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# Heat transport in phononic-like membranes: modeling and comparison with modulated nano-wires

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## Abstract

The thermal conductivity of phononic-like membranes and their analogous nano-wires are computed with both Molecular Dynamics and Monte Carlo simulations. Using both methods, the thermal conductivity of the porous membranes with cylindrical pores is found to be lower than the nano-wire's one for the same scattering surface to volume. This work confirms experimental observations by Nomura *et al* [1] and Yu *et al* [2] for similar systems. The lower thermal conductivity of membranes is attributed to the different orientation of the scattering surfaces either at the pores or at free surfaces and not to coherent effects. The comparison between the porous membranes and nano-wires with periodic cylindrical modulations shows that thermal transport is hindered further when there are surfaces perpendicular to the heat flow. These results show that **coherent effects have no impact on thermal transport in both kind of nano-structures at room temperature.**

*Keywords:* Nano-structuration, Silicon, Molecular Dynamics, Monte Carlo, thermal conductivity

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## 1. Introduction

During the last decades, increased interest has been observed to tailor different physical properties of nano-structures and nano-structured materials. Unique characteristics and effects are found in nano-structured semi-conductors compared to their bulk properties. Silicon is the most common semi-conductor on Earth and is a non-pollutant material. Therefore, nano-structured Silicon has been intensively studied experimentally and theoretically for its optical [3, 4] or thermal properties [5, 6, 7] among a plethora of other properties. The importance of thermal management of nano-structures has arisen as the electronic devices became smaller and more powerful. Nano-structured semi-conductors are widely used for energy thermoelectric conversion [8, 9] or in photovoltaic devices [10].

Efficiency of thermoelectric materials depends on their electrical to thermal conductivities ratio (figure of merit), thus the thermal conductivity (TC) has to be very low. However, current thermoelectric materials have a poor figure of merit and cannot be massively used for energy production. Then, the aim of the nano-structuration of semi-conductors is often to reduce the thermal transport by multilength scale hierarchical structuring with purpose to increase the density of interface or introducing point or extended defects. On the other hand as electrons have a much lower mean free path than phonons [11], it can be assumed that their conductivity is preserved in most of the nano-structured semi-conductors.

Historically, the study of heat transfer in composite materials began with Maxwell [12] and Lord Rayleigh [13] at the end of the 19<sup>th</sup> century. Thereafter, **thermal transport in nano-structured compounds gained interest, including porous and nano-porous materials** [14, 15, 16]. Different kinds of nano-structuration are possible today, **especially with the fast development of fabrication methods**. The TC of super-lattices alternating layers of different semi-conductors have been intensively investigated during the last decade [17, 18, 19]. In such structures, band folding plays a key role in TC lowering. The reduc-

tion of the thermal transport was also observed in thin films [20, 21, 22, 23] and nano-wires [24, 25, 26, 27, 28, 29]. In the recent years, several studies are devoted to thermal behavior of bulk nano-porous systems [30, 31, 32, 33], or nano-porous membranes [34, 35, 36, 37, 38].

35 Recently, a new method has been proposed to reduce thermal transport in periodic nano-structures. By analogy to the photonic crystals, which are also known as photonic band gap materials as there are forbidden photon propagation frequencies [39, 40], an artificially and periodically structured material could **remove** phonons of certain frequencies [41, 36, 42, 43, 44]. These phonon  
40 band gaps are due to scattering and interference phenomena, the latter being known as coherent effects. If the prohibited phonon modes are heat carriers, the TC would be further reduced [45]. Abnormally low TCs have been experimentally observed in periodically nano-structured Silicon [2] and this was attributed to these coherent effects.

45 Nomura *et al* compared the experimental TCs of membranes with periodic cylindrical pores to those of nano-wires [1]. They found that thermal transport is weaker in membranes, despite their low scattering surface to volume ratio compared to nano-wires with similar characteristic size. This might be due to phononic effects (*i.e.* **any effect related to a modification of phonon dispersion properties like band flattening, band gap ... or coherent scattering of phonon**  
50 **due to the periodicity of the hole pattern**), but authors mentioned that the “local angles between local and global heat flux” could be responsible of this phenomenon [1]. In other words, they point out the different impact of scattering surfaces on thermal transport according to their spatial orientation compared  
55 to the direction of the main thermal gradient. At this stage a simple schematic description of phonon transport can be depicted. When the TC is measured along the growth direction of a nano-wire, all scattering surfaces of the system are parallel to the heat flux. If phonons are diffusely scattered at the free surfaces, half of them are back-scattered (Diffuse Mismatch Model). In contrast,  
60 in the “phononic crystal” (hollow membrane) the surface of the pore (which is here a part of the scattering surfaces with upper and lower boundaries) is

mainly perpendicular to the heat flux (see fig. 1a). Then, the back-scattering of phonons in the membrane is increased as compared to the nano-wire and the TC of the membrane is reduced.

65 In this work, the same strategy as Nomura *et al* has been exploited, making the comparison between porous membranes and nano-wires with two numerical techniques: Monte Carlo solving of the BTE and Molecular Dynamics. The comparison between the two nano-structured materials shows the importance of the orientation of the scattering surfaces on thermal transport. Technical  
70 details about the computations of the TC with these two methods are presented in section 2, then the geometries of the modeled systems are defined in section 3. TC experimental results and numerical simulation results are compared in section 4. In the same section, the phonon densities of states computed with Molecular Dynamics are presented to give physical insights. Finally, in section  
75 5 modulated nano-wires are modeled and their TC is given in comparison to membrane's TC with the same geometric parameters.

