

Low Thermal Conductivity through Dense Particle Packings with Optimum Disorder

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Heat transport plays a critical role in modern batteries, electrodes, and capacitors. This is caused by the ongoing miniaturization of such nanotechnological devices, which increases the local power density and hence temperature. Even worse, the introduction of heterostructures and interfaces is often accompanied by a reduction in thermal conductivity, which can ultimately lead to the failure of the entire device. Surprisingly, a fundamental understanding of the governing heat transport processes even in simple systems, such as binary particle mixtures is still missing. This contribution closes this gap and elucidates how strongly the polydispersity of a model particulate system influences the effective thermal conductivity across such a heterogeneous system. In a combined experimental and modeling approach, well-defined mixtures of monodisperse particles with varying size ratios are investigated. The transition from order to disorder can reduce the effective thermal conductivity by as much as $\approx 50\%$. This is caused by an increase in the thermal transport path length and is governed by the number of interparticle contact points. These results are of general importance for many particulate and heterostructured materials and will help to conceive improved device layouts with more reliable heat dissipation or conservation properties in the future.

Materials with low thermal conductivity are employed in many fields such as clothing, refrigeration, building insulation, and thermoelectrics.^[1] Concepts to reduce the thermal conductivity of a given material either target the material composition or its nano-, meso-, or microstructure. Generally, for bulk materials, a high thermal conductivity is found in crystalline solids where phonons are able to transport thermal energy over several hundred nanometers based on a well-defined crystal lattice.^[2–5] In contrary, low thermal conductivities are

mostly found in disordered, amorphous materials. Based on an increased scattering at the disordered structure, the mean free path of phonons is strongly reduced, resulting in diffusive thermal transport.^[6,7] Allen et al.^[8,9] proposed three different vibrational modes, namely diffusons, propagons, and locons, to describe thermal transport in amorphous matter. Increasing phonon scattering in bulk materials, subsequently leads to a reduction in thermal conductivity. In dense materials this can be achieved by layered structures,^[10,11] doping,^[12,13] or the embedding of nanoparticles,^[14,15] where particularly crystalline solids are strongly affected. Zhang and Minnich investigated how nanoparticle clusters with a particular size distribution can lower the thermal conductivity in crystalline SiGe alloys even below its amorphous limit.^[14]

Besides the chemical composition of a certain material, the influence of the overall structure is of high importance, too. The most obvious and well-known structural influence is given by the intro-

duction of porosity. This severely decreases the density of a bulk material and consequently reduces the effective thermal conductivity. Depending on the cell size of the porous material, highly insulating properties are accessible.^[16–19] Moreover, classical porous, granular matter becomes increasingly important for a range of applications, which involve heterostructures and interfaces. For instance, thermal management in high-density storage devices such as batteries or supercapacitors is a critical safety concern.^[20–22]

Colloidal assembly structures have been proven to be particular suitable to investigate the influence of 3D nanostructuring on the effective thermal transport in granular matter.^[23] The thermal conductivity of colloidal crystals is mainly governed by the geometrical constrictions at the interparticle contact points, and the material of the particles itself.^[24–26] While most colloidal assembly structures targeted periodically ordered materials, the controlled introduction of disorder also showed to provide fundamental insights, for instance, into the physics of phononic bandgaps in the hypersonic regime.^[27]

In this work, we provide a conceptual understanding of the influence of structural order on the thermal transport properties in particulate mesostructures. Therefore, binary colloidal

