

Nanoscale phonon dynamics in self-assembled nanoparticle lattices

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Chang Qian^{1,7}, Ethan Stanifer^{2,7}, Zhan Ma³, Lehan Yao¹, Binbin Luo¹, Chang Liu¹, Jiahui Li¹, Puquan Pan¹, Wenxiao Pan¹✉, Xiaoming Mao²✉ & Qian Chen^{1,4,5,6}✉

Geometry and topology endow mechanical frames with unusual properties from shape morphing to phonon wave manipulation, enabling emerging technologies. Despite important advances in macroscopic frames, the realization and phonon imaging of nanoscale mechanical metamaterials has remained challenging. Here we extend the principle of topologically engineered mechanical frames to self-assembled nanoparticle lattices, resolving phonon dynamics using liquid-phase transmission electron microscopy. The vibrations of nanoparticles in Maxwell lattices are used to measure properties that have been difficult to obtain, such as phonon band structures, nanoscale spring constants and nonlinear lattice deformation paths. Studies of five different lattices reveal that these properties are modulated by nanoscale colloidal interactions. Our discrete mechanical model and simulations capture these interactions and the critical role of effects beyond nearest neighbours, bridging mechanical metamaterials with nanoparticle self-assembly. Our study provides opportunities for understanding and manufacturing self-assembled nanostructures for phonon manipulation, offering solution processability, transformability and emergent functions at underexplored scales of length, frequency and energy density.

Topological design principles enable unique properties in various systems, from the visually striking curved voids in the MAXXI Museum¹ to shape-morphing actuators for soft robotics² and topological metamaterials³ inspired by the discovery of topological insulators⁴. In such metamaterials, topology control can engineer phonons and photons with remarkable phenomena such as unidirectional edge states and reconfigurable waveguiding⁵. For example, Maxwell lattices, a special class of topologically engineered mechanical frames, exhibit marginal stability⁶. They are porous systems with structural degeneracy subextensive in system size, leading to transformability and topologically protected floppy modes^{3,7}, all of which are important for

applications in shock absorption, stress focusing and non-reciprocal wave transmission^{8,9}. Owing to their broad relevance, topologically engineered mechanical frames have been extensively realized at the macroscopic scale^{7,9,10} and recently at the nanoscale using lithography or printing^{11–13}. Quantitatively, their phonon properties are characterized by phonon frequencies and wave eigenmodes as functions of wave vectors, known as phonon band structures, providing information on the wave propagation direction and velocity, which is essential for phonon design and manipulation in metamaterials.

Meanwhile, self-assembly of colloidal nanoparticles (NPs; <100 nm in size) has attracted extensive attention for its ability to

¹Department of Materials Science and Engineering, Grainger College of Engineering, University of Illinois, Urbana, IL, USA. ²Department of Physics, University of Michigan, Ann Arbor, MI, USA. ³Department of Mechanical Engineering, University of Wisconsin-Madison, Madison, WI, USA.

⁴Department of Chemistry, University of Illinois, Urbana, IL, USA. ⁵Beckman Institute for Advanced Science and Technology, University of Illinois, Urbana, IL, USA. ⁶Materials Research Laboratory, University of Illinois, Urbana, IL, USA. ⁷These authors contributed equally: Chang Qian, Ethan Stanifer.