## 2. Simulation methods

### 2.1. Molecular Dynamics

Molecular Dynamics simulations are performed with *LAMMPS* [46]. Equilibrium Molecular Dynamics (EMD) method is used to determine the TC via  
80 the Green-Kubo formula [47]:

$$k_{xy} = \frac{\mathcal{V}}{k_B T^2} \int_0^{+\infty} \langle J_x(t) J_y(0) \rangle dt \quad (1)$$

where  $x$  and  $y$  subscripts denote space directions,  $\mathcal{V}$  is the system's volume,  $J$  is the heat flux,  $t$  is the time,  $T$  is the system's temperature and  $k_B$  the Boltzmann constant. Then, the TC can be obtained for all directions. For  
85 membranes, the flux auto-correlation function is calculated in  $x$  and  $y$  directions ( $J_x(t)J_x(0)$  and  $J_y(t)J_y(0)$ , respectively). The in-plane TC is the average of the two thermal conductivities in direction  $x$  and  $y$  (see fig. 1a). For nano-wires,

the flux auto-correlation function is calculated only for  $x$  direction which is the growth direction of nano-wires (see fig. 1b). The interactions between the atoms  
90 are described with the Stillinger-Weber potential [48] with modified coefficients  
by Vink *et al* [49] as this latest parameterization is able to describe thermal  
transport in Silicon, in both crystalline and amorphous phases.

The time step is set to 0.5 fs in all EMD runs. At the beginning of the  
simulation, the system is relaxed at  $T = 300$  K with a NVT ensemble during  
95 200 ps. Then the computation of the TC is performed every 40 ps under a NVT  
ensemble, estimating the flux fluctuations correlation every 10 fs, for a total  
duration of 10 ns. The TC is averaged over the second half of the simulation,  
when the steady state is established, in order to reduce the uncertainty on the  
results [50]. Moreover, each simulation is repeated 10 times with different seeds  
100 and the TC is averaged. Periodic boundary conditions are applied on surfaces  
perpendicular to the directions of interest (nanowire's growth direction, mem-  
brane's  $x$  and  $y$  directions), while non-periodic and shrink-wrapped boundary  
conditions are applied on the free surfaces. Size effects, i.e. influence of the  
simulation box size, have been considered by testing the model on cubic box  
105 with edge length of 5, 10, 15 and 20  $a_0$ . For these for cases mean value of bulk  
TC remains the same, only errorbar increases when the box gets smaller. In the  
bulk crystalline Silicon case, the TC is estimated to be  $k = 164 \pm 21$  W/m K.  
That is in good agreement with experimental values [51, 52]. It can be noted  
that classical Molecular Dynamics are only valid above Debye temperature  $T_\theta$   
110 (645 K for silicon). For temperature below  $T_\theta$  a quantum correction is usually  
needed, but it has been shown that even at half the Debye temperature thermal  
properties computed without quantum correction were only 15% lower than the  
experimental values [53]. Thus, as it has been often shown in the litterature,  
classical MD allow to recover the thermal conductivity with a good accuracy  
115 [32, 21, 30].

With Molecular Dynamics, the phonon's Density of States (DOS) of the  
system can also be extracted from the trajectories of atoms. Indeed, the dis-  
placement of atoms can be decomposed by Fourier transform to extract the

density of frequencies of phonons. In this work, the *specden* plugin of the *VMD*  
 120 *Signal Processing Plugin Package* [54] was used to calculate the phonon DOS  
 of the porous membranes.

## 2.2. Monte Carlo

The Monte Carlo technique is based on the resolution of the Boltzmann  
 Transport Equation (BTE) in the relaxation time approximation (eq. 2) [33, 24],  
 125 where  $f$  is the phonon's distribution function,  $v_g$  is the group velocity,  $\tau$  is the  
 relaxation time, while exponent "0" denotes thermal equilibrium:

$$\frac{\partial f}{\partial t} + \vec{v}_g \cdot \vec{\nabla} f = \frac{f^0 - f}{\tau(\omega, T)} \quad (2)$$

In this approach, phonons are considered as particles with wave properties (pul-  
 sation, group velocity and polarization) and their displacements and interactions  
 are modeled through several steps:

- 130 • Design of the geometry of the structure. Parameters such as size and  
 boundary conditions are defined, then the system is divided into 20 cells  
 in the  $x$  direction.
- Initialization of phonon population with random space positions, deter-  
 mining their characteristics according to the spectral properties of the  
 135 medium (Bose-Einstein distribution, dispersion curves and density of states).  
 These properties are those of the bulk crystalline Silicon, so coherent  
 phononic effects cannot appear in the results obtained with Monte Carlo.  
 A weak temperature gradient is applied in the  $x$  direction by initializ-  
 ing more phonons in the first cell (Bose-Einstein distribution at higher  
 140 temperature).
- Drift of the phonons during the time step, knowing their initial posi-  
 tion and their group velocity. This step is represented by the advective  
 term  $\vec{v}_g \cdot \vec{\nabla} f$  in the BTE. Reflections at the boundaries and the pores are  
 achieved during this step. For membranes specular reflection (periodic  
 145 boundary) is assumed in the  $y$  direction, whereas diffuse reflection is set

in the  $z$  direction (see fig. 1a). For nano-wires, reflection at the edge of a cell are both diffuse in  $y$  and  $z$  directions (see fig. 1b). The reflection at the pores can be set to entirely specular or purely diffuse.