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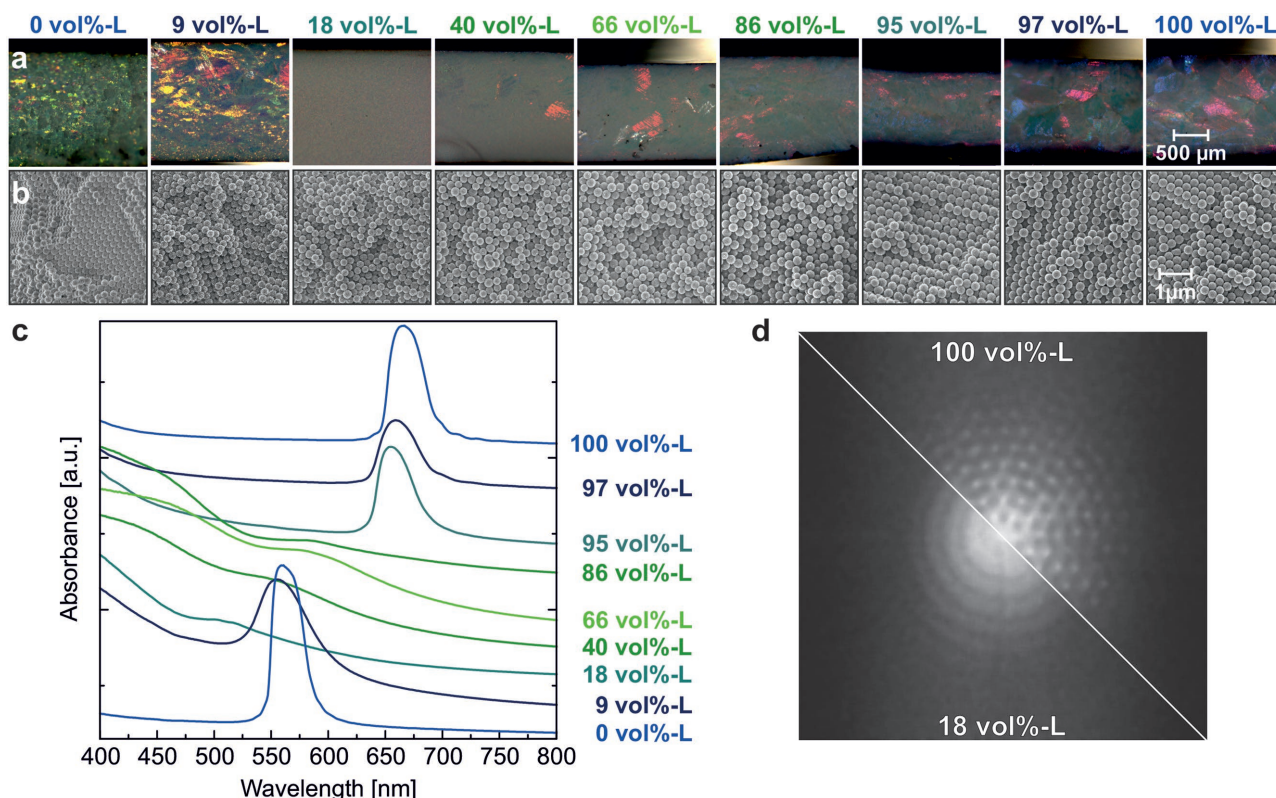


Figure 1. Structural characterization of binary colloidal assemblies. a) Optical and b) scanning electron microscopy side view images of the edges of split colloidal monoliths. c) UV-vis transmission spectra measured on dip-coated assemblies. d) Fast Fourier transformation (FFT) images from scanning electron microscopy images with a mixing ratio of 18 vol% L compared to a FFT image of 100 vol% L colloidal crystal.

assemblies were fabricated from two monodisperse, differently sized polystyrene (PS) particles. These building blocks are easily accessible by common polymerization techniques^[28,29] and their self-assembly into superstructures is well-established.^[30] By mixing two differently sized particles, it is possible to control the structural order of the resulting colloidal assembly. We clarify the underlying effect of the thermal conductivity reduction by finite element modeling combined with molecular dynamic simulations. We further demonstrate how to reduce heat transport in disordered binary assemblies in a rational way.

Binary colloidal assemblies of PS particles possessing a diameter of 243 nm (S) and 306 nm (L) were fabricated by evaporation-induced self-assembly (size ratio ≈ 0.8). For spectroscopic characterization, binary assemblies were additionally immobilized on glass slides by dip-coating of 3 wt% aqueous particle dispersions. The mixing ratio ranged from 0 to 100 vol% L. Optical microscopy and scanning electron images of the edges of split monoliths are shown in **Figure 1a,b** and provide a qualitative expression of how the mixing ratio translates into order and disorder.

From optical microscopy (**Figure 1a**), strong opalescent colors are visible for samples consisting of only one particle type (0 and 100 vol% L) as well as for binary assemblies only containing a small amount of differently sized specimen (9, 95, and 97 vol% L). This is due to Bragg reflection. The difference in color between 0 and 100 vol% L monoliths arises from the size dependence of the Bragg reflectivity. Different

colors within one monolith can be attributed to the angle dependence of the Bragg law, based on different crystal planes exposed to the surface.

For other mixing ratios, only weak overall Bragg reflection (66 and 86 vol% L) or almost only diffuse scattering (18 and 40 vol% L) is visible. At these mixing ratios, the polydispersity of the binary particle dispersion prevents large area particle crystallization. Noteworthy, some embedded crystalline regions are observable for several intermediate mixing ratios (40, 66, and 86 vol% L). This can be explained by the strong tendency of demixing in binary colloidal dispersions.^[31–33] The slow self-assembly process (several days) of the dispersion enables the formation of phase separated, multicrystalline, and amorphous areas.

