



Optimization of the random multilayer structure to break the random-alloy limit of thermal conductivity

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A low lattice thermal conductivity (κ) is desired for thermoelectrics, and a highly anisotropic κ is essential for applications such as magnetic layers for heat-assisted magnetic recording, where a high cross-plane (perpendicular to layer) κ is needed to ensure fast writing while a low in-plane κ is required to avoid interaction between adjacent bits of data. In this work, we conduct molecular dynamics simulations to investigate the κ of superlattice (SL), random multilayer (RML) and alloy, and reveal that RML can have 1–2 orders of magnitude higher anisotropy in κ than SL and alloy. We systematically explore how the κ of SL, RML, and alloy changes relative to each other for different bond strength, interface roughness, atomic mass, and structure size, which provides guidance for choosing materials and structural parameters to build RMLs with optimal performance for specific applications. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4913319>]

Reducing the lattice thermal conductivity (κ) is an essential route to develop thermoelectric materials with high figure of merit. Previous attempts to reduce κ focused on fabricating nanostructures with enhanced phonon scatterings, for example, nanocomposites/nanocrystals with grain-boundary scattering,^{1,2} superlattices with interface scattering,³ alloys with mass/bond-difference scattering,⁴ nanowires with boundary roughness scattering,⁵ etc. In our earlier work,⁶ we showed that the κ of superlattice (SL) could be significantly reduced by randomizing the thicknesses of its layers. For the resulted random multilayer (RML), the reduction in κ is caused by phonon localization instead of enhanced phonon scattering, which can offer a new class of strategies to reduce κ .

The SL structure has attracted extensive attention owing to the feasibility to aggressively enhance phonon-interface scattering without deteriorating electron mobility significantly. It was also reported that SL can break the corresponding random alloy thermal conductivity limit.^{7,8} However, it has been widely observed that the κ of SL cannot be continuously reduced by decreasing its period length p .^{6–11} When p is very small, coherent phonons arising from the SL phonon spectra dominate heat conduction, and these phonons are not scattered by the interfaces. Creating roughness or species mixing at the interfaces was proposed to reduce κ by disturbing coherent phonon transport;¹² however, this also deteriorates electrical conductivity. In common thermoelectric materials, the electron mean-free-path (MFP) is significantly shorter than the phonon MFP.¹³ This allows us to engineer the RML system such that the layer thickness is comparable to or longer than the electron MFP but shorter than the MFP of coherent phonons. As a result, electrons become incoherent while phonons remain coherent, and thereby, the coherent phonons will be localized in RML, while electron transport will not be affected much. Despite our limited knowledge that RML could have lower κ than SL,⁶ and that sometimes SL could have lower κ than alloy, there is no

systematic study on how the κ of these structures change relative to each other when various structural parameters are varied, or when different materials are used.

In addition, a highly anisotropic κ is essential for various applications.^{14,15} For example, the magnetic layers used for heat-assisted magnetic recording requires a high κ in the direction perpendicular to the layer to ensure fast thermally aided writing, while a low κ parallel to the layer to avoid the thermal interaction between adjacent bits of data.¹⁴ The anisotropic κ of SLs has drawn significant attention¹⁶ but that of RMLs has never been studied. In this work, we investigate the thermal transport in multilayer structures with different interface condition, average period length, bond strength, and atomic mass, so as to gain a knowledge of the benefit of using them as low- κ or anisotropic thermal materials. This work will provide practical guidance to choose the best materials and optimal structural parameters to achieve the lowest κ or highest anisotropy with the layered structure.