- Collisions of the phonons during the time step. This step is represented by the right hand side term of the BTE  $(f^0 - f)/\tau(\omega, T)$  and brings the system back to equilibrium after the drift phase by modifying the phonon's properties. It takes into account the phonon scattering due to impurities and anharmonic processes (phonon-phonon interactions) thanks to the semi-empirical lifetime of Holland [55]. Thus, the Normal and Umklapp processes are differentiated.
- Thermalization of the first and last cells according to the temperature gradient. All the phonons in these thermostats are deleted then replaced by new ones in order to impose the hot and cold temperatures of the gradient.

During MC simulation, the three last steps are repeated for a total duration of about 200 ns. A steady state is usually reached after tens of nanoseconds (depending on the thermal resistance), when the temperature gradient becomes linear between the two thermostats. The heat flux and the temperature of each cell during the steady state are computed from the properties of phonons (pulsation and velocity) at every time step. Finally, temperatures and flux are averaged over the steady state and the TC is extracted according to the Fourier's law (eq. 3 with  $S$  the cross-section). The code which performed all these steps was developed by our work team (more details can be found in refs [56, 33, 24] and was validated by retrieving the bulk crystalline Silicon conductivity:  $k \simeq 148$  W/m K. In this work, the typical time step is  $\Delta t = 1$  ps and the temperature gradient is set from 299 to 301 K for structures with characteristic length  $L_x$  of 4800 nm.

$$\frac{\vec{J}}{S} = -k \times \vec{\nabla}T \quad (3)$$



### 3. Modeled systems

Three nano-scale geometries of Silicon are modeled in the current work:

- 175 • phononic-like nano-porous membranes (np-memb)
- nano-wires with constant cross-section (NW)
- nano-wires with modulated cross-section (m-NW)

As in ref [1], membranes with cylindrical nano-pores (np-memb) are compared to nano-wires (NW) with dimensions adjusted in a way that the nano-wires just fit in the space between the pores of the membranes (fig. 1a and 1b). So the width of a nano-wire is equal to the neck  $n = a - d$  with  $a$  the periodicity of the equivalent porous membrane and  $d$  the diameter of the pores. Both in-plane TC of membranes and TC of NWs are considered along the  $x$  direction. Due to the lower material volume and the greater scattering surface of the NW compared to the membrane, it was expected that the NW has lower TC than the membrane. But the opposite behavior was observed by Nomura *et al* [1] and Yu *et al* [2]: the NW has a greater TC than the membrane. Both of these two works [1, 2] were based on experimental TC measurements. The current work confirms this behavior numerically.

190 The two geometries have been modeled with both numerical methods (Molecular Dynamics and Monte Carlo) but with different characteristic sizes. With Molecular Dynamics, the thickness of the membrane is kept constant at  $e = 15a_0 = 8.145$  nm, the diameter of the pores is set to  $d = 10a_0 = 5.43$  nm while the periodicity of the membrane varies between 15 and 34  $a_0$  (8.145 and 18.5 nm, respectively) with  $a_0 \simeq 5.43\text{\AA}$  the lattice constant. Thus, the equivalent NW's height is always 15  $a_0$  and its width varies between 5 and 24  $a_0$  (neck between the pores of the membrane). With Monte Carlo, the periodicity and the thickness of the membrane are respectively set to  $a = 240$  nm and  $e = 145$  nm (comparable to the experimentally fabricated membranes of Nomura *et al*), while the diameter  $d$  of the pores varies between 0 and 220 nm (zero corresponds to membranes without pores). Thus, the height of the equivalent

NW is kept at  $e = 145$  nm and its width varies between 220 and 0 nm. We have chosen different sets of values for the two methods because of the limitations due to computational cost for MD on one hand and the validity scale of MC on the other hand, **keeping a similar ratio  $n/e$  for both methods.**

A third equivalent system has been modeled (fig. 1c). **It is a modulated nano-wire (m-NW) where hollows with the shape of a half-cylinder are periodically set along the  $x$  axis (length of the m-NW) at both ends of the structure in the  $y$  direction. In order to compare the new system with the porous membrane, the half-cylinders have the same diameter  $d$  as the pores, while the maximum width of the m-NW is equal to the periodicity of the membrane. Thus, the minimum width in the narrow part of the m-NW is equal to the neck of the membrane. The TC is always computed along the  $x$  axis. Now the only difference between this latest configuration and the phononic-like membrane is the boundary condition along  $y$  axis: periodic for the membrane and fixed for the m-NW.**

To summarize we intent to study three different systems; i.e. a phononic membrane, a nanowire and a modulated nanowire. In phononic membranes it has already be demonstrated [1, 58] that when energy carrier MFPs become smaller than a characteristic size the TC is affected. This characteristic size can be given by: i) the surface to volume ratio when boundaries dominate the transport, or ii) the neck of the np-memb when the distance between holes is very small[58]. In the first case ( $L = S/\mathcal{V}$ ), such behavior can be explained in the frame of the Casimir limit theory [59] which well describe thin films and nanowires. In the second case ( $L = n$ ), the characteristic length is the neck of the nanostructure and physic of transport is ruled by the constriction effect also known as "ballistic transport" [60, 61]. In the latter case, one can refer to studies dealing with modulated and constricted nanowires [24] that exhibit similar features. Hereafter, we are going to investigate the TC of the three systems and try to see if the suggested mechanisms rules effectively heat transport in np-memb.