✉e-mail: wpan9@wisc.edu; maox@umich.edu; qchen20@illinois.edu

create scalable, solution-processable and reconfigurable structures of precise control over topology, owing to the tunability of NP properties such as shape, composition and inter-NP interaction^{14,15}. However, research on NP-assembled lattices as mechanical frames is scant^{16–18}, with their phonon band structures largely unexplored. NP-assembled mechanical frames can access unique frequency ranges (megahertz to terahertz) that are crucial for phonon manipulation in optomechanical devices, mechano-logic and thermal transport (Supplementary Fig. 1, Supplementary Note 1 and Supplementary Tables 1 and 2)^{19–21}. NP-assembled lattices also hold promise as novel metamaterials^{22,23} by coupling the tailored optical, electronic and magnetic properties of NPs with the mechanical aspects of lattices^{14,24,25}. Meanwhile, current methods such as those using digital cameras, laser vibrometry and first-principle models used in macroscopic frames^{26,27} are not applicable to NP-assembled lattices due to resolution limitations and restricted frequency ranges (Supplementary Note 1 and Supplementary Table 3). Whereas ensemble inelastic neutron scattering has measured the phonon density of states of quantum dot lattices¹⁹, it does not measure the phonon band structures needed for quantitative phonon design. Electron energy-loss spectroscopy used for atomic lattices²⁸ cannot cover the frequency range of NP-assembled lattices, and optical microscopy lacks the spatial resolution for NPs^{29,30}. Owing to a lack of experimental data, the theoretical framework of mechanical metamaterials has yet to account for factors such as NP shape anisotropy, thermal fluctuations and complexities of inter-NP interactions, critical for NP-assembled mechanical frames.

Here we bridge topologically engineered mechanical frames with NP-assembled lattices, presenting the theoretical framework and experimental measurement of phonon band structures in NP-assembled lattices such as Maxwell and hexagonal lattices. Phonon band structures of colloidal assemblies were also previously noted as dispersion relations²⁹, although not in the classical sense as particle systems are overdamped in solution. A key feature of Maxwell lattices is a perfect hinge that constrains longitudinal motion while allowing rotational freedom (Fig. 1a), and it is realized here with anisotropic gold nanocubes. Liquid-phase transmission electron microscopy (TEM)^{31–33}—which images real-time dynamics in solution at atomic to nanometre resolution—is adapted to a phonon-mode nanoscopy (PMN) platform, to measure phonon band structures without previous knowledge of the inter-NP interaction. This real-space imaging capability (Supplementary Note 1.3) contrasts with ensemble phonon measurements, enabling the unambiguous separation and study of the modes of interest with high precision, such as the highly anisotropic floppy modes in Maxwell lattices carrying directional propagation of low-frequency phonons. These modes lead to unconventional nonlinear lattice deformation paths and extensive lattice reconfiguration. The PMN workflow is also applied to ‘overconstrained’ hexagonal lattices assembled from gold nanorods and triangular nanoprisms, which show isotropic phonon band structures without floppy modes, suppressing reconfiguration. By integrating PMN with coarse-grained (CG) inter-NP interaction calculations, we elucidate the quantitative tunability of phonon band structures by lattice structure and inter-NP interactions. Notably, these interactions extend beyond the traditional central-force potentials in mechanics theories³⁴ to include entropic effects in addition to many-body interactions and those beyond nearest neighbours (NNs) in nanoassemblies³⁵. Our study of phonon mode structures in NP-assembled lattices paves the way for understanding phonon wave propagation (Supplementary Notes 1.3 and 1.4) at the nanoscale and unlocking the full potential of next-generation NP-based mechanical metamaterials, achieving phonon manipulation in these systems such as crystalline lattices¹⁴ and amorphous networks³⁶.

Self-assembly of a nanoscale Maxwell lattice

Whereas most studies on NP-assembled lattices lead to close packing^{14,37}, topologically engineered mechanical frames with theoretically predicted superior properties are often open lattices. A major challenge in obtaining open lattices from self-assembly lies in their mechanical

stability: how are these lattices to be prevented from collapsing into close packing? Polymer ligands on the NPs can increase the lattice spacing, although the lattice structure still tends to be close-packed³⁸.

To address this challenge, we first focus on Maxwell lattices, which are on the verge of mechanical instability. We use the shape anisotropy of NPs to control the stability of these lattices, which are characterized by the balance between the degrees of freedom of the building blocks and the constraints from interactions between them^{6,7}. In the simplified case of point-like building blocks and central-force potentials that are radially symmetric, this balance takes the form $\langle z \rangle = 2d$, where $\langle z \rangle$ denotes the average coordination number of the building blocks (Supplementary Fig. 5) and d is the dimension of space. For anisotropic NPs, deviations from central-force potentials create a distinction between ‘strong’ central-force interactions between the NPs (usually NN bonds) and ‘weak’ interactions beyond the NNs (for example, potentials that depend on the bond angles). Maxwell’s counting rule includes only strongly interacting neighbours in z . We thus introduce a parameter, Maxwellness, to measure the ratio of the leading-order weak interactions to strong interactions. The limit of ideal Maxwell lattices is reached when this ratio goes to zero, whereas lattice stability requires some weak interactions to prevent unbounded floppy modes that can cause collapsing, favouring a Maxwellness of slightly non-zero.

