. (1) on the whole range investigated [15 nm - 1.2  $\mu\text{m}$ ]. The measurements by BB-FDTR are performed for lengths larger than 300 nm, with the normalized thermal conductivity also increasing from 0.5  
50 to 1. The reduction of thermal conductivity, defined as  $\kappa_{\text{bulk}} - \kappa_{AJ}(L)$ , for a feature size (film thickness, nanowire diameter) is plotted in Fig. 2. For silicon,

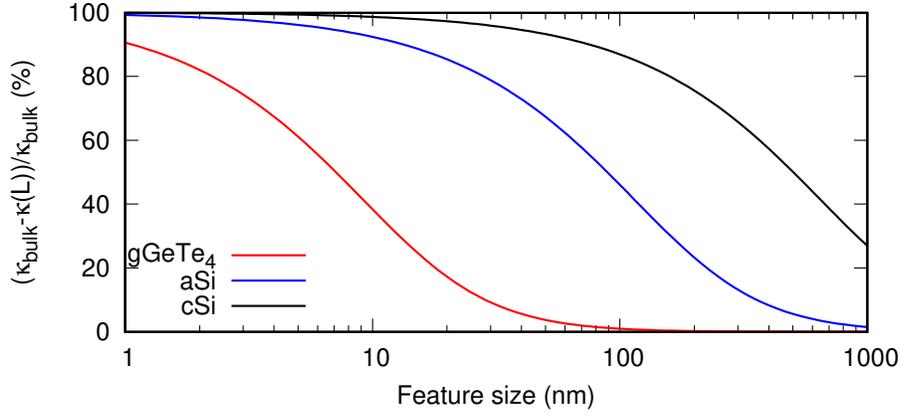


Figure 2: Thermal conductivity reduction as a function of a feature size. Lines correspond to the law expressed by Eq. (1) [8] adjusted to experiments (aSi [4]) or to calculations (cSi [6] and gGeTe<sub>4</sub> [10]).

the thermal conductivity is reduced by 30% as a result of microstructuration ( $L=1 \mu\text{m}$ ). The reduction reaches 80-90% when the size decreases below 100 nm.

55 Having established the size dependence of the thermal conductivity in a crystalline system when approaching the nanometer scale of observation, we turn to the behavior of specific disordered systems, by considering first amorphous silicon. A plateau experimentally observed at  $30 < L < 100$  nm is attributed to the contribution of non-propagative modes (diffusons) [4] (Fig. 1). For  $L > 100$ ,  
60 a variation of the thermal conductivity with  $L$  is measured. The evolution for  $L > 100$  nm can be fitted to Eq. (1) (see Fig.1), leading to the conclusion that in this system propagative modes do exist up to  $1 \mu\text{m}$ . Fig. 2 shows that nanostructuration reduces the propagative component by 20 % at 200 nm (Fig. 2). In glassy SiO<sub>2</sub> instead, the thermal conductivity is constant in the range  
65 of BB-FDTR measurements, i.e. for lengths greater than 60 nm. This calls for further evidence to be collected on disordered network systems bearing some similarity with glassy SiO<sub>2</sub> (predominant fourfold (twofold) coordination of the tetravalent (divalent) atom).

We have met this goal by studying glassy  $\text{GeTe}_4$  by first-principles modelling  
70 [10]. The thermal conductivity of glassy  $\text{GeTe}_4$  was obtained by resorting to  
first-principles molecular dynamics [11], ensuring a quantitative description of  
the atomic structure based on the account of chemical bonding [12]. Application  
of the AEMD methodology provides the thermal conductivity of glassy  $\text{GeTe}_4$   
for cells dimensions up to 6 nm. The results show a dependence of the thermal  
75 conductivity on length (Fig.1). Quite remarkably, this dependence follows Eq.  
(1) and leads to a bulk thermal conductivity in excellent agreement with the  
measured value [13], thereby substantiating the atomic scale description of the  
heat transport in this material.

Interestingly, for  $L > 60$  nm, the thermal conductivity of glassy  $\text{GeTe}_4$  is  
80 constant, much in the same way as measurements performed for the silica glass  
(see Fig. 1). One may argue whether glassy  $\text{GeTe}_4$  is a peculiar case or it  
is representative of a general behavior typical of disordered materials, at least  
for those featuring a network topology. The present results are very much in  
favor of this second hypothesis since they demonstrate that propagative modes  
85 could in principle exist in any disordered material, although they do not travel  
distances as large as in crystals. This result opens new perspectives in terms of  
thermal management at short scales. For example, in phase-change memories,  
heat control is crucial to enable phase shift with a reduced supplied power. The  
dimension of the phase-change material in contact with the heater falls in the  
90 decananometric range. In Fig. 2, we see that the extrapolation of our AEMD  
results predicts a reduction of thermal conductivity of 15-20% at 20 nm, 35-  
40% at 10 nm and 60-65% at 5 nm for glassy  $\text{GeTe}_4$ . This reduction would  
undoubtedly prevent heating and therefore phase switching, thereby worsening  
the performances of such heat-based switching device.

95 In summary, a combined analysis based on the use of three different ap-  
proaches to investigate the size dependence of thermal conductivity allows con-  
cluding that disordered network forming systems are characterized by the exist-  
ence of propagative heat modes. This differs drastically from any conjecture  
favoring diffusons against propagons (either diffusive or ballistic) as modes of

100 heat transport in the presence of topological structural disorder. As a direct  
consequence, the thermal conductivity of such disordered materials is reduced  
at scales typical of applications in nanotechnology.

### Conflicts of interest

There are no conflicts of interest to declare.

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### Data availability

The raw/processed data required to reproduce these findings are available  
from the corresponding author on reasonable request.

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