## 4. Comparison between phononic-like membranes and nano-wires

### 4.1. Molecular Dynamics

The TCs obtained with means of Molecular Dynamics are summarized in  
 235 table 1. The ratio of scattering surface  $S$  to volume  $\mathcal{V}$  is provided for each  
 configuration as it usually controls the TC of isotropic and homogeneous porous  
 media. This parameter is differently calculated for membranes and NWs (eq.  
 4). In spite of its lower  $S/\mathcal{V}$  ratio, the TC of the membrane is systematically  
 lower than NW's one, as previously experimentally observed by Yu and Nomura  
 240 [2, 1]. As Molecular Dynamics are a numerical technique, this observation does  
 not come from experimental uncertainty or exterior perturbations.

Table 1: Comparison between the TCs of porous membranes and equivalent NWs. The  $S/\mathcal{V}$  ratio is given for each configuration. The TC of the membrane is systematically lower, despite its lower  $S/\mathcal{V}$  ratio.

Neck $n$ ( $a_0$ )	$k$ (W/m K)		$S/\mathcal{V}$ ( $\text{nm}^{-1}$ )	
	membrane	nano-wire	membrane	nano-wire
5	3.4±0.3	14.0±1.9	0.64	0.98
10	8.6±0.5	22.1±2.3	0.43	0.61
15	15.2±1.9	26.7±2.7	0.35	0.49
<b>24</b>	<b>22.7±2.0</b>	<b>32.8±3.3</b>	<b>0.16</b>	<b>0.22</b>

$$\frac{S}{\mathcal{V}} = \begin{cases} \frac{\pi de + 2(a^2 - \frac{\pi d^2}{4})}{ea^2(1-\phi)} & \text{for a membrane} \\ \frac{2(e+n)}{e \times n} & \text{for the equivalent nano-wire} \end{cases} \quad (4)$$

The reduction of the TC of the membranes compared to their equivalent  
 NW ranges from **30** to 75% depending on the “neck” size. This reduction is  
 more pronounced when the neck is small. In figure 2, the TC of both systems  
 245 is plotted in terms of neck size. **The ratio  $k_{NW}/k_{np-memb}$  (blue crosses, right  
 blue axis) decreases when the neck size increases. We assume that for neck sizes  
 larger than the phonon mean free path, the nano-wire's TC might be smaller**

than the membrane's one. Due to computational time issues we could not test this hypothesis with EMD.

250 Three assumptions can be considered to explain why the membrane's TC is much lower compared to NW's one:

1. Phononic effects might be dominant at low temperatures in the phononic-like membranes because of the periodicity of the porosity. Is this the case at room temperature? Band folding and band gap could occur in the dispersion curves and it would drastically lower the TC.  
255
2. The effect of the orientation of the scattering surface is important, as supposed by Nomura [1] and demonstrated in ref [57]. In a NW, all scattering surfaces are parallel to the direction of measurement ( $x$  axis), while in membranes this surface is the combination of free surfaces (membrane's walls parallel to  $x$  axis) and pore surfaces (curved surface, sometimes perpendicular or tangential to  $x$  axis). The surfaces perpendicular to the direction of TC measurement could prevent the thermal transport more efficiently than the parallel surfaces (lateral surfaces of a NW).  
260
3. In the simulation, it is possible that the roughness is more important for the pore surfaces, which are curved, than for the free surfaces, which are flat. A part of the phonons could be reflected specularly by free surfaces of the membrane while the pores would diffuse them. The NW having no pores, all its scattering surface would be partially specular and its TC would be greater than expected in purely diffusive case.  
265

270 In figure 3, the DOS of the three membranes are compared to the one of the membrane of same thickness without pores. No direct band gap due to the porosity is observed at 300 K and the modifications compared to the non-porous membrane are negligible except for the smaller system. In the latter, the TO and TA peaks are reduced. The TO polarized phonons contribute very little to the thermal transport in Silicon at room temperature [62], so the reduction of the TO peak should have no significant influence on the TC. However the TA polarized phonons are the main heat carriers, so the reduction in this peak could

further lower the TC. This could explain why the reduction of the TC compared to the NW's one is so large for the membrane with the smallest periodicity. But  
280 for the two largest systems, the reduction in the TC does not seem to be due to phononic effects.