Scanning electron microscopy (SEM) images validate the optical impression (**Figure 1b**). The pure colloidal crystals feature a high degree of crystalline particle ordering. In contrast, for intermediate mixing ratios, only a random packing of the particles is observed. This is additionally highlighted by fast Fourier transformation (FFT) images of the SEM images illustrated in **Figure 1d**. Whereas distinct reflexes are visible for 100 vol% L due to the hexagonal symmetry of the particle lattice, only smeared Debye–Scherrer rings are obtained for 18 vol% L monoliths. The smearing is based on the disordered mesostructure, whereas the observed Debye–Scherrer rings arise from the different particle diameters present within the monoliths.

We further quantify the intrinsic order of the binary colloidal films by UV-vis transmission spectra of dip-coated samples,

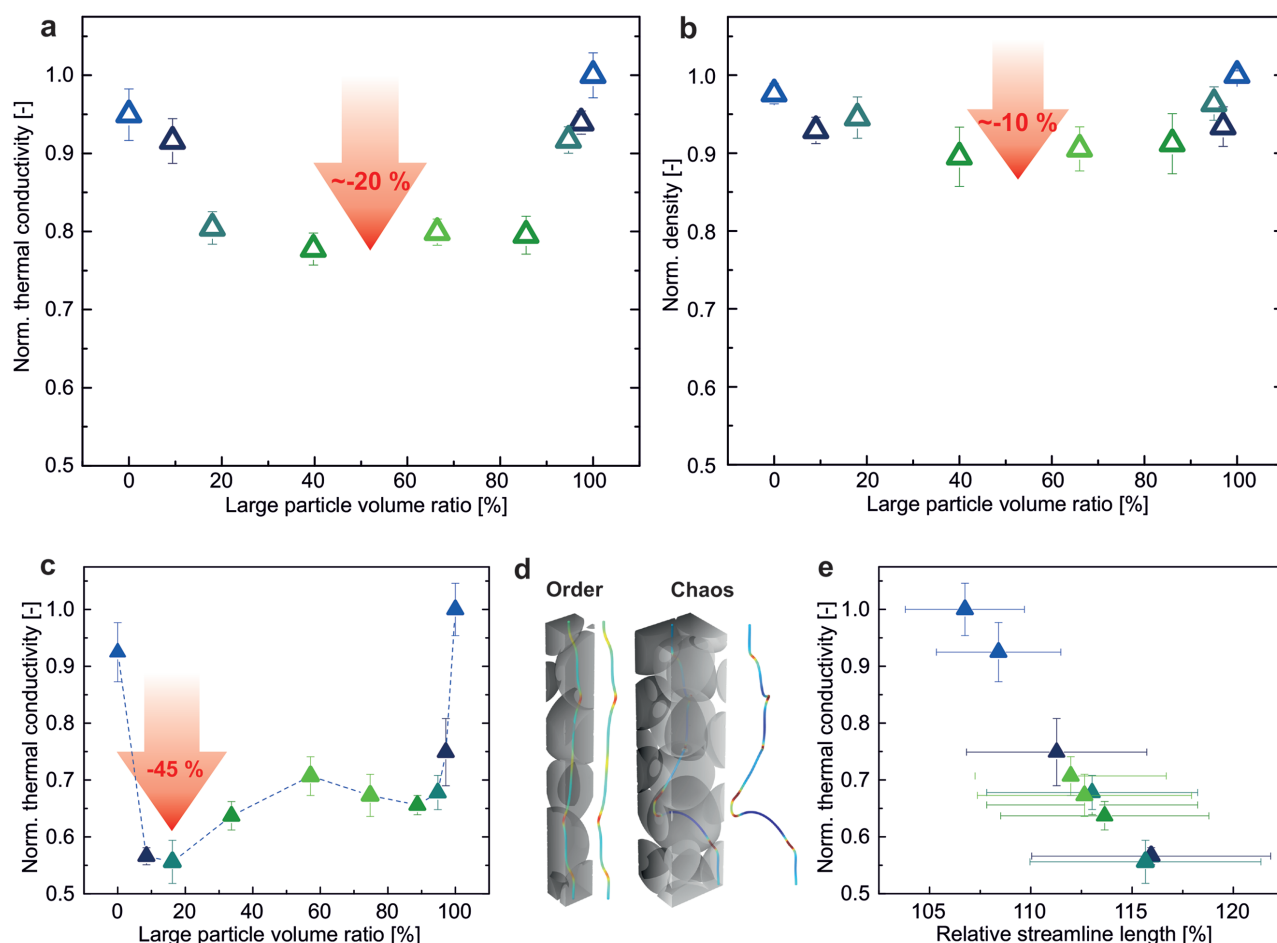


Figure 2. Thermal conductivity of the investigated assemblies with a size ratio of 0.8. Color code indicates ordered (bluish) and disordered (greenish) assemblies. a) Normalized thermal conductivity of binary PS colloidal assemblies possessing different mixing ratios. The red arrow indicates the reduction of the thermal conductivity due to the introduced disorder. b) Normalized density of the colloidal assemblies. c) Thermal conductivity versus volume fraction of large particles obtained by FEM. d) Exemplary streamlines present within a crystalline and a disordered assembly with a size ratio of 0.8 and 16 vol% L. e) Thermal conductivity versus relative streamline length of various size ratios. Error bars in (c) and (e) arise from three individual simulations boxes at three different directions in space.

displayed in Figure 1c. A strong Bragg peak is visible for 0 vol% L colloidal crystals at a wavelength of 559 nm. At small mixing ratios of 9 vol% L, the Bragg peak broadens and the maxima is less allocable due to the disturbance of the crystal lattice. A further increase of the large particle volume fraction to 18 vol% L leads to a vanishing of the Bragg peak. No distinct Bragg peaks are observable for intermediate mixing ratios from 44 to 86 vol% L, indicating a randomly packed structure. The Bragg peak of the larger particle species reoccurs at 95 vol% L and reaches a maximum intensity for 100 vol% L at a wavelength 667 nm.

Optical microscopy, SEM, and UV-vis characterization prove the highly crystalline nature of the homo-particle ensembles, which define the edges of the mixture phase diagram. The long-range order is quickly lost, when mixing two particles with a size ratio of 0.8. Depending on the assembly process a complete suppression of crystallinity can be found (dip-coating) or small, multicrystalline regions caused by demixing prevail (dispersion drying).

Laser flash analysis (LFA) was performed on colloidal monoliths obtained from evaporation-induced self-assembly. By determining the sample density and specific heat capacity, it is possible to calculate the specimen's effective thermal conductivity (see the Supporting Information for details). The thermal conductivity, normalized to the maximum initial value of the pure colloidal assemblies, as well as the normalized thermal conductivity of intermediate mixing ratios are shown in Figure 2a. The color code helps to separate ordered samples (bluish) from randomly packed assemblies (greenish) and correspond to the mixing ratios given in Figure 1.

Homo-particle colloidal assemblies (mixing ratio 0 and 100 vol% L) show a thermal conductivity of 73 and 77 mW m⁻¹ K⁻¹ in absolute numbers, respectively. At small mixing ratios of differently sized particles, the thermal conductivity slightly drops to ≈93% of the initial value. For intermediate mixing ratios, the thermal conductivity drops significantly to ≈80%. This reduction can only partially be explained by the reduced density of the intermediate assemblies as displayed in Figure 2b.

The reduction of the density for intermediate mixing ratios originates from the prevented close packing of the particles during assembly. This leads to a space filling which deviates from the theoretical maximum of 74%. Still, the density only decreases to $\approx 90\%$ of its initial value. Therefore, an additional effect is present, which is responsible for the overall reduction of the thermal conductivity to 80%.

To elucidate this additional contribution, we performed finite element method (FEM) modeling on binary particle mixtures possessing a size ratio of 0.8. The required virtual assemblies were obtained by molecular dynamic (MD) simulations of the assembly process. Exemplary particle assemblies obtained from MD simulations are shown in Figure S2a (Supporting Information). We found highly crystalline particle assemblies at the edges of the mixing diagram. In contrast to our experimental findings, the crystallization process is already fully prevented at very small mixing ratios (Figure S2a, left, Supporting Information). This is caused by the lack of demixing or phase separation of the particles due to the short assembly time-scale used for the MD simulation. FFT images of 0 and 9 vol% L assemblies from MD simulation are compared to the experiment in Figure S2a (Supporting Information), right. Thus, the fully amorphous structure obtained from the MD simulation can be regarded as an ideally disordered case. Experimentally, some degree of crystallization will be difficult to exclude owing to the long timescale allowed for the self-assembly process. FEM has been conducted using the software COMSOL Multiphysics. Details on the modeling are described in the Supporting Information. The calculated thermal conductivity against the volume fraction of large particles is displayed in Figure 2c. Analogous to Figure 2a, the color code indicates ordered (bluish) and disordered assemblies (green). The mixing diagram shows a similar trend for the thermal conductivity as observed for the experiment, with high thermal conductivities for ordered, and a reduced thermal conductivity for disordered assemblies. A minimum thermal conductivity of only 55% of the initial value is observed at a volume fraction of ≈ 16 vol% L. This is an almost twofold enhancement of the insulation capability caused by the disordered structure, and it is significantly lower compared to the experimental results. We ascribe this deviation to the structural difference between the MD simulation and the experiment. As outlined before, by MD simulation one can observe a more disordered distribution of both particle types within the monolith, leading to a stronger reduction of the thermal conductivity.

