Nanoscale Disorder Generates Subdiffusive Heat Transport in Self-Assembled Nanocrystal Films

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ABSTRACT: Investigating the impact of nanoscale heterogeneity on heat transport requires a spatiotemporal probe of temperature on the length and time scales intrinsic to heat navigating nanoscale defects. Here, we use stroboscopic optical scattering microscopy to visualize nanoscale heat transport in disordered films of gold nanocrystals. We find that heat transport appears subdiffusive at the nanoscale. Finite element simulations show that tortuosity of the heat flow underlying the subdiffusive transport, owing to a distribution of nonconductive voids. Thus, while heat travels diffusively through contiguous regions of the film, the tortuosity causes heat to navigate circuitous pathways that make the observed mean-squared expansion of an initially localized temperature distribution appear subdiffusive on length scales comparable to the voids. Our approach should be broadly applicable to uncover the impact of both designed and unintended heterogeneities in a wide range of materials and devices that can affect more commonly used spatially averaged thermal transport measurements.

KEYWORDS: Heat transport, time-resolved microscopy, subdiffusion, self-assembled nanocrystals, tortuosity, thermoreflectance

At the nanoscale, heat flow must navigate length scales intrinsic to material heterogeneities. This process contributes to the macroscopic thermal properties of a material but is typically aggregated into bulk parameters that can obfuscate microscopic origins. It is well-known that, in the cases of electronic and mass transport, heterogeneity has impacts beyond a simple reduction in diffusivity, leading to fundamentally different transport regimes such as subdiffusive behavior. Subdiffusion refers to a mean-squared expansion of an initially localized heat distribution evolving as \(t^\alpha\), where \(\alpha < 1\), such that the effective thermal conductivity falls off as a power law with the length scale traversed, tending to zero in the infinite limit. The ability to observe such behavior on the appropriate microscopic scales should therefore lead to mechanistic insights about the impact of defects on thermal transport.

The challenge of measuring nanoscale heat transport in heterogeneous media is that it requires a direct indicator of heat flow on the length and time scales of the encounters with nanoscale defects. Typically, thermal conductivity is measured on length scales orders of magnitude greater than the size of individual defects, yielding an average quantity. Ultrafast optical pump–probe measurements of thin films do not typically image heat spreading, and length-dependent steady-state thermal resistance measurements lack dynamical information and require constraining sample geometries and mechanical properties. Although adequate in the limit that the scale measured far exceeds those of material heterogeneities, the nanoscale heat transport properties, e.g., subdiffusion, may differ substantially from those obtained with typical measurements. Furthermore, the ability to obtain the combined spatial and temporal information required to establish relationships between nanoscale heterogeneity and nanoscale heat transport behavior has been lagging behind that of optical spatiotemporal techniques that probe electronic excited states in optoelectronic materials because their contrast mechanisms generally do not directly report on heat.

Here, we take advantage of the unique ability of the recently developed stroboscopic optical scattering microscopy (stroboSCAT) to spatiotemporally resolve nanoscale heat transport in films of colloidal Au nanocrystals (NCs). By virtue of its sensitivity to heat-induced local index of refraction changes, we resolve the expansion of a diffraction-limited heat pulse at room temperature with tens of nanometers and \(\sim 100\) ps sensitivity. We find that heat transport in these NC films appears subdiffusive on the length and time scales of the measurement (\(100\) ps–\(100\) ns and \(30\)–\(300\) nm). By simulating...
heat transport in geometries constructed to approximate transmission electron micrograph (TEM) images of similar NC films, we find that subdiffusion emerges mechanistically when voids are present in the films on scales within our sensitivity range. We learn that heat transport is locally diffusive on the small length scales between voids but that the voids lead to subdiffusive nanoscale heat transport by constraining heat flow along more protracted, circuitous paths. In fact, recasting the mean-squared expansion from direct space to a geodesic metric recovers diffusive behavior. At scales longer than the scale of voids, heat transport again appears diffusive but with a lower conductivity than is observed in the microscopic contiguous regions of the film. We anticipate that this recent ability to detect heat transport on the scale of heterogeneities will find use with a broad range of systems for which heat is expected to flow through both deliberately and unintentionally introduced nanoscale heterogeneities, including both imperfect materials and phononic devices.\textsuperscript{34,35} It also illustrates the extent to which bulk transport can be improved by demonstrating the true nanoscale intrinsic limit of the diffusivity.