#### 4.2. Monte Carlo

The TCs calculated with Monte Carlo are plotted in the figure 4. For the membranes, two cases are considered: the reflection of phonons at the pore  
285 boundaries can be specular or diffuse. The TC is systematically lower when diffuse conditions are applied on the pore surface. Our geometric parameter values are based on the fabricated and measured membranes of Anufriev *et al* [58]. Their results have been added in the figure for comparison (stars). The numerical values are in pretty good agreement with the experimental ones. Indeed, the Monte Carlo method underestimates the experimental TC but the  
290 trend is the same and the uncertainty on the measurement is unknown. Once more, the TC of the NW is greater than the membrane's one when the neck is small, regardless of the reflection condition on the pores. Two regimes are observed in the figure 4:

- 295 • When the neck size is reduced (smaller than 150 nm) because of the great diameter of the pore ( $d > 90$  nm), the TC of the NW is larger than the membrane's one.
- When the pore's diameter is small, the neck is large (greater than 150 nm) and the TC is lower for the NW than in nano-porous membranes.

300 Molecular dynamics results and experimental values of refs [1, 2] belong without doubt in the first regime. Here, for the plotted Monte Carlo results, the crossing of the two curves occurs at a critical neck size  $n_c = 150$  nm. The periodicity of the membrane is 240 nm, so the ratio  $n_c/a = 150/240$  is close to 2/3. In order to check if this finding is general, a systematic study on the periodicity and the thickness of the membranes has been performed with Monte Carlo (2  
305 thicknesses and 4 periodicities are depicted in figures added in supplementary

data). For all studied cases the  $n_c$  does not depend on the membrane thickness but only on the periodicity. Moreover, the crossing of the TC of the two nano-structures occurs when the neck size is roughly equal to 2/3 of the periodicity (tab. 2). Corresponding graphs are given in supplementary materials section.

Table 2: Critical neck size  $n_c$  for different periodicities and thicknesses of membranes. When the neck is greater than  $n_c$ , the TC of the equivalent nano-wire is lower than the TC of the membrane. When the neck is less than  $n_c$ , thermal transport is further reduced in the membrane than in the nano-wire. The ratio  $n_c/a$  is always close to 2/3.

$a$ (nm)	$e = 145$ nm (MC)		$e = 80$ nm (MC)	
	$n_c$ (nm)	$n_c/a$	$n_c$ (nm)	$n_c/a$
160	100	0.625	105	0.66
200	125	0.625	125	0.625
240	150	0.625	160	0.67
280	185	0.66	190	0.68

The TC of the phononic-like membrane is about 60-80% of the NW's one when the neck is small. As for the Molecular Dynamics results, the discrepancy between np-memb and NW increases when the neck size decreases, but the inverse behavior was observed by Nomura *et al.* In order to compare the two systems, we plotted the TC versus the  $S/\mathcal{V}$  ratio (fig. 5). Considering the  $S/\mathcal{V}$  ratio, the first regime is already reached for  $d > 30$  nm (4<sup>th</sup> point). So, at same  $S/\mathcal{V}$  ratio, the TC of the NW is less than the TC of the porous membrane only when the pore diameter is very small compared to the periodicity ( $d \ll a$  with  $a = 240$  nm here).

In section 2.2, we mentioned that intrinsically the Monte Carlo method does not take into account the phononic effects due to the periodicity of the porosity. However, the TC of the phononic-like membrane is still lower than the TC of the NW for a same  $S/\mathcal{V}$  ratio. Then the first hypothesis of the section 4.1 (phononic effects) is insufficient to explain this behavior. Combined with the DOS in the figure 3, the MC results lead to the exclusion of this hypothesis.

The third assumption (specular reflections) can also be eliminated with the Monte Carlo simulations. Indeed, with this numerical method, the reflections of the particles on the membrane's and NW's exterior surfaces are systematically diffuse. Concerning the pore's surfaces, the reflection type can be set to purely specular or diffuse at the beginning of the simulation. So, even with the pore condition set to specular and the exterior walls entirely diffuse, the porous membrane can have a TC lower than the NW for a same  $S/\mathcal{V}$ . So the third hypothesis of the section 4.1 can also be excluded. There is only left the second one, *i.e.* the surfaces of the pores, which are curved and partially perpendicular to the direction of measurement, are more efficient to reduce the thermal transport than the exterior surfaces, which are parallel to the  $x$  axis. In order to evaluate this assumption, an other comparable system (third one depicted in section 3) has been modeled with Monte Carlo and Molecular Dynamics.

## 5. Modulated nano-wires

In this section, the TC of the third modeled system is investigated. If the orientation of the scattering surfaces is the main reason of the larger reduction of the TC in the porous membranes compared to the NWs without modulations, then the TC of the equivalent modulated NWs (m-NWs) with periodic and cylindrical modulations would always be less than or equal to the membrane's one. It is expected that the TC of the m-NW is much less than the membrane's one when  $d$  is small because of the back-scattering which occurs on the free surface perpendicular to the  $y$  direction only in the m-NW (the periodic conditions perpendicular to  $y$  axis in the membrane do not reduce the thermal transport). When  $d$  approaches to  $a$ , the impact of the  $y$  boundary conditions on thermal transport is less important as reflections on the cylinders become more frequent than free surface scattering. So the TCs of the two systems should be the same. This is exactly what is observed in figure 6.

With Monte Carlo, the m-NW has been modeled with dimensions comparable to those of the systems of the previous section (4.2): the height of the

355 m-NW is equal to the thickness of the membrane ( $e = 145$  nm), its maximum  
width is  $a = 240$  nm and the diameter  $d$  of the cylinders varies between 0 and  
220 nm. For the membrane, the two cases of specular and diffuse reflections on  
the pores were investigated. In order to compare the new system to the mem-  
brane one, both reflection conditions on the cylindrical modulations have been  
360 tested, while the reflections occurring on the walls between two modulations are  
always diffuse.