We use gold nanocubes with slight corner truncation (edge length $L_e = 63.1$ nm, truncation length $L_t = 17.2$ nm) (Fig. 1b,c and Supplementary Figs. 2 and 3) as the building blocks for the Maxwell lattices. The nanocubes are negatively charged and dispersed in water due to electrostatic repulsion (E_{el}). Liquid-phase TEM imaging is performed at low electron dose rates (that is, 8.9–14.4 electrons per square ångström per second ($e^- \text{Å}^{-2} \text{s}^{-1}$)), where beam effects have been well-studied for aqueous solutions and have been proved to be negligible (Supplementary Note 2)³¹. For our PMN analysis, the lattices remain in equilibrium (Supplementary Fig. 4 and Supplementary Note 2). Increasing the ionic strength I via a flow of phosphate-buffered saline (PBS; pH = 8, $I = 22$ –110 mM) makes the inter-NP van der Waals attraction (E_{vdW}) overwhelm the screened E_{el} , triggering the assembly into a single-layer rhombic lattice (Supplementary Fig. 6 and Supplementary Video 1). Each NP in the rhombic lattice has strong interactions from four NN bonds and thus has $\langle z \rangle = 4$ as a Maxwell lattice in the $d = 2$ spatial dimension (Fig. 1d,e). The rhombic lattice maintains a stable bond length l (for example, $l = 77.3 \pm 2.4$ nm at $I = 22$ mM; Fig. 1d–g) and a bimodal distribution of the bond angle θ (Fig. 1f, Supplementary Figs. 7–9 and Supplementary Notes 3 and 4), suggesting a high enough Maxwellness to ensure structural stability and a low enough Maxwellness to permit floppy modes (Fig. 1b). The bond angle histogram in Fig. 1f is converted to a free energy diagram with two potential wells connected by an energy barrier, $E_b = 0.80 k_B T$ per rhombus, which can be overcome by thermal fluctuations to enable reconfiguration of the rhombuses between degenerate left- and right-leaning states (Fig. 1g and Supplementary Note 4), not observed in close packing³¹.

Both CG modelling, which describes the inter-NP interactions, and Brownian dynamics (BD) simulations, which track the assembly process, pinpoint the importance of beyond-NN interactions. Figure 1i shows the CG models of ligand-coated gold cubes (Supplementary Note 4) to calculate the pairwise interaction E_{tot} according to equation (1) (see the example in Fig. 1h):

$$E_{tot} = E_{vdW} + E_{el}. \quad (1)$$

When only the NN interaction is considered, the CG model suggests a square lattice ($\theta = 90^\circ$) at the energy minimum. By contrast, considering next-NN (NNN) interactions and beyond converges to global energy minima split at two θ values (Fig. 1i, Supplementary Figs. 9–11 and Supplementary Notes 4 and 5), with the system saddled at a square lattice (Fig. 1j). The saddle point is metastable and can fall into the global minimum of a rhombic lattice, consistent with our BD simulation