We investigate binary SL, RML, and alloy systems composed of two base materials. The SL and RML are created via layer-by-layer stacking of face-centered-cubic unit cells (UC) of two different materials alternatively along the [100] direction. If all the layers of the same material have the same thickness, the resulted structure is SL; in contrast, if the layer thickness is random, it is a RML. Specifically, the RMLs simulated in this work are created from the corresponding N -layer SLs in the following way: (1) Randomly select a layer from the N layers. The selected layer must have at least 2-UC-thick of atoms, or the selection is repeated until a thick enough layer is selected. (2) Move 1 UC thick of atoms from this layer to another randomly chosen layer of the same material; in this way, we have modified the thicknesses of two individual layers but maintained the total thickness of each material unchanged. (3) Repeat the above steps for $160 \times N$ times. We also study SL with interface roughness in the form of interfacial species mixing.¹⁷ It is created by mixing one atomic monolayer of each of the materials at the interface, thereby forming a two-monolayer (1 UC) thick

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interface mixing region. The atomic structures of RML and rough SL can be found in the supplementary materials.¹⁸

The interatomic interactions are modeled by the Lennard-Jones (LJ) potential

$$\phi_{ij}(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right], \quad (1)$$

where ϕ_{ij} and r_{ij} are the pairwise interaction potential energy and the distance between atoms i and j , and σ and ϵ are the zero-potential-energy pair separation and the potential well depth, respectively. The same σ as that in solid argon¹⁹ was used to model all the atomic interactions in our simulations, while ϵ is increased from 0.0104 eV (van der Waals force in argon) to 0.1664 eV, unless otherwise mentioned, to mimic covalent bonds as appeared in most SLs and alloys fabricated so far, e.g., Si/Ge. The only difference between the two base materials is their atomic masses, which are, respectively, 40 g/mol and 90 g/mol unless otherwise mentioned.

Herein, we conduct molecular dynamics (MD) simulations using the LAMMPS package.²⁰ Equilibrium MD (EMD) simulations with the Green-Kubo method²¹ are used to compute the bulk-limit κ from the heat current autocorrelation function (HCACF) as

$$\kappa_\nu = \frac{V}{k_B T^2} \int_0^\tau \langle J_\nu(\tau) J_\nu(0) \rangle d\tau, \quad (2)$$

with V denoting the volume of the structure, T the temperature, k_B the Boltzmann constant, ν the direction of heat flux J and $\langle \rangle$ the auto-correlation operator. The periodic boundary condition is applied to all directions. The heat flux \vec{J} is computed as

$$\vec{J}(t) = \frac{1}{V} \left\{ \frac{1}{2} \sum_{i,j,i \neq j} \vec{r}_{ij} (\vec{F}_{ij} \cdot \vec{v}_i) + \sum_{i,j,k} \vec{r}_{ij} [\vec{F}_j(ijk) \cdot \vec{v}_j] \right\}, \quad (3)$$

where \vec{v} denotes the velocity of atom i , and \vec{r} and \vec{F} are the distance and the two/three-body interaction between different atoms (i, j , or k). The convection term in the original full

heat flux formulation²¹ is not included in our calculations since it causes wild oscillations in the HCACF, making it difficult to extract the saturated value. Removing this term helps smooth the HCACF without affecting the validity of the Green-Kubo calculation.¹⁶ Supercells with a cross-sectional area of 8 UC \times 8 UC and a length up to 512 UC (64 UC for short-period SLs and RMLs) are used to ensure the convergence of simulation results with respect to supercell size. More details on the convergence test can be found in the supplementary materials.¹⁸ Our EMD simulations are conducted with a time step size of 1 fs for 16 million steps. More details on our EMD simulations can be found elsewhere.²² The nonequilibrium MD (NEMD) technique has been used to reveal size-dependent thermal transport properties,^{23,24} which will be used here to explore how the total structure length affects κ . The setup of our NEMD simulation is the same as that in our earlier work.⁶

It is well known that the cross-plane thermal conductivity κ_\perp of a SL is usually different from its in-plane value κ_\parallel .³ However, κ_\parallel of RMLs has never been studied. A knowledge of the existence and magnitude of anisotropy in RMLs is essential for its applications.

Figures 1(a) and 1(b) show the κ_\perp and κ_\parallel of SL, RML, and rough SL. As shown in Fig. 1(a), κ_\perp of SL decreases with increasing period length p at short p 's and then increases at long p 's, while κ_\perp of both RML and rough SL increases monotonically with p . The non-monotonic trend for SL arises from a competition between coherent and incoherent phonons, i.e., coherent phonon conductivity decreases with increasing p due to reduced group velocities while incoherent phonon conductivity increases with p due to reduced phonon-interface scatterings.⁶ In RML and rough SL, thermal transport is almost solely contributed by incoherent phonons, so their κ_\perp increases with the increase in p as a result of decreased interface density. It is worth noting that κ_\perp of RML is not necessarily higher or lower than that of alloy, but it is more beneficial to use RML with smaller p , resulting from the localization of coherent phonons and extensive interface scattering of incoherent ones.