To experimentally monitor nanoscale heat transport in Au NC films, we use stroboSCAT microscopy. stroboSCAT\textsuperscript{3} is a recently developed time-resolved interferometric optical scattering microscopy that can track both electronic and thermal energy flow at the nanoscale.\textsuperscript{26,33,36–38} stroboSCAT measures transient changes to a material’s local optical polarizability induced by a focused ultrafast pump laser pulse (Figure 1).\textsuperscript{33} These changes are measured by interferometrically detecting scattered probe light from the sample on a camera in wide-field and comparing it to a reference image taken in the absence of a pump pulse (Figure 1a).\textsuperscript{33} In the Au NC films, the resulting differential image contrast maps the spatial distribution of heat in the sample, as reflected by the transient change of the scattering cross-section of the NCs.\textsuperscript{3,37,39–41} Its time evolution is determined by repeating the measurement with progressively longer pump–probe delays (Figure 1b). We report the signal as $\Delta R(t)/R$ since the experiment is performed in a reflection geometry, where the scattered light is detected at the field level via interference with light reflected from the substrate–sample interface.\textsuperscript{33,42,43}

Specifically, films of 4.4 nm diameter Au NCs capped with dodecanethiol (DDT) ligands were dropcast onto glass slides from a colloidal solution (Figure S1, Methods). We illuminate the Au NC film at room temperature with a 405 nm pump light pulse ($\sim$100 ps), focused to a spot size with a full-width at half-maximum (fwhm) of 590 nm (Figure 1a). The electrons excited at the d–s interband transition rapidly equilibrate with the lattice via electron–phonon coupling within the NCs within the duration of the pulse,\textsuperscript{37} and we visualize the time-dependent optical field profile of the resulting heat distribution with a wide-field 635 nm wavelength probe light.

Figure 1. (a) Schematic of the stroboSCAT experiment, in which the sample is excited with a focused pump light pulse and then the subsequent heat diffusion is imaged using a wide-field probe pulse after a controlled time delay. (b) Representative ground-state scattering image (pump off) and stroboSCAT time series on a 120 nm thick region of a film of 4.4 nm Au NCs with DDT ligands. (c) Representative mean-squared expansion curves of thin and thick regions of two different 4.4 nm Au–DDT films. The mean-squared expansion curve of a 10 nm thick region is fit to give a single value of $\alpha$ of 0.7 \pm 0.1. A 120 nm thick region of an identically prepared film is fit over 0.1–10 ns to give $\alpha = 0.6 \pm 0.1$ and separately over 3–100 ns to give $\alpha = 1.0 \pm 0.1$. (d) Thickness dependence of $\alpha$ for different regions of a single 4.4 nm Au–DDT film, where $\alpha$ was fit over 1–100 ns in each case. The subdiffusive regime ($\alpha < 1$) is shaded gray, and the diffusive regime ($\alpha = 1$) is indicated with a dashed line. See raw data in Figure S2a.
pulse, detuned from the plasmon resonance peak at 514 nm, over a 0.1–100 ns time window (Figure 1a). With a 2σ-integrated excitation fluence of ~9 μJ/cm², we estimate an average initial change in temperature on the order of a few Kelvin. The region of elevated temperature appears as negative (dark) contrast (Figure 1b). By taking an azimuthal average of the spatial distribution of the transient scattering profile and fitting to a Gaussian function, we monitor in-plane heat diffusion, quantified by the mean-squared expansion, \( \sigma^2(t) - \sigma^2(0) \), with a few tens of nanometers spatial sensitivity that is determined by the signal-to-noise ratio rather than the diffraction limit (Figure 1c). We observe an associated root-mean-squared expansion of the heat profile from ~30 out to ~300 nm depending on the region interrogated in the film, corresponding to a range of 4 to 40 NC–NC center-to-center distances (Figures 1c and S2).