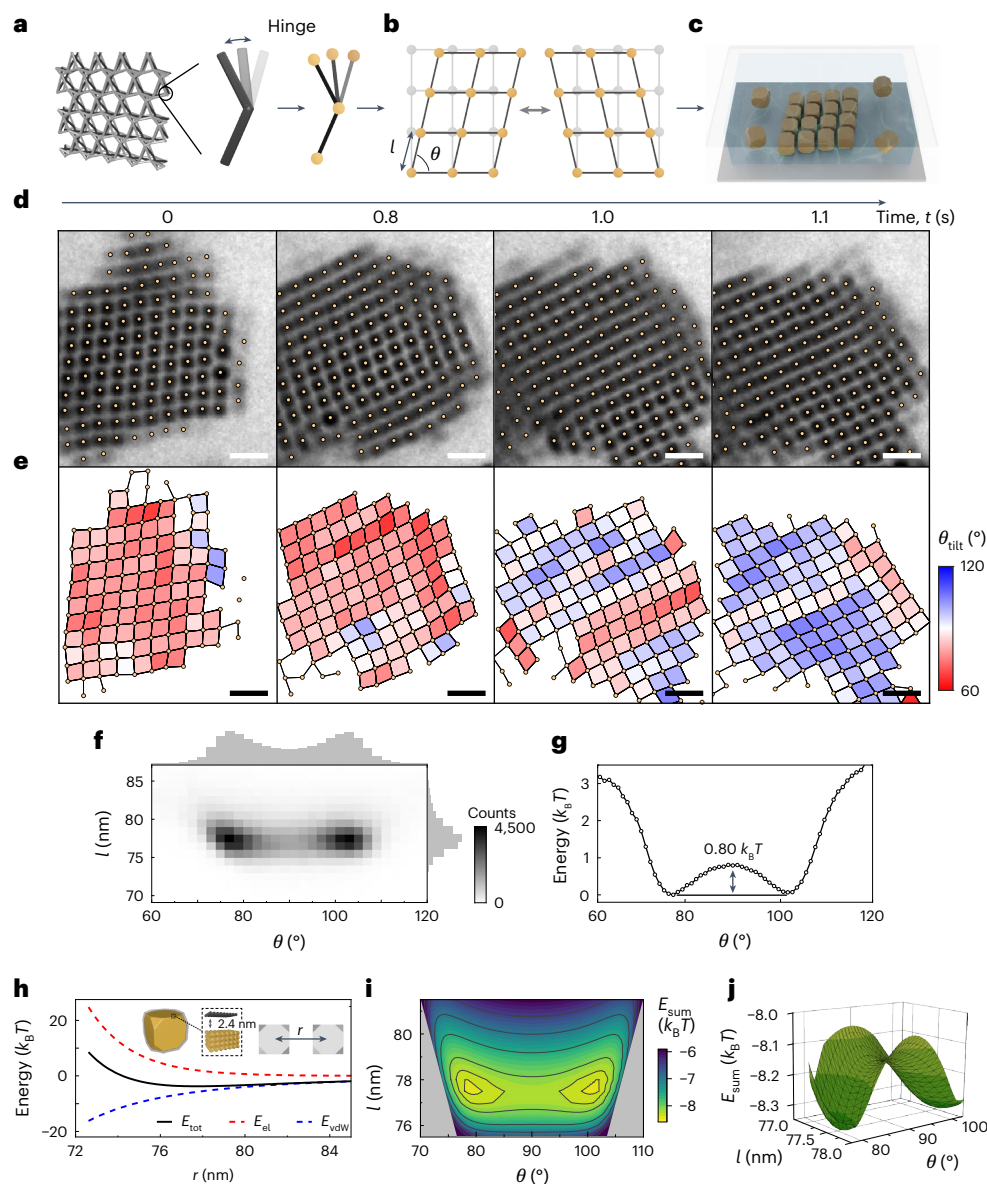


Fig. 1 | Self-assembled Maxwell lattice from gold nanocubes with structural degeneracy. **a**, Schematics of macroscopic (kagome bilayer⁵¹) Maxwell lattices and a hinge exhibiting rotational freedom. **b**, Schematic of a rhombic lattice with structural degeneracy, where the bond angle θ and bond length l are noted. **c**, Self-assembly of gold nanocubes into a rhombic Maxwell lattice in a silicon nitride (SiN_4) chamber via liquid-phase TEM. **d, e**, Time-lapse liquid-phase TEM images overlaid with tracked NP centroids (yellow filled circles) (**d**) and the bond network with rhombuses coloured according to θ_{tilt} (**e**), which describes the angle at which each rhombus leans. The definition of θ_{tilt} is given in Supplementary Fig. 9. Ionic strength $I = 22$ mM; electron dose rate = 10.9 electrons per square ångström per second ($e^- \text{Å}^{-2} \text{s}^{-1}$). Scale bars, 150 nm. **f**, Histogram of rhombuses