For diffuse conditions on the cylinders, the TC of the m-NW is systematically  
lower or equal to the membrane's one, but the two conductivities merge when  
the neck becomes smaller than 100 nm. The same behavior is observed with  
365 specular reflections on the cylinders:  $k_{m-NW} \leq k_{np-memb}$  and the two curves  
converge when the neck is reduced. This means that the thermal transport is less  
hindered in NWs than in porous membranes with same characteristic dimensions  
surely because of the orientation of the scattering surfaces. Comparing figures 4  
and 6 it is observed that both types of NW (with and without modulations) have  
370 lower TC than their equivalent membranes for neck sizes larger than 150 nm.

In figure 7, results are plotted in terms of  $S/\mathcal{V}$  ratio. For a same  $S/\mathcal{V}$ , the TC  
of the m-NW is more important than the membrane's one. This is coherent with  
the previous observation: in both systems, a part of the scattering surface is  
parallel to the measurement direction (fixed boundary conditions perpendicular  
375 to the  $z$  axis), but in the m-NW there is also the free surface between the  
cylinders perpendicular to the  $y$  direction which is parallel to the  $x$  axis. So a  
more important fraction of the scattering surface is parallel to the measurement  
direction in the m-NW. Therefore it is logic that the thermal transport is more  
reduced in the membrane for a same  $S/\mathcal{V}$  ratio. When  $S/\mathcal{V}$  increases (*i.e* when  
380 the diameter increases), the difference in the TC between membranes and m-  
NW disappears, as the scattering surface perpendicular to the  $y$  axis between  
the modulations is less and less influential.

The orientation of the scattering surfaces is an important parameter for  
the TC, this is also retrieved by Molecular Dynamics as it will be shown at the  
385 following. A m-NW with dimensions comparable to those of the systems studied



in the section 4.1 has been modeled with MD. The maximum width of the m-NW was set to  $15 a_0$  and the diameter of the cylinders is  $10 a_0$ , so the neck is equal to  $5 a_0$ . Then this m-NW has to be compared with the membrane of the first line in the table 1 ( $a = 15a_0$ ,  $d = 10a_0$  and  $n = a - d = 5a_0$ ). With Molecular Dynamics, the TC of the m-NW is found to be  $3.3 \pm 0.4$  W/m K and its  $S/\mathcal{V}$  ratio is equal to  $0.77 \text{ nm}^{-1}$ . This is very close to the TC of the equivalent membrane ( $3.4 \pm 0.3$  W/m K, see fig. 2). This definitely confirms that the difference between the TC of membranes and NWs is due to the orientation of the scattering surfaces compared to the direction of TC measurement. Moreover, the DOS of the nano-wires with and without modulations have been computed and the m-NW has exactly the same DOS as the equivalent membrane and the  $5 a_0$  width NW. With these results, we can conclude that phononic effects do not dominate the TC of these systems **at room temperature, and the reduction of the TC is due to the phonon scattering at the surfaces of the nano-structures.**

## 6. Conclusion

This work provides insights about the thermal conductivity (TC) of phononic-like membranes and nano-wires with and without width modulations. Experimental results of Anufriev *et al* [58] have been retrieved and observations of Yu *et al* [1] are confirmed with two independent and complementary numerical techniques. The difference between the TC of periodic porous membranes and nano-wires' one is explained with geometric considerations by modeling an equivalent modulated nano-wire. In this system, a part of the scattering surface is perpendicular to the direction of measurement, as in the porous membrane. This leads to a reduced TC compared to a simple nano-wire, proving that the orientation of the scattering surface is important.

It is shown that the phononic effects in the periodic membrane **do not exist** at 300 K. The surface's orientation is enough to explain the lower TC of the porous membrane compared to the nano-wire's one for most of the systems. Ultra-low TCs observed by Yu *et al* [2] concern nano-structured Silicon for temperature

415 comprised between 100 and 300 K. The current work achieved at room temperature does not show any coherent effect on the studied structures. Further investigation at lower temperatures is necessary to verify possible “phononic” behavior for the origin of the TC lowering.

Finally, even if phononic effects are negligible, the  $S/\mathcal{V}$  ratio is not sufficient  
420 to describe the thermal behavior of nano-structured materials because it does not take into account the scattering surface’s geometry. A generalization of the TC appraisal in such nano-structures could possibly be achieved by introducing correction factors defining the orientation of the different scattering surfaces in the  $S/\mathcal{V}$  parameter.

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#### **Supplementary materials**

In this section we present the TCs calculated with MC of nano-porous membranes of different thicknesses (80 nm, fig. 8, and 145 nm, fig. 9) and periodicities  
435 (160 nm, 200 nm, 240 nm and 280 nm) as a function of the neck. The TCs of equivalent nano-wires with height of 80 nm and 145 nm have been computed too for the sake of comparison. Then the critical neck size  $n_c$ , corresponding to the crossing of the curve of the membrane with the nano-wire’s one, has been extracted for each periodicity and thickness. When the neck is smaller than  $n_c$ ,  
440 the TC of the nano-wire is larger than the membrane’s one. When the neck is smaller than  $n_c$ , the membrane has a larger TC than the nano-wire. The critical neck values  $n_c$  for all configurations can be found in table 2.

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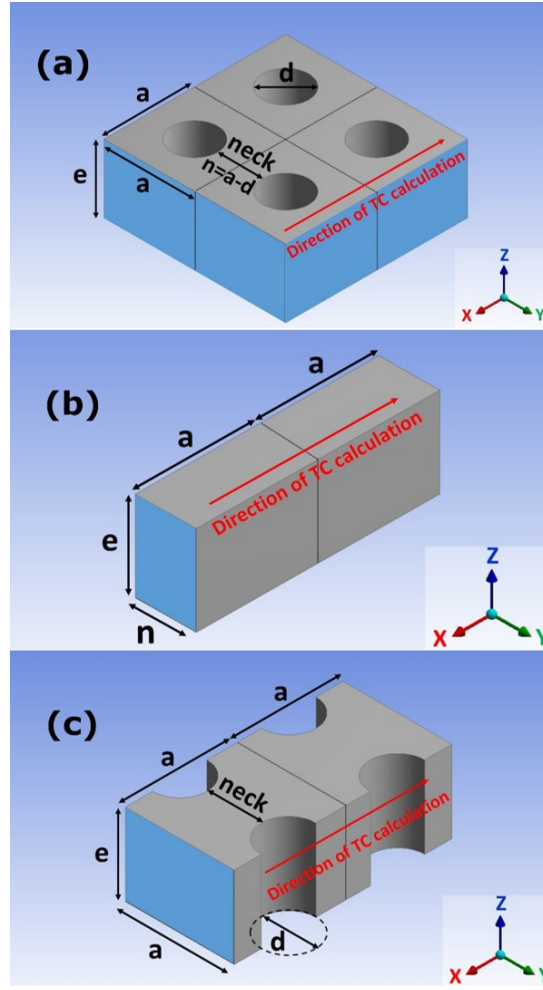


Figure 1: Schematic representation of the modeled systems. **(a)** phononic-like nano-porous membranes (np-memb). Blue faces indicate periodic boundary conditions in these directions, the other direction is not periodic as it is the direction of the thickness of the membrane. **(b)** equivalent nano-wire (NW) whose width is equal to the neck between two adjacent pores in the porous membrane. The height is equal to the thickness of the membrane. The blue face indicates a periodic boundary condition in this direction (length of the nano-wire), the other directions are not periodic (walls of the nano-wire). **(c)** equivalent modulated nano-wire (m-NW). Its width is equal to the periodicity  $a$  of the porous membrane and is modulated by periodic and cylindrical constrictions with the same diameter  $d$  as the pores. Thus, the minimum width is equal to the neck between two neighbouring pores in the membrane. The blue face indicates a periodic boundary condition in this direction (length of the m-NW), the other directions are not periodic (walls of the m-NW).

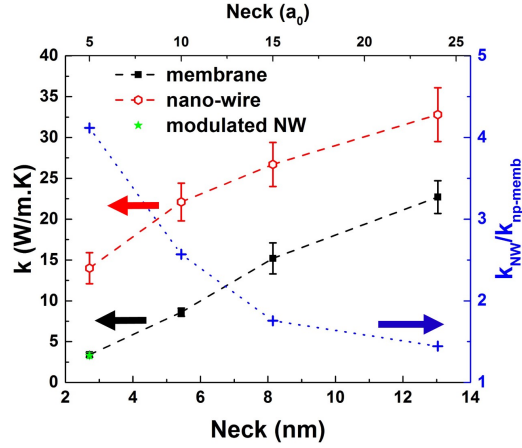


Figure 2: TC (computed by MD) of porous membranes and equivalent NWs versus neck size, calculated with EMD (left axis). The ratio of the TC of the NW to membrane's one is given for each neck size (right axis).

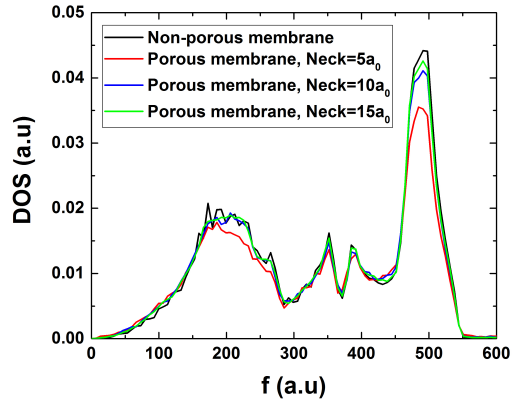


Figure 3: Phonon Density of State (DOS) of the nano-porous membranes compared to the DOS of a membrane of same thickness without pore. Modifications in phonons populations due to the porosity do not seem to be important for thermal transport.

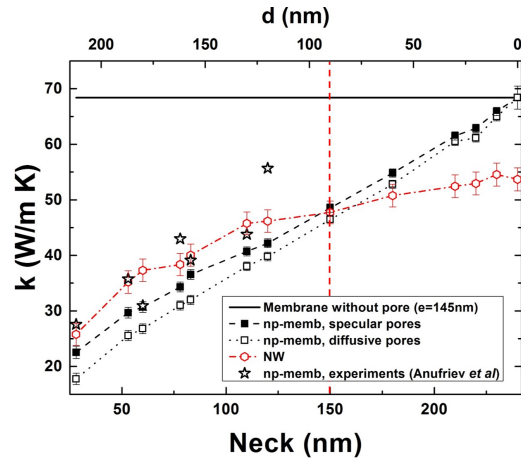


Figure 4: TCs (calculated by MC) of nano-porous membranes and equivalent NWs in terms of the neck size. When the latter is small, the TC of the NW is once more greater than the membrane's TC. Experimental results for membranes with the same geometric configuration can be found in ref [58].