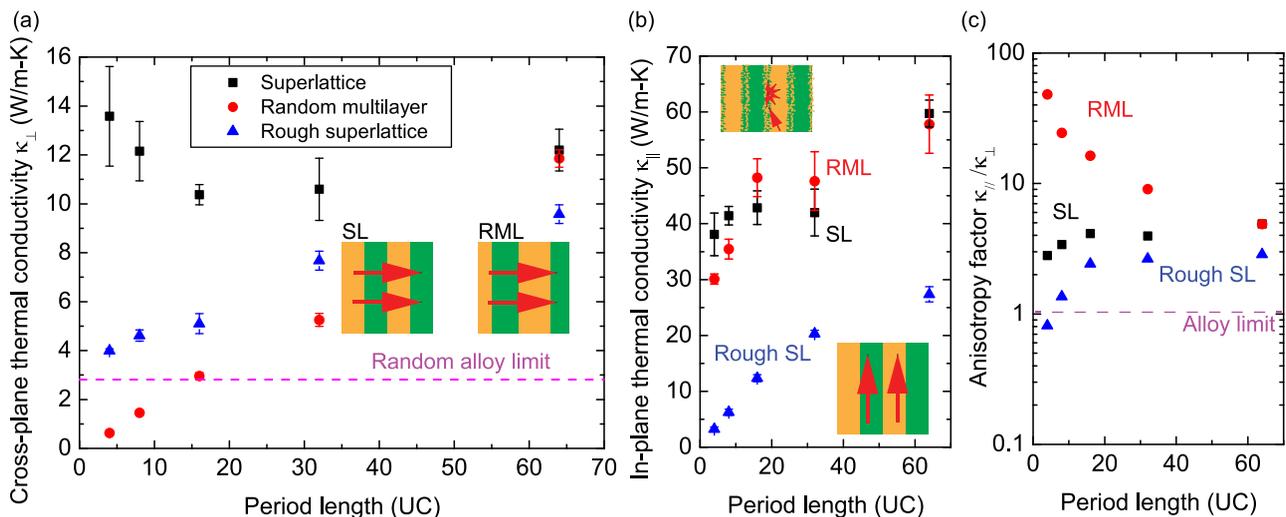


FIG. 1. (a) Cross-plane thermal conductivity, (b) in-plane thermal conductivity, and (c) anisotropy factor of superlattice with smooth interface, random multilayer, and superlattice with interface roughness.

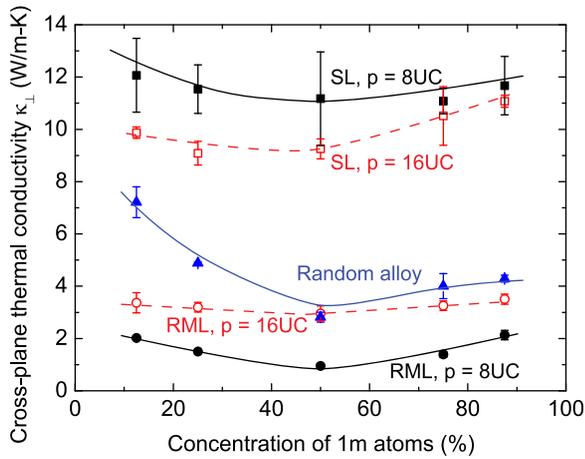


FIG. 2. The cross-plane thermal conductivity of superlattice, random multilayer, and random alloy as a function of the concentration of 1 m atoms. Lines are guides for the eyes.