of certain l and θ values in Supplementary Video 1. **g**, Free energy of rhombuses (expressed via $k_B T$) as a function of θ derived from **f** (all l values combined). k_B , Boltzmann constant; T , temperature. **h**, CG modelling of the interaction energy types E_{vdW} , E_{el} and E_{tot} for an NP pair as a function of the centre-to-centre distance r . Right inset: schematic showing the NP orientation for the interaction (with the side facets of the NPs aligned). Left inset: schematic shown the CG model of a gold nanocube (gold) with ligands (black) (Supplementary Note 4). **i**, Diagram showing the sum of interaction energy (E_{sum}) of multiple pairs between the central NP and a surrounding NP as a function of θ and l up to the second NNs, which is sufficient for predicting the stable assembly structure. **j**, Saddle-point feature of the energy diagram in **i**.

(Supplementary Fig. 12, Supplementary Note 6 and Supplementary Video 2). The NNN interactions are needed to stabilize Maxwell lattices. At a fixed l with varied θ , the interaction change of diagonal NNN pairs can overwhelm that of the NN pairs, favouring the rhombic lattice. Meanwhile, the NNN interactions are much weaker than the NN interactions (for example, $5.1 k_B T$ for NN attraction and $1.1 k_B T$ for NNN attraction at $I = 27$ mM), preventing the lattices from transforming into hexagonal lattices.

This use of beyond-NN interactions to assemble bistable rhombic lattices contrasts with previous studies (Supplementary Note 4.2)^{39–41}. The importance of interactions beyond NNs can be unique for NP

systems, where the range of colloidal interactions is on a par with or exceeds the size of the NPs. In the BD simulations, we develop a deep-neural-network-based machine learning (ML) method to account for the large system size and complex inter-NP interactions beyond NNs, to achieve the fast prediction of self-assembly dynamics (Supplementary Fig. 12 and Supplementary Note 6).

PMN workflow to map phonon band structures

The defining mechanical feature of Maxwell lattices is the existence of floppy phonon modes⁷, which can take the form of soft planewave modes along certain high-symmetry directions in the bulk phonon