Our measurements point to subdiffusive heat transport in the colloidal NC films over a substantial portion of the three orders of magnitude of time delays considered. Figure 1c shows representative mean-squared expansion curves collected in thin and thick regions of two identically prepared films (see Figure S2 for all curves). Fitting each data set to \( \sigma^2(t) - \sigma^2(0) \propto t^\alpha \) yields different values of the exponent \( \alpha \) in different regions of a given film (Figures 1d and S2). In many regions, we find \( \alpha < 1 \), suggesting subdiffusion. The exponent \( \alpha \) increases with film thickness, as determined by atomic force microscopy correlated to the same regions of a film probed with stroboSCAT (Figure S3), starting from 0.53 at a thickness of 9 nm up to ~1 for a 120 nm-thick region of the same film (Figure 1d). The value of \( \alpha \) also varies over the time window measured in some locations in the film. For example, in the 120 nm-thick region of the 4.4 nm NC film in Figure 1c the slope of the mean-squared expansion on the log–log plot appears to increase with time, becoming approximately diffusive after ~10 ns, and was therefore fit piecewise. Around this time delay, we observe root-mean-squared expansions of ~40–140 nm, depending on the film thickness. The expansion during the diffusive time window of the 120 nm-thick film corresponds to a heat diffusion coefficient of \( (3.0 \pm 0.2) \times 10^{-3} \text{ cm}^2 \text{ s}^{-1} \), or thermal conductivity of approximately 0.3 W m⁻¹ K⁻¹, similar to that of a previous study of analogous NC films (see Supporting Information). Subdiffusive transport behavior is consistently observed in multiple films and over multiple regions within each one (Figures 1c,d and S2) and does not strongly depend on NC size, e.g., a film of 5.7 nm NCs exhibits analogous behavior to the 4.4 nm NC film (Figure S2), which is consistent with macroscopic thermal conductivity measurements. Finally, in contrast to the
subdiffusive behavior observed in the colloidal NC films, identical stroboSCAT measurements on a ~6 nm thick (continuous) polycrystalline Au film show normal diffusion with $\alpha = 1.0 \pm 0.1$, a diffusion coefficient of $(1.1 \pm 0.1) \times 10^{-1} \text{ cm}^2 \text{s}^{-1}$, and thermal conductivity of $27 \pm 2 \text{ W m}^{-1} \text{K}^{-1}$ (see Supporting Information, Figure S4).

We hypothesize that the subdiffusive behavior in these NC films originates from spatial disorder in the NC packing that forces heat to navigate a geometrically restricted environment induced by voids. While the nanoscale heterogeneities themselves are not directly resolved by the optical scattering technique, we support this correlation between subdiffusive behavior and the presence of voids below with the combination of the film thickness dependence of $\alpha$ (Figure 1d), heat transport simulations based on TEM images of a NC film (Figure 2a), and the normal diffusive behavior observed in polycrystalline Au (Figure S4). Specificaly, the TEM image of an incomplete monolayer of 5.7 nm Au–DDT NCs (Figure 2a) shows voids on length scales ranging from single NC vacancies to a few hundreds of nanometers. The 4.4 nm NCs exhibit packing behavior that is qualitatively similar to that of the 5.7 nm NCs in Figure 2a. While NCs may self-assemble on the surfaces of the glass slides used for stroboSCAT experiments differently than they do on carbon TEM grids, it is reasonable to expect that the NC films in the stroboSCAT experiments have a similar structure to that in Figure 2a.

Even in multilayer regions of a film on TEM grids, similar voids are apparent (Figure S5), suggesting a likeness especially to thinner regions of the film. The below analysis suggests that normal diffusion occurs in the moderately well-packed regions and that the subdiffusion stems from heat having to circumnavigate the voids.

To test the hypothesis that voids can give rise to the experimentally observed subdiffusive behavior, we carry out finite element heat transport simulations in a disordered Au–DDT NC composite film (Figure 2b, S6) that approximates the experimental condition in the TEM image of Figure 2a. Simulations are initialized using a Gaussian profile (fwhm = 76 nm) of elevated temperature with a peak deviation from the background of $\Delta T = 1 \text{ K}$ in the Au NC cores (Figure S7), reflecting the stroboSCAT experiments within the constraints of simulation tractability (see below). Fourier’s equation is solved as a function of space and time to map the heat expansion subject to the boundary conditions dictated by the nonconductive voids and the NC–ligand interfacial resistance (Figure 2b, Methods). Figure 2c shows how the simulated temperature profile expands over time from 0 to 100 ns in the TEM-inspired film configuration with local spatial disorder and voids. Consistent with ultrafast electron diffraction observations, on the shortest time scales beneath our experimental time resolution (~100 ps), heat transport is virtually instantaneous within the NC cores and transports across the NC–ligand interface such that the subsequent evolution is limited by the relatively slow conduction in the ligand material (Figure S8). As heat flows around the voids over 100 ps–100 ns, the profile develops anisotropy. Mimicking the stroboSCAT analysis, the temperature profiles are azimuthally averaged and then fit to a Gaussian function to obtain the mean-squared expansion (Figure 2d), revealing a subdiffusive exponent of $\alpha = 0.80$ (Figure 2d, red).

Interestingly, filling the voids with ligand material (Figures S6 and S7) recovers the diffusive behavior with near-unity $\alpha$, despite the disorder in the NC positions (Figure 2d, orange).

Both this result and a simulation on a perfectly ordered hexagonal lattice without voids (Figure 2d, gray) yield $\alpha = 0.98$, differing only slightly in their diffusion coefficients, likely due to the differing volume fraction of the highly conductive Au. Note that the deviation between these results and $\alpha = 1$ is likely noise due to a combination of factors, such as simulation tolerance, resolution, and fitting, and provides an estimate of the magnitude of the uncertainty in the approach. Small increases or decreases to the inter-NC separation disorder (Figures S6 and S7), characterized by $\sigma_0/(d)$, the separation’s standard deviation normalized to its mean, introduce changes to the resulting $\alpha$ increasing from 0.80 for 13% disorder to 0.87 for 0% disorder (Figure 2e, blue) and decreasing to 0.76 for 20% disorder (Figure 2e, purple). This tuning of the extent of subdiffusivity can be rationalized in terms of the relative number and size of voids that disrupt the local connectivity in the film (Figure S6). Our findings suggest that even though dense regions of a NC solid can display essentially crystalline local order even in submonolayer regions of a film (Figure S5b), subdiffusive transport can still occur on scales comparable to any voids.

The resemblance between the simulated subdiffusive heat transport and the experimental stroboSCAT data suggests that the simulations capture the essential underlying physics. The value of $\alpha$ in the TEM image-based simulation geometry lies roughly in the middle of the range of experimental values found in different regions of the dropcast NC films. The precise value of $\alpha$ depends on the local NC packing order (Figure 2e) and likely also on the size distribution and arrangement of voids, which can feasibly change in different films and different regions of the same film. Additionally, the size of the simulation geometry and consequently the initial temperature distribution size were limited by computational power. Separately, the magnitude of the mean-squared expansion found in the simulations underestimates those of the experiments by a factor of 1–20, with the largest deviations occurring at early times. This quantitative discrepancy could be due to the impact of the inherently 3D geometry of the films measured in experiments, the interaction with the glass substrate altering the experimentally observed mean-squared expansion, or overestimates of the ligand thermal or density parameters employed in the simulations (Methods), due, for example, to ligand coverage. In addition, our simple model does not account for the possibility of ballistic phonon/electron transport within NC cores or between NC cores that are in direct contact, which could enhance the transport over small distances at early times in particular.48

To further validate our void-induced subdiffusivity hypothesis, we compare the simulated temperature map to a map of geodesic distances in the simulated film and show that diffusive transport is recovered in geodesic space. The geodesic distance ($l_{\text{geo}}$) between two points is the length of the shortest path between them through contiguous material (i.e., in the solid phase, avoiding voids). Figure 3 compares a contour map of the geodesic distance from the central NC (Figure 3a) to a contour map of the temperature after 100 ns of evolution (Figure 3b), using the geometry of Figure 2b (Figure S9). The initial condition used in this simulation elevates the temperature of the central NC alone (Figure S7e). Moving out from the center, voids disrupt the path connectivity, making the shortest, geodesic distance one that curves to circumnavigate voids. The boxed regions in Figure 3a show representative locations where contours curve radially inward on the more
radially distant sides of voids, resulting in notable increases in $l_{\text{min}}$ relative to the radial distance $r$ from the central NC. The temperature map at 100 ns (Figure 3b) bears a strong resemblance to the geodesic map (Figure 3a) in that temperature contours curve radially inward on the more radially distant sides of voids (boxed regions of Figure 3b). In fact, plotting the mean-squared expansion along the geodesic coordinate as a function of time, $\langle l_{\text{min}}^2(t) \rangle$, recovers the diffusive behavior, with $\alpha = 0.99$ (Figure 3c, Figure S9).

Additional correlations between local void area fraction, local geodesic distance, and the “instantaneous” exponent $\alpha(t)$ appear in Figures S9 and S10 and associated text.

Altogether, the observation that we recover diffusive behavior in geodesic space suggests that the voids are responsible for the nanoscale subdiffusive heat expansion measured in Euclidean space. Conceptually, radial heat expansion slows as the heat flow lines wrap around the voids, actually moving over a distance of $l_{\text{min}}$ rather than $r$. Thus, while locally heat flows diffusively according to the heat diffusion equation through contiguous regions of the film, the boundary conditions imparted by the voids cause heat to navigate circuitous pathways that make the observed mean-squared expansion subdiffusive on the scale of the voids. On scales distinctly smaller (Figure 3c) or larger (Figure 1c) than voids, diffusive behavior is still observed.

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Figure 3. (a) Contour maps of the geodesic distance from the central NC in nanometers and (b) the temperature 100 ns after raising the temperature of the central NC by $\Delta T = 1$ K for the same simulation landscape as in Figure 2. The central NC core is indicated with a red dot. (c) Log–log plot of the mean-squared expansion along the geodesic distance as a function of time, $\langle l_{\text{min}}^2(t) \rangle$, for the same simulation.
measurements reveal anomalous diffusion and the scales on which it occurs can provide important microscopic information on the origins of suboptimal conduction at larger scales. For example, the distribution of sizes, shapes, and locations of voids could potentially lead to different transport behaviors associated with their characteristic scales that impact macroscopic flow in various ways.15,49

The nanoscale structurefunction relationships that we have shown can pave the way to conceptualizing and designing subdiffusive heat transport in a range of systems beyond NC arrays, such as low-dimensional nanostructures and amorphous polymers.25,51 Because the mechanism of nanoscale subdiffusive heat transport found here is geometric in nature, it could apply wherever heat must navigate indirect pathways. For example, this picture could explain the subdiffusive transport inferred in planar π-conjugated molecular nanoribbons, provided that defects in the single crystalline structure were imposing transport barriers to circumnavigate.25 Furthermore, in bulk amorphous polymers, where thermal conductivity is strongly suppressed compared to that in individual molecular chains due to the tortuous path taken by thermal vibrations, it would be interesting to explore whether heat transmits subdiffusively.51 Tortuosity-based design principles for heat management could be intentionally leveraged,34 for example, to control the path of heat flow or to tailor heat flow over specific length scales.

We have presented an observation of, and a mechanistic model for, nanoscale subdiffusive heat transport in composite Au NC–ligand films. Together, the experiments and simulations demonstrate that subdiffusive heat transport can occur at the scale of realistic voids in disordered nanoparticle solids, and we suggest that it is likely to occur in other materials with similar heterogeneities. Locally, heat travels diffusively in contiguous regions of the film, but tortuosity makes the transport subdiffusive on length scales of the voids. Beyond heat transport, the nature of the heterogeneity studied here would lead to subdiffusive electronic or mass transport as well, which could also be captured using stroboSCAT, either separately or in combination. Furthermore, stroboSCAT could be used to map nanoscale heat flow in a wide range of systems, potentially revealing the role of defects and heterogeneities and also enabling realistic comparison of transport in deliberately nanostructured or microstructured devices with performance anticipated by their ideal design. Moreover, combined with temperature calibration, this approach could be adapted to construct absolute temperature maps of high interest for far-from-equilibrium thermodynamics studies at the nanoscale.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.1c00413.

Methods, TEM images, mean-squared expansion curves for Au NC films and polycrystalline Au film, atomic force micrograph images, thermal diffusivity and conductivity calculations, simulation geometries, simulated temperature maps, geodesic distance analysis, and correlation between subdiffusive exponent, voids and geodesic distance (PDF)

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge H. L. Weaver, J. G. Raybin, and J. C. Portner for helpful discussions. This work, including all stroboSCAT measurements and interpretation, were primarily funded through the “Photonics at Thermodynamic Limits” Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under award no. DE-SC0019140. Data interpretation was also supported by the SIMES Institute for Energy Sciences from the Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division, under contract DE-AC02-76SF00515. Sample preparation and
characterization were supported by the Office of Basic Energy Sciences, the U.S. Department of Energy, under award no. DE-SC0019375. Simulations were performed in the Molecular Graphics and Computation Facility, College of Chemistry, UC Berkeley which is funded by NIH S10OD023532. J.K.U. acknowledges support from the Camille and Henry Dreyfus Foundation’s Postdoctoral Program in Environmental Chemistry (data collection and initial simulations) and the Arnold O. Beckman Postdoctoral Fellowship in Chemical Sciences from the Arnold and Mabel Beckman Foundation (manuscript preparation). N.S.G. and D.V.T. also acknowledge Alfred P. Sloan Research Fellowships, David and Lucile Packard Foundation Fellowships for Science and Engineering, and Camille and Henry Dreyfus Teacher-Scholar Awards.

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