Figure 1(b) displays the in-plane κ 's. Different from the κ_{\perp} 's shown in Fig. 1(a), κ_{\parallel} of smooth SL and RML are almost the same and much higher than their κ_{\perp} 's. This indicates that the phonon localization in the cross-plane direction does not affect in-plane phonon transport significantly, which could lead to enhanced anisotropy in κ for such layered structure. However, κ_{\parallel} of rough SL is remarkably lower than that of smooth SL and RML. This is because the interfaces in rough SLs scatter phonons diffusely and the backscattering of forward propagating phonons causes substantial thermal resistance. In contrast, interfaces are smooth in perfect SL and RML, in which phonons are scattered specularly at the interfaces without backscattering.

To quantify the anisotropy in κ , we define the anisotropy factor as $\kappa_{\parallel}/\kappa_{\perp}$. We compare the anisotropy factors of SL, RML, and rough SL in Fig. 1(c). It is noticeable that the anisotropy in RML can be 1 order of magnitude higher than smooth SL, and almost 2 orders of magnitude higher than rough SL, when the period length is short.

The dependence of κ on composition in random alloys has been extensively studied to explore the optimal composition for lowest κ .²⁵ Herein, we compare such composition dependence for SL and RML with that for alloys in Fig. 2. We denote the atoms with atomic mass of 40 g/mol as 1 m and the others of 90 g/mol as 2.25 m. It is obvious that there is a minimum κ of alloy at around 50%, but there is no significant composition dependence of κ_{\perp} in SL and RML, which is a result of the dominance of interface scattering.

There is a wide span of atomic mass and bond strength in materials that have been used to make SLs or alloys, for example, Si/Ge,²⁶ AlAs/GaAs,²⁷ Bi₂Te₃/Sb₂Te₃,⁷ etc. As a result, these structures have very different phonon properties. The difference between the κ_{\perp} of SL and RML relies greatly on the phonon MFP of the base materials,⁶ but it is not clear how the κ_{\perp} of SL, RML, and alloy change relative to each other when different base materials are used.

To explore this question, we first study two systems with different mass ratios. The first system is composed of two materials with atomic mass of 40 g/mol and 60 g/mol, respectively, and thereby denoted as 1 m–1.50 m. Similarly, the second system with 40 g/mol and 90 g/mol masses is denoted as 1 m–2.25 m. Figure 3(a) depicts the value of κ_{\perp} relative to the corresponding alloy limit for the two systems. Notably, materials with larger mass mismatch (1 m–2.25 m) benefit more from the RML structure, i.e., they see a much lower κ_{RML} than κ_{alloy} . This also happens in SLs with large period length p . The reason is that it is less likely for incoherent phonons, which are the dominant heat carriers in RML and large- p SL, to transmit across interfaces when there is larger mass mismatch. Differently, short period SLs do not see much reduction in κ_{\perp} when the mass difference enlarges, owing to the fact that the dominating coherent phonons are not scattered at the mass-mismatched interfaces.

We also study another two systems with different bond strength ratio. The first system consists of two base materials of which the ϵ is 1 and 16 times of the ϵ for argon, and accordingly, denoted as 1 ϵ –16 ϵ . Similarly, the second system of which the ϵ is 4 and 16 times of that for argon is denoted as 4 ϵ –16 ϵ . In both systems, all the atoms have a mass of 40 g/mol. In Fig. 3(b), it is obvious that RMLs with larger bond strength mismatch (1 ϵ –16 ϵ) shows more benefit than those with less mismatch (4 ϵ –16 ϵ). It is interesting to note that the 1 ϵ –16 ϵ SLs also shatter the random alloy limit significantly, which is a consequence of the high thermal resistance of the interfaces.

Finally, we explore the dependence of κ_{\perp} on the structure length, since—in experiments—the sample lengths varies in a wide range from nanometer to micrometer where κ may differ from the bulk limit. Our NEMD (symbols) and EMD (dashed lines) results are shown in Fig. 4, where κ_{\perp} increases with the number of periods, i.e., the total length, and approaches the bulk-limit κ_{\perp} . Therefore, a reliable comparison between the κ of different structures should be between samples of the same length, and samples consisting

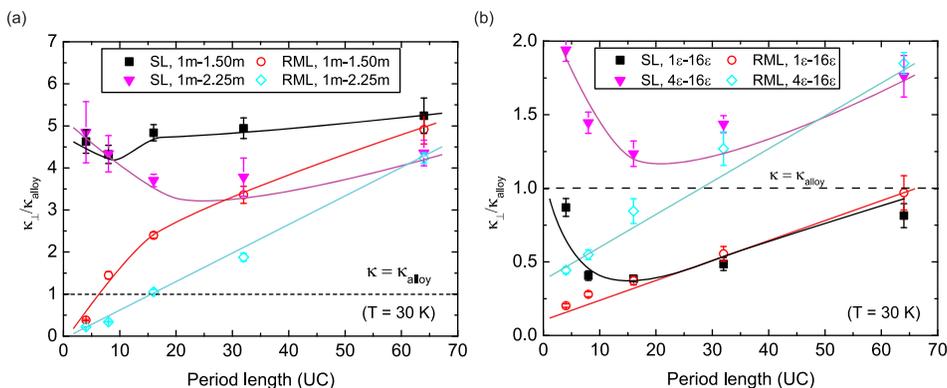


FIG. 3. The cross-plane thermal conductivity of superlattice and random multilayer relative to the alloy limit ($\kappa_{\perp}/\kappa_{\text{alloy}}$) for different (a) mass mismatch and (b) bond strength mismatch. Lines are guides for the eyes.

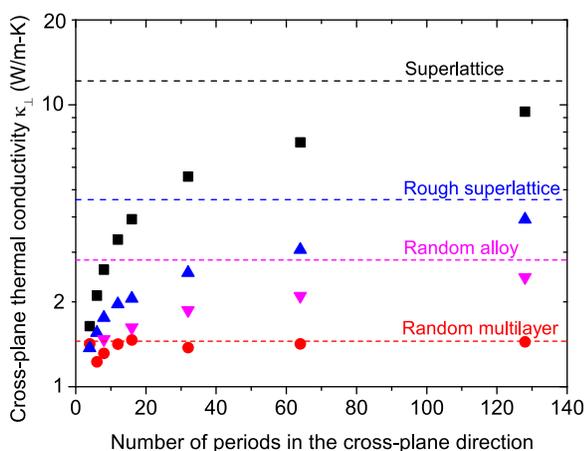


FIG. 4. The cross-plane thermal conductivity of SL, RML, rough SL, and random alloy as a function of structure length predicted in NEMD simulations. The discrete symbols are the κ_{\perp} 's obtained in our NEMD simulations on structures of different length, while dashed lines are bulk-limit κ_{\perp} 's from our EMD simulations.

of more layers are more likely to show significant difference between κ_{SL} and κ_{RML} .

Before we conclude this paper, it will be beneficial to discuss the feasibility of utilizing RMLs to achieve a lower κ_{\perp} than that of SL by using the same materials and fabrication techniques as used for SLs before. As mentioned above, a non-monotonic relation between κ_{\perp} and p of SLs with a minimum κ_{\perp} signifies an important role played by coherent phonons, which has already been experimentally observed for different SLs.^{7,10,28} Another manifestation of significant coherent phonon contribution is that κ_{\perp} increases linearly with the increase in total length of the SL in the experiment of Luckyanova *et al.*²⁹ It is promising to see a lower κ_{\perp} in RML than SL in the above systems due to the localization of coherent phonons. However, an observation of κ increasing with SL length does not guarantee coherent phonon conduction. For example, the κ of both rough SL and that of RML increases notably with total length in Fig. 4, but this increase is due to ballistic transport rather than coherent phonons.

In summary, we computed the bulk-limit κ of SL, RML, and alloy using EMD simulations and size-dependent κ using NEMD simulations. The cross-plane κ of RML was found to be lower than or comparable to that of rough SL, but the in-plane κ of RML can be much higher than rough SL. As a result, RML can have 1–2 orders of magnitude higher anisotropy in κ than SL. RMLs with short period length and large lattice mismatch (bond strength or atomic mass) were shown to be promising to break the alloy limit. Our work provides

guidance for building RMLs with ultra-low κ or highly anisotropic κ tensor.

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