To explain the origin of the thermal conductivity reduction beyond the decrease in density, we utilized FEM to analyze the length of the thermal transport pathway through such a particulate assembly structure. This can be done by evaluating the length of heat flux streamlines, which reach from the hot to the cold side of the simulation box. Figure 2d shows two individual cases through an ordered (100 vol% L) and disordered (≈ 16 vol% L) particle ensemble. Whereas in the ordered case, a rather straight and unperturbed streamline is obtained, the introduction of disorder strongly bents and perturbs the thermal transport path. The statistic evaluation over the entire simulation box is given in Figure 2e, where we normalized the streamline length on the length of the simulation box. One finds a direct correlation between the streamline length and

the thermal conductivity reduction. This finding can be intuitively explained by a sort of effective thermal length, which differs from the plain geometric size of the box. One may draw an analogy to the concept of the diffusive optical path in a particulate powder, which is governed by the scattering cross section of the constituting sphere.^[34]

Most interestingly, the FEM simulation finds a strongly asymmetric shape of the thermal conductivity reduction with two minima at moderately high and low mixing ratios, respectively. These are not found in the experiment, presumably due to the presence of mesocrystalline domains, embedded in the amorphous structure. We now want to understand the origin of these minima and how the thermal conductivity could be reduced even further. This question could be rephrased to how the thermal streamline length can be further increased in such colloidal superstructures. We, therefore, return to MD simulation and evaluate the local structure around one particle more explicitly. We did this in a twofold way: (1) Using the radial distribution function we evaluate the number of particles surrounding a center particle, which are within the local space of about +10% of the respective particle diameter. (2) Using the individual coordinates of each particle pair, we extracted the number of touching spheres around a central particle. We term the first one “next neighbors”, and the second one “contact neighbors”. Quite expectedly, when introducing disorder the average number of next and contact neighbors is reduced. For crystalline assemblies, one can find an average number of next neighbors per particles of ≈ 12 , based on the face-centered cubic symmetry. For all disordered intermediate mixing ratios, the number of next neighbors is reduced to ≈ 10 (Figure S2b, Supporting Information). The next contact neighbor analysis yields ≈ 8 owing to the more rigorous exclusion criterion. One can imagine that this reduction leads to less pathways for heat to travel through the particle structures and therefore reduces the thermal conductivity of the assemblies. However, we find that the mean number of next neighbor particles merely reaches a broad plateau, and does not explain the asymmetric shape shown in Figure 2c. We, therefore, evaluated the next neighbor particle histograms explicitly. This is shown in Figure 3, where we present the next neighbor histograms at selected mixing ratios (bottom row). We chose a special illustration, to highlight the structural heterogeneity, when heat travels through such a system. We, therefore, present a projection of all particles with the same number of next neighbors that can be found within the simulated box. The color code indicates particles possessing the same number of next neighbors from high (blue) to low (red). It therefore provides a direct impression of how many particles are clustered around one central sphere.

For mixing ratios of 0 and 100 vol% L almost every particle possesses 12 next neighbors. This indicates a nearly fully crystalline face-centered cubic assembly, with few line and point defects being visible. The next neighbor distribution function quickly broadens at intermediate mixing ratios. Most importantly, this distribution function shows a strongly asymmetric behavior. For mixing ratios of 9–66 vol% L, even more than 12 next neighbors per particles are present within the assembly, whereas for high mixing ratios, the number of next neighbors is limited to 12. For a low number of large particles (small mixing ratios), it is possible that one large particle is decorated by a

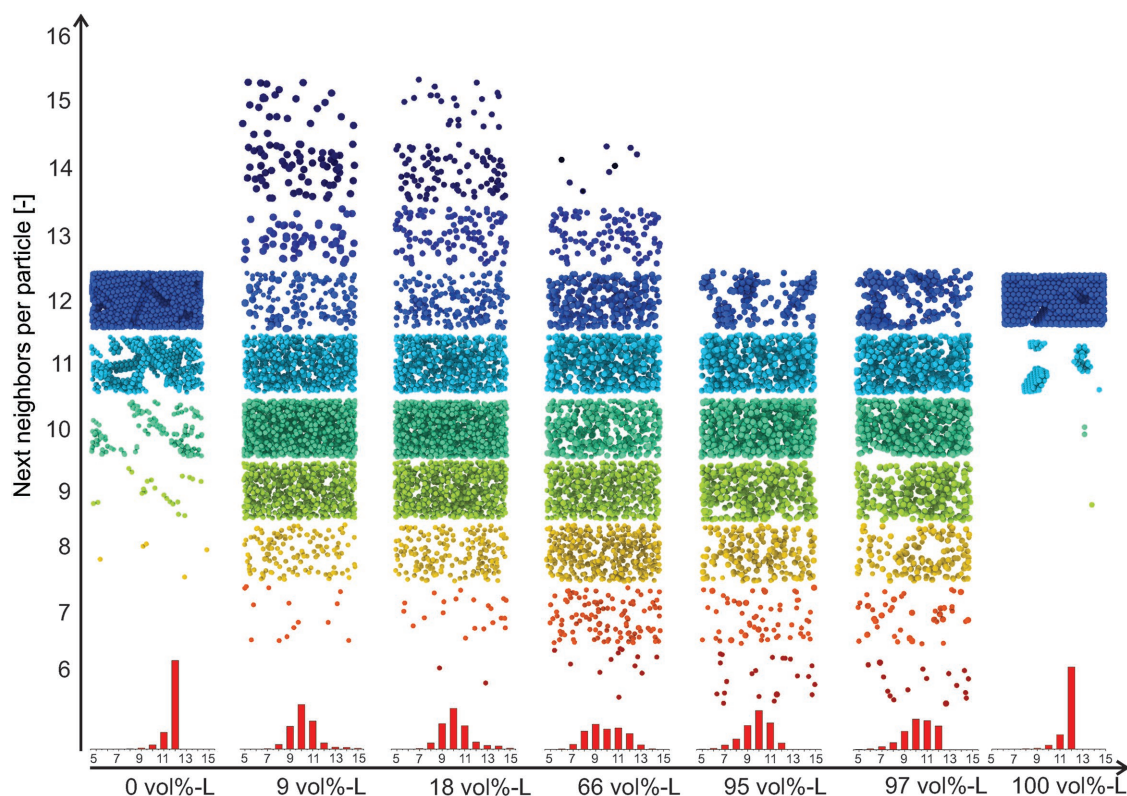


Figure 3. Molecular dynamics simulations of the assembly process of a binary particle mixture. Number of next neighbors per particle against volume fraction of large particles. Size ratio is 0.8. Projection of the assemblies visualizes the particles possessing the indicated number of neighbors. Histograms show the relative frequency of particle neighbors per particle present within the different assemblies.

high number of smaller particles. In contrary, for high mixing ratios of large particles, it is geometrically not possible to decorate a small particle with a high number of large particles, since there is simply not sufficient space. This asymmetry is less pronounced when considering the contact neighbors (Figure S5, Supporting Information). The average contact number stays constant with a tendency toward fewer contact points at the minimum volume fraction ≈ 20 vol% L. This discrepancy between a constant or reduced number of *contact* neighbor particles compared to the evolution of many *next* neighbor particles hints toward the importance of a jammed particle corona in close vicinity to the central bead.

We also conducted a thorough analysis of the interparticle constriction effect in the Supporting Information (Figures S6–S8, Supporting Information). We, therefore, analyzed the average interparticle contact area and relate this to the contact neighbor distribution. Using an ideal face-centered cubic reference system we show that a reduction of the interparticle contact area leads to an increase in thermal path length caused by a stronger bending of the heat flux stream lines (Figure S6b, Supporting Information). However, the changes of the interparticle contact area play a secondary role compared to the introduction of disorder and consequently to the thermal path length.

The consequence of the asymmetric next neighbor distribution for the effective thermal length is rather surprising. A reduction of the number of next neighbor particles indeed leads to a reduction in thermal conductivity. However, even

more efficient is the introduction of a certain amount of many jammed and not necessarily directly contacting particles, since this leads to an even stronger disturbance of the streamline length due to a geometric extension of the predetermined thermal transport path. This is accompanied by a minimum of the total number of interparticle contact points within the simulation volume (Figure S5, Supporting Information).

To clarify how this transport pathway is governed by the size mismatch of the two particles, we varied the size ratio of the particles between 0.9 and 0.54 at the mixing ratio around 20 vol% L, which showed the lowest thermal conductivity. Noteworthy for this data set, the experimental samples were prepared by filtration to speed up the assembly time and therefore obtain particle structures, which are more comparable to the MD assemblies. Both, experiment and FEM simulation, show a systematic decrease of the thermal conductivity with a decreasing size ratio from 0.9 to 0.54 (Figure 4d). The increase of the thermal conductivity for the smallest size ratio (0.54) for the experiment can be explained by an increasing tendency to demix as outlined above. One also needs to take into account that fully crystalline binary assemblies can be obtained for size ratios of <0.41 owing to the octahedral voids in face-centered cubic structures, which we approach with this small size ratio.^[35]

Figure 4a compares the heat flux density of the particle assemblies from size ratios of 0.54, 0.8, and 0.9 to the heat flux density of a fully crystalline assembly (size ratio: 1.0). Crystalline assemblies feature uniform and straight streamlines

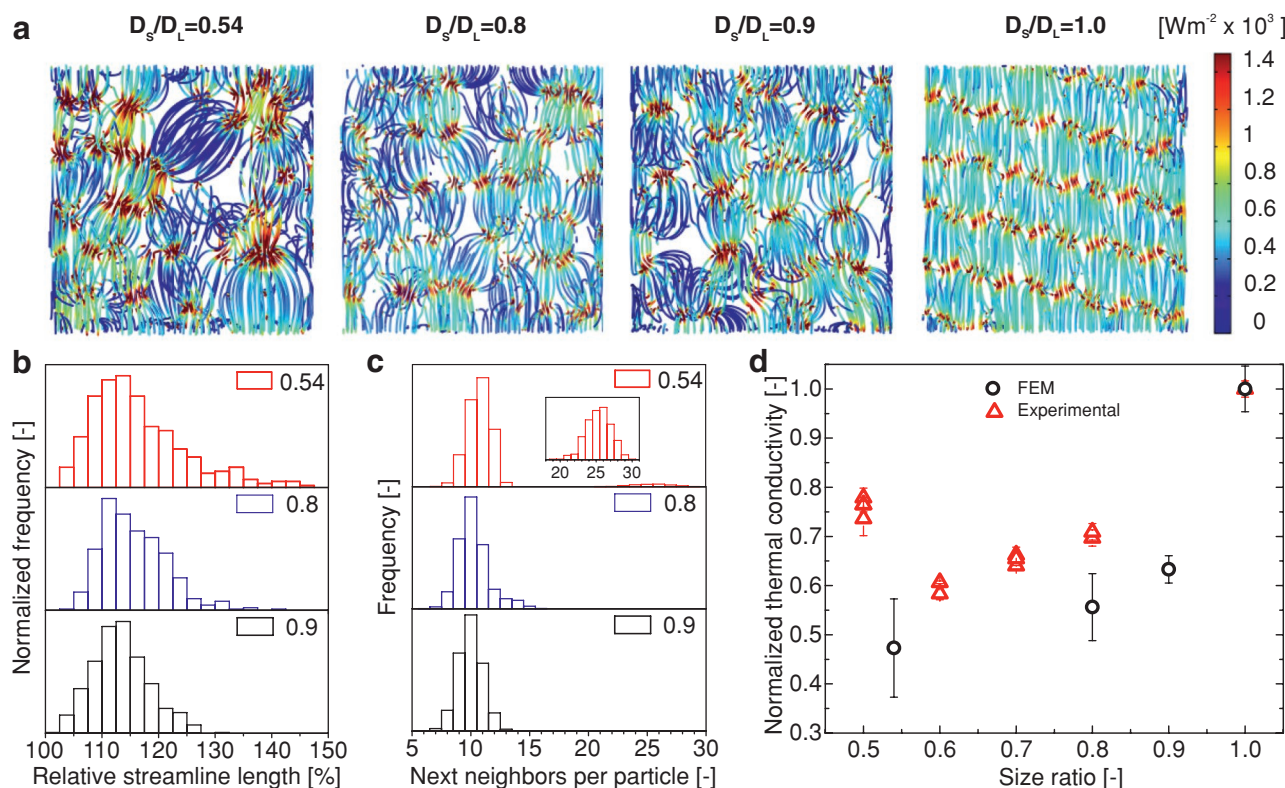


Figure 4. Influence of the size ratio (D_S/D_L) on the thermal conductivity at ~ 20 vol% L. a) Comparison of the heat flux densities of particle assemblies possessing different size ratios. b) Histograms of the streamline length and c) next neighbors per particle of the assemblies. d) Resulting thermal conductivity from FEM compared to experimental data.

(Figure 4a, 1.0), whereas a decreasing size ratio evokes a high degree of distortion. This is especially obvious for the heat flux density of the size ratio 0.54, where one large particle heavily impedes the heat flux through the entire particle box. The qualitative impression from the heat flux density images is verified by comparing the relative streamline lengths of the different size ratios (Figure 4b). The smaller the size ratio, the higher the number of long streamlines, which can reach up to 140% relative to the length of the simulation box. This indicates that the less the particle sizes match, the stronger the heat flux is bent along the particle network, leading to an elongation of the thermal transport path.

The higher fraction of long streamlines coincides with a broadening of the next neighbor distribution function with decreasing size ratio (Figure 4c). The broadening increases the number of >10 next neighbors, indicating an increasing decoration of a large particle with small particles. However, due to the small number of large particles at this volume fraction and size ratio combination (about 4% number ratio of large particles) this effect is not visible in the average number of neighbors for the whole assembly. Only when looking at the detailed next neighbor histograms the results from the heat flux simulations can be understood (Figure 4c). For a size ratio of 0.54 a second fraction with even 25–30 next neighbors is found. Looking at the contact neighbor distribution for this sample, the number of touching spheres remains rather constant at about 8 (Figure S5, Supporting Information). This highlights the evolution of a densely jammed corona, where

a small amount of large particle clusters are decorated with smaller spheres. This constitutes an efficient way to increase the thermal path length. Overall, the larger mismatch between the two particle sizes led to a thermal conductivity reduction by 40% (size ratio 0.6) in the experiment and 53% (size ratio 0.54) in the FEM simulation. We finally also checked, whether 19 vol% L represents the absolute minimum with respect to the mixing ratio. We, indeed, find the highest fraction of >25 next neighbor particles for this mixing ratio (Figure S4, Supporting Information). Higher or lower mixing ratios (± 5 vol% L) lead rapidly to a reduced number of next neighbors. Therefore, a mixing ratio of 19 vol% L of large particles is sufficient to strongly reduce the effective thermal transport across a binary particle mixture.

We finally compare this disorder derived thermal insulation effect to the thermal conductivity of known polymer materials. The unique properties of colloidal crystals and especially colloidal glasses can be inferred from the Ashby plot in Figure 5.^[36] It shows a direct relation between the thermal conductivity and the polymer density. Using polymer foams, highly insulating materials are accessible, however, at the expense of the materials density. Transitioning from colloidal crystals to colloidal glasses, retains the materials density to a large extent, while the thermal conductivity decreases. This opens the avenue to design highly insulating granular materials at a retained high density.

In summary, we investigated the influence of order and disorder in particle mixtures on their thermal transport

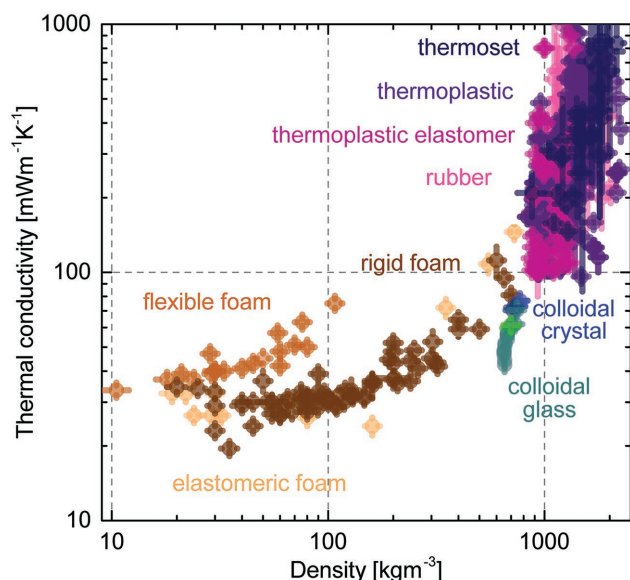


Figure 5. Ashby plot of density versus thermal conductivity of bulk and foam polymer materials. The introduction of disorder to a colloidal ensemble reduces the thermal conductivity (measured in vacuum) while retaining a comparatively high density.

properties. We therefore choose a controlled mixture of binary latex particles as a model system. In a combined approach, which comprised experimental characterization, MD simulation as well as FEM, we were able to relate the observed reduction in thermal conductivity to the local environment of the colloidal particles. Quite surprisingly, the increase of next neighbor contact points at low mixing ratios and at a high size mismatch between the binary spheres, represents the most efficient way to attain a minimum thermal conductivity. This is achieved at a comparatively high density. The decisive concept is the increase in the effective thermal length, across which the thermal energy needs to be transported. Overall, disorder in a binary colloidal glass can reduce the thermal conductivity by as much as $\approx 50\%$ compared to its single phase, crystalline counterpart. Our findings are of high importance for heterostructured and particulate materials, for applications where a high insulation, but also a good heat dissipation are paramount. Owing to the diffusive thermal transport in our system, our findings are of conceptual nature and applicable to many other nano-, micro-, and macrostructured materials, beyond simple latex beads. Most importantly, we want to stress the relevance of the concept of an effective thermal length, which cannot only be increased by constriction but may be even more strongly affected by additional pathways and detours.

Experimental Section

Details on the particle synthesis, binary colloidal self-assembly methods, and characterization methods, as well as a detailed description of the thermal transport characterization by laser flash analysis, molecular dynamics simulations, finite element modeling, complementary contact particle analysis, and a discussion on the influence of the particle contact area can be found in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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colloidal glass, next neighbor correlation, photonic crystal, powder sintering, thermal transport

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