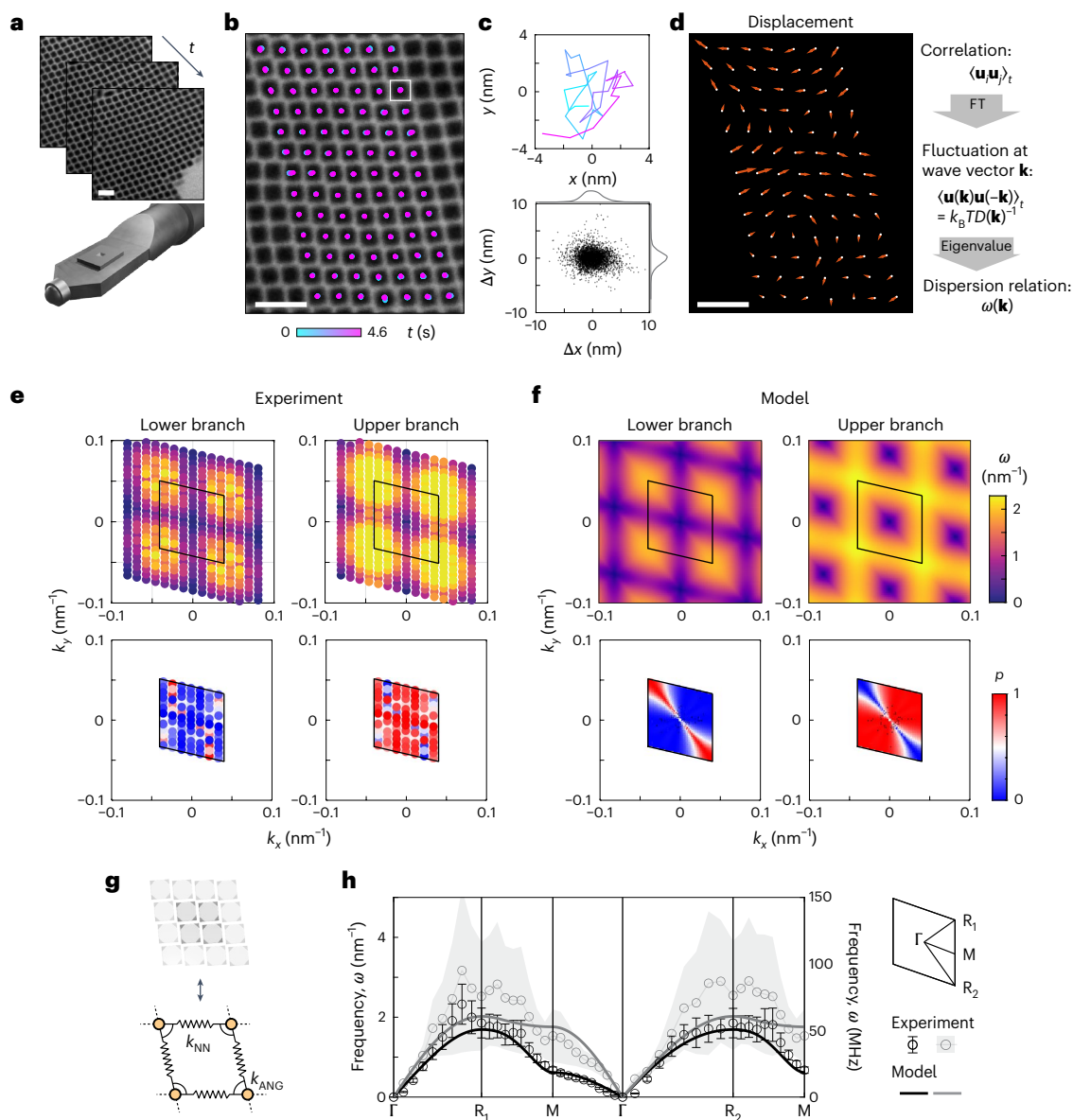


Fig. 2 | Direct imaging of phonon dynamics and integrated theoretical framework to extract phonon band structures using PMN. **a**, Illustration of the time-lapse liquid-phase TEM videos of the lattices, where NPs vibrate locally at the lattice sites. Scale bar, 200 nm. **b**, Drift-corrected trajectory mapped over a selected region of a stable rhombus lattice. The trajectory is coloured to the elapsed time, t . $t = 22$ mM; electron dose rate = $10.9 \text{ e}^- \text{ \AA}^{-2} \text{ s}^{-1}$. The vibrations of individual NPs at the lattice sites are sensitive to the geometric and interaction constraints imposed by their neighbours. The free NPs otherwise diffuse rapidly, essential for annealing defects and growing into large crystals (Supplementary Note 10.1). Scale bar, 200 nm. **c**, Top: expanded single-NP trajectory corresponding to the NP highlighted by the white box in **b**. Bottom: histogram of the instantaneous displacements (Δx and Δy) of NPs from their time-averaged centroid positions. Statistics include all of the NPs in **b**. **d**, Example of the instantaneous displacement of the NPs in one frame, from which correlations of the displacements are calculated to derive the dynamical matrix D and the phonon band structures (details in Supplementary Note 9). Scale bar, 200 nm. FT, Fourier transform. **e, f**, Phonon frequency (ω , top row) and polarization (p , bottom row; 1 for longitudinal and 0 for transverse waves) values

from experiment (**e**) and the model (**f**) plotted based on the spring constants (k_{NNN} , k_{ANG}) fitted to the phonon band structures measured in PMN, in the space of wave vectors (k_x , k_y). **g**, Discrete mechanical model of one rhombus in the lattice, consisting of four NN springs and four angular springs. k_{NN} , NN spring constant; k_{ANG} , angular spring constant. **h**, Phonon band structures along high-symmetry paths. The number of datapoints in the phonon frequencies and the phonon band structures are determined by the number of resolvable wave vectors, which is proportional to the lattice size (Supplementary Note 9.2). Two units of frequency are shown following procedures detailed in Supplementary Table 15. The lower branch (black) has higher precision than the higher branch (grey) as it is a mode of large displacements and is well sampled in liquid-phase TEM. The errors of the lower branch frequency are marked as error bars, and those of the upper branch frequency are denoted by the grey shading. The errors (vertical range of the bars or of the shading) are calculated following procedures listed in Supplementary Note 9.2. This error calculation and presentation is consistently implemented for all of the phonon frequency and phonon band structure graphs in this work. Data on the pixel size and errors of tracking are given in Supplementary Tables 4 and 5.

spectra, in the case of rhombic lattices, or floppy modes exponentially localized at the edges or interfaces of the lattice, depending on the type of Maxwell lattice⁷. Inspired by the work on phonon mode mapping using optical microscopy^{29,30,42}, we adapt liquid-phase TEM

into a PMN platform to image the phonon dynamics directly and measure the phonon band structures of the NP-assembled lattices. Much like single-particle tracking beyond diffraction-limited imaging in optical microscopy⁴³, subnanometre-resolution tracking of NP

centroids is achieved in liquid-phase TEM (Supplementary Note 3). The PMN workflow also propagates the effects of tracking error and displacement-sampling statistics to the calculations of phonon band structures and nanoscale spring constants (Supplementary Note 9.2 and Supplementary Tables 4–6).

The fundamental assumption of PMN is that the assembled structure experiences small vibrations around a stable configuration under thermal fluctuations³⁰, which is satisfied in our NP system between structural reconfiguration (Fig. 2a, Supplementary Figs. 4 and 13 and Supplementary Note 7). Following equilibrium statistical mechanics, the correlation functions of NP vibrations are related to the dynamical matrix D via

$$\langle \mathbf{u}_i \mathbf{u}_j \rangle_t = k_B T D_{ij}^{-1}, \quad (2)$$

where i and j labels the NPs tracked in liquid-phase TEM and $\mathbf{u}$ is the displacement vector of an NP per frame from its time-averaged position after drift correction (Fig. 2b–d, Supplementary Fig. 14, Supplementary Note 8 and Supplementary Video 3). The correlation function is equal-time. Thus, D does not describe temporal decay or diffusion, and there is no mass involved as inputs (Supplementary Note 9.1). This method can thus apply to different damping conditions (Supplementary Note 1.2) and is not affected by possible sluggish motions of NPs (Supplementary Note 10.1). The NPs exhibit vibrations up to 10.6 nm from lattice sites (Fig. 2c and Supplementary Table 13).

Phonon band structures are then measured for NP-assembled lattices (Supplementary Note 1) from the dynamical matrix in Fourier space $D(\mathbf{k})$, where eigenvectors are denoted as the wave polarization of the modes, giving 1 for longitudinal waves and 0 for transverse waves (Fig. 2e, Supplementary Fig. 15 and Supplementary Note 9). Here we observe two acoustic branches because $D(\mathbf{k})$ is a 2×2 matrix, leading to two branches of modes: we only consider displacements in the x – y plane, and the NP rotations are observed to be tightly confined, providing small entropic corrections to the spring constants (Supplementary Figs. 17 and 18, Supplementary Note 11 and Supplementary Table 8). The low values of polarization for the lower branch indicate that it is dominated by transverse waves where NPs slide past each other. By contrast, the upper branch is dominated by longitudinal waves, indicating bond length changes of higher energies.

This PMN method measures the critical properties of mechanical metamaterials (Supplementary Note 1.3), for which it requires only high-spatial-resolution tracking of the instantaneous vibrations of the NPs, not the inter-NP interactions, with a measurable frequency range about 0.1 MHz to 100 GHz (Supplementary Note 1 and Supplementary Fig. 16). Note that our control analysis on a simulated lattice with random, non-correlated vibrations shows no phonon structures (Supplementary Note 10.3).

Phonon behaviours governed by inter-NP interactions

To understand the phonon band structures, we develop a discrete mechanical model (Fig. 2g and Supplementary Notes 9.3–9.5) that describes the NP-assembled lattices as beads of mass connected by ‘effective’ springs. This model consists of two sets of potentials: one connects NNs and represents the strong interaction (equation (3)):

$$V_{\text{NN}}(l) = \frac{k_{\text{NN}}}{2}(l - l_0)^2, \quad (3)$$

where k_{NN} is the spring constant and l_0 is the equilibrium bond length; the other is a bistable angular (ANG) potential to account for the weak interactions, that is, beyond-NN, three-body and bistable interactions (equation (4)):

$$V_{\text{ANG}}(\theta) = k_{\text{ANG}}(\theta - \theta_0)^2(\theta + \theta_0 - 180^\circ)^2, \quad (4)$$

where k_{ANG} is the strength of the ANG potential, and θ_0 and $180^\circ - \theta_0$ are the two equilibrium bond angles, corresponding to the left- and right-leaning rhombus configurations, respectively. Here, k_{ANG} controls both the stiffness of the ANG spring when expanded around the local minima and the barrier between them (Supplementary Note 9.3).

This step of PMN fits the experimentally measured dynamic matrix to that predicted from our discrete mechanical model, to extract the spring stiffness and the Maxwellness of the lattice. For clarity, a phonon band structure is plotted along the high-symmetry paths in the example of $I = 22$ mM (Fig. 2h). A branch of floppy modes with low frequency sits between the Γ and M points in the first Brillouin zone, corresponding to the zero modes in an ideal Maxwell lattice. The fitting (Fig. 2e, f and Supplementary Note 9.4) yields $k_{\text{NN}} = 0.77 \pm 0.03 k_B T \text{ nm}^{-2}$ and $k_{\text{ANG}} = (1.34 \pm 0.11) \times 10^{-4} k_B T \text{ deg}^{-4}$. These parameters describe that a mechanical deformation associated with an energy of $1 k_B T$ leads to a small longitudinal stretching of an NN bond by 1.6 nm and a high angular fluctuation of 7.2° . The Maxwellness M is calculated via

$$M = k'_{\text{ANG}}/k_{\text{NN}}, \quad (5)$$

where k_{ANG} is normalized to k'_{ANG} to make M dimensionless (Supplementary Fig. 16, Supplementary Note 9.5 and Supplementary Table 7). At $I = 22$ mM, $M = 0.031 \pm 0.003$, suggesting closeness to an ideal Maxwell lattice and robustness under thermal fluctuation. By comparison, for macroscopic structures, $M = 0$ is often achieved using rigid struts with a low hinge friction⁹. Our result demonstrates the design of NP-based materials with both longitudinal stability and rotational freedom.

The phonon modes mapped via PMN fit well with our discrete mechanical model at the harmonic level, although inter-NP interactions are complex. To rationalize this agreement, we make a comparative study of the sets of k_{NN} and k'_{ANG} derived from the CG-modelled inter-NP interaction and from PMN analysis for rhombic lattices at different ionic strengths (Supplementary Fig. 19 and Supplementary Video 4). In ab initio CG models, within local fluctuations around the equilibrium lattice, both the NN interaction and the ANG potential are well fitted with our discrete mechanical models (Fig. 3a, b, Supplementary Note 12 and Supplementary Table 7), with matching fitting parameters of k_{NN} and k'_{ANG} (Fig. 3a–g and Table 1), suggesting that thermal fluctuations smooth the complex forms of inter-NP interactions, enabling simple effective models for lattice dynamics with slight discrepancies. As I is increased, k_{NN} and k'_{ANG} increase substantially, indicating steeper inter-NP interaction potentials. Macroscopically, previous work has shown that the strength of inter-NP interactions determines the plastic or elastic deformation of NP-assembled lattices upon indentation⁴⁴. We show that variations in inter-NP interactions manifest as the coefficients controlling the mechanical strength and flexibility of nanoframes.

Applying PMN to other lattices and spatial mapping

PMN readily extends to other NP self-assemblies. Taking hexagonal lattices as an example of closely packed non-Maxwell lattices ($\langle z \rangle = 6 > 2d$, overconstrained), we find that no floppy modes arise in their phonon band structures except the trivial translational modes at $\mathbf{k} = 0$. The phonon structure is isotropic at small $\mathbf{k}$, for both the hexagonal lattices assembled from standing gold nanorