

## Regular article

# On the minimum limit to thermal conductivity of multi-atom component crystalline solid solutions based on impurity mass scattering



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## ABSTRACT

We investigate the effect of mass disorder on the thermal conductivity of Lennard-Jones based multi-component solid solutions via classical molecular dynamics simulations. In agreement with Klemens' perturbation theory, the thermal conductivity reduction due to mass scattering alone is found to reach a critical point, whereby adding more impurity atoms in the solid solution does not reduce the thermal conductivity. A further decrease in thermal conductivity requires a change in local strain-field, which together with mass defect scattering can lead to ultralow thermal conductivities in solid solutions, surpassing the theoretical minimum limits of the corresponding amorphous phases.

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The scattering of higher frequency phonons in crystalline solid solutions results in a significantly lower thermal conductivity as compared to the pure crystals [1–3]. This was first theorized by Klemens in a model of thermal conductivity in which the phonon scattering rates with crystalline impurities have a quartic dependence on the frequency [4]. Klemens' seminal work suggested that the impurities in crystals, such as local changes in atomic mass or bonding environment, will influence the high frequency vibrations much more-so than the low frequency phonons in a similar process to Rayleigh scattering of photons [5–7]. Building upon this work, Abeles proposed a virtual crystal approximation (VCA) to predict the thermal conductivity of solid solutions, which was based on extending Klemens' perturbation theory of isolated impurities to a crystalline alloy with multiple atomic species spanning large atomic percentages, such as  $\text{Si}_{1-x}\text{Ge}_x$ , where  $0 \leq x \leq 1$  (i.e., non-dilute)[8]. Thus, the strength of alloy scattering in the VCA framework depends on perturbations due to mass, strain field and alloy concentration [8,9].

Going beyond binary alloys, the VCA framework has been applied to ternary [10–12] and quaternary [13,14] alloys to gauge the relative roles of mass, bond and volume difference scattering on the thermal conductivity reduction. Koh et al. [14] have shown that for PbTe based alloys, the effect of changes in atomic radius and

bonding outweigh that due to mass differences in the resulting phonon thermal conductivity. Their results have been corroborated by more rigorous first principles-based molecular dynamics simulations on PbTeSe by Murakami et al. [12], where the authors attribute the experimentally observed reduction in thermal conductivity to the local force-field difference between the alloyed constituents. Similarly, for InGaN alloys at intermediate compositions, the large reduction in the thermal conductivity has been attributed to scattering mechanisms beyond that due to scattering by mass disorder, whereas, for high and low alloy concentrations, it was observed that mass disorder alone in the scattering cross-section term could accurately replicate the experimental results [11]. Taken together, engineering solid solutions with considerable mass and force field differences between the constituent atoms can present opportunities to push the limits of thermal transport in alloys by taking advantage of the force-field and mass disorder scattering.

Recently, the advent of engineering configurational entropy into metal-oxide solid solutions by populating the sublattice with many distinct cations [15] has brought fourth the potential to utilize the aforementioned strategies to fabricate materials that possess ultralow thermal conductivities. Most notably, Rost et al. [15] demonstrated the ability to fabricate entropy stabilized oxides with five cation components, creating, for example, a single phase rock salt crystal with Mg, Ni, Co, Cu and Zn (i.e., a solid solution of  $\text{Mg}_x\text{Ni}_x\text{Co}_x\text{Cu}_x\text{Zn}_x\text{O}$ ,  $x = 0.2$ ). The phonon thermal transport in non-metal crystalline solid solutions with five (or more) different elemental species offers the ability to push the limits of traditionally assumed phonon scattering theory, such as the VCA approaches

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described previously. In this regard, it becomes necessary to understand the relative contributions of mass and bond disorder to the thermal conductivity of solid solutions with four or five different atomic species to effectively engineer ultralow thermal conductivity materials. Moreover, the important questions then become: i) what are the lower limits to thermal conductivity of a crystalline alloy with five (or more) different masses? ii) what role does changes in bond strengths have relative to the mass scattering rates? and iii) can this provide an avenue to reduce the thermal conductivity of crystalline systems below the minimum limit to thermal conductivity traditionally associated with amorphous phases? Our present manuscript seeks to answer these questions via molecular dynamics simulations.

Thus, in this study we gauge the effect of mass disorder on thermal conductivity beyond quaternary alloys. For this purpose, we use nonequilibrium molecular dynamics (NEMD) simulations to predict the thermal conductivities of Lennard-Jones (LJ) based solid solutions with one to five component atoms in the crystalline system. In agreement with the VCA, we show that for multi-component alloys, the thermal conductivity reaches a minimum, whereby adding more impurity atoms in the solid solution does not affect the thermal conductivity. Our molecular dynamics simulations suggest that to further lower the thermal conductivity of multi-component alloys, the local strain field needs to be perturbed by changing the interatomic force-field. Furthermore, we demonstrate that with additional scattering driven by changes in the local force-field (i.e., phonon scattering due to changes in bonding and/or volume), the NEMD predicted thermal conductivity of a crystalline alloy can be reduced below the corresponding amorphous phase of the host atoms. This suggests that for solid solutions with five or more atomic species, engineering local strain to enable additional phonon scattering can lead to covalently bonded, isotropic crystalline materials with ultralow thermal conductivities that can be lower than the predicted minimum limit of the corresponding amorphous phases, a feat that has traditionally only been realized in weakly bonded crystals and/or anisotropic layered solids [16–22].

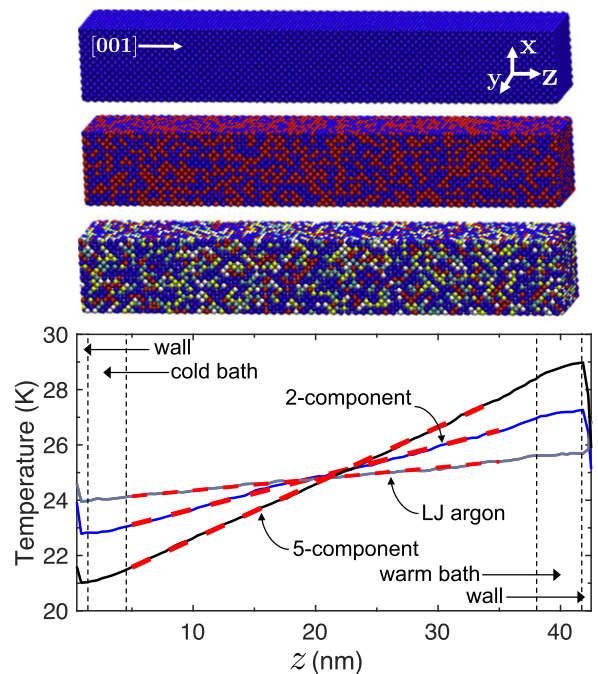
We employ the widely used 12-6 Lennard Jones (LJ) potential,  $U(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ , where  $U$  is the interatomic potential,  $r$  is the interatomic separation, and  $\sigma$  and  $\epsilon$  are the LJ length and energy parameters, respectively. For computational efficiency the cutoff distance is set to  $2.5\sigma$  for all the simulations and the time step is set to 1 fs throughout the simulations. As we are interested in understanding the general effect of mass impurity scattering on thermal transport in multi-atom component crystalline solid solutions as opposed to material specific properties, the use of the LJ potential is sufficient to provide this translational insight. For simplicity, the length and energy parameters are modeled for argon ( $\sigma = 3.405 \text{ \AA}$  and  $\epsilon = 10.3 \text{ meV}$ , respectively) with the lattice constant  $a_0 = 1.56\sigma$  and arranged in an fcc lattice. The sizes of the computational domains are  $10a_0 \times 10a_0 \times 80a_0$  with periodic boundary conditions applied in the  $x$ - and  $y$ -directions, whereas, fixed boundaries with 4 monolayers of atoms at each end are placed in the  $z$ -direction for the NEMD simulations. Schematics of the computational domains for (from top to bottom) LJ argon, 2-component and 5-component alloys (with 50% alloy concentration) are shown in the top panel of Fig. 1. For all multi-component alloys, the impurity masses are equally (and randomly) distributed throughout the host crystalline lattice at the prescribed alloy concentration.

Initially, the structures are equilibrated under the Nose-Hoover thermostat [23], the number of atoms, volume and temperature of the simulation are held constant followed by the NPT integration (which is the isothermal-isobaric ensemble with the number of particles, pressure and temperature of the system held constant) for another 2 ns at 0 bar pressure. We note that for our typical simulations on these LJ-based structures, the temperature fluctuations dissipate in  $\sim 100$  ps and likewise the barostat takes  $\sim 1$  ns for the pressure oscillations to reside. After equilibration, the thermostat

and barostat are removed and a fixed amount of energy is added per time step to a warm bath at one end and removing the equal amount of energy from a cool bath at the other end (with the lengths of the baths at  $10a_0$  in the  $z$ -direction) under a microcanonical ensemble with the number of particles, volume and energy held constant. The addition and removal of energy is carried out at a rate of  $7 \text{ meV ps}^{-1}$  for a total of 12 ns. The temperature profiles for the first 5 ns of the NEMD simulations are discarded in order for the system to reach steady state. This is followed by the sampling of temperature profiles every 0.1 ps for the rest of 7 ns to obtain time-averaged steady-state temperature profiles for our structures. Examples of these temperature profiles for LJ argon, 2-component and 5-component alloys are shown in the bottom panel of Fig. 1. This approach of calculating a temperature gradient in the  $z$ -direction is used to predict the thermal conductivity by invoking the Fourier law,  $Q = -\kappa \partial T / \partial z$ , where the applied flux,  $Q$ , is in the  $z$ -direction and  $\kappa$  and  $T$  are the thermal conductivity and temperature, respectively.

Fig. 2 shows the NEMD-predicted thermal conductivity as a function of temperature for LJ argon. For comparison, we also include the thermal conductivity predictions using the Green-Kubo approach from Ref. [24] in Fig. 2 (open square symbols). The agreement between the two approaches implemented to calculate the thermal conductivities suggests that size effects do not distort the predictions from our NEMD simulations. The errorbars for the NEMD predictions are representative of four different simulations with varying initial conditions.

To understand the effect of increasing the number of atomic species (and the mass disorder thereof) to a binary solid solution on the thermal conductivity, we apply the VCA by only considering perturbations due to mass scattering for our LJ system. For an isotropic



**Fig. 1.** (Top panels) Schematics of LJ argon, 2-component and 5-component alloys (from top to bottom). For the alloys, the impurity atoms (in equal concentrations) make up 50% of the computational domains with the blue color atoms representing the atoms in the host lattice. (Bottom panel) Time-averaged steady-state temperature profiles for the computational domains shown in the top panel. The temperature gradient and the applied heat flux are used to predict the thermal conductivity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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