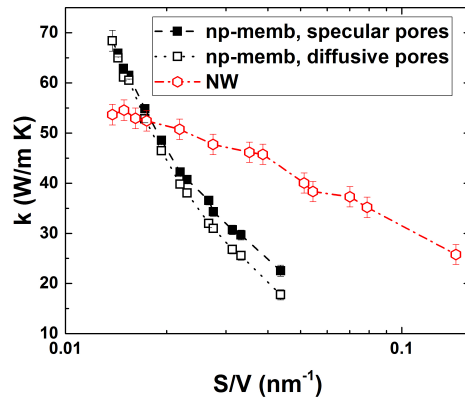


Figure 5: TCs (calculated by MC) of nano-porous membranes and equivalent NWs in terms of the  $S/V$  ratio.

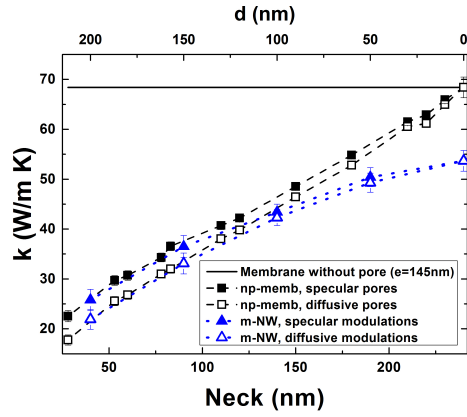


Figure 6: TCs computed with Monte Carlo of nanoporous membranes (np-memb) and equivalent modulated nano-wires (m-NW) in terms of the neck size.

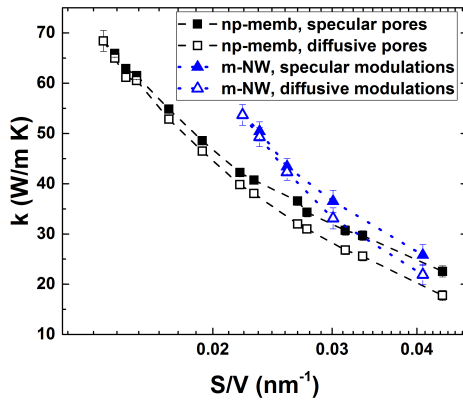


Figure 7: TCs computed with Monte Carlo of nanoporous membranes and equivalent m-NWs in terms of the  $S/V$  ratio.

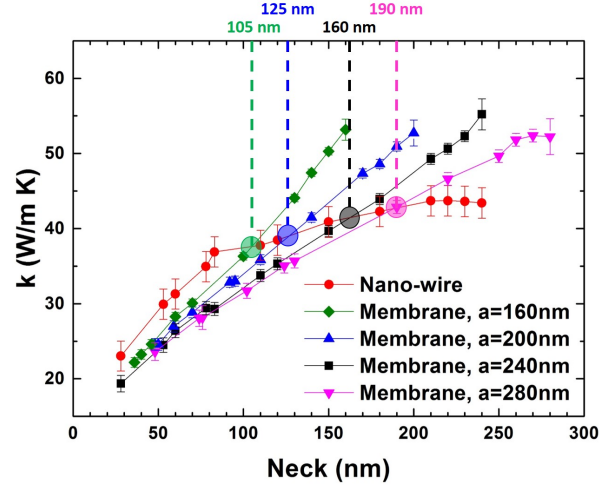


Figure 8: TCs (computed by MC) of membranes with thickness of 80 nm for various periodicities compared to the TC of the nano-wire with height of 80 nm. The values of the critical neck size  $n_c$  for which membrane's TC is equal to NW's one can be found in table 2.

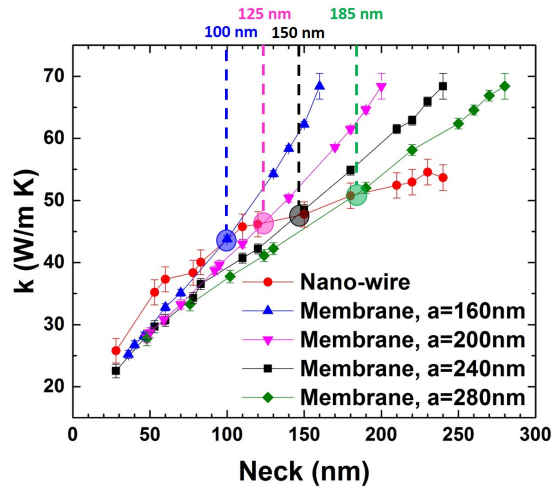


Figure 9: TCs (computed by MC) of membranes with thickness of 145 nm for various periodicities compared to the TC of a nano-wire with height of 145 nm. The values of the critical neck size  $n_c$  for which membrane's TC is equal to NW's one can be found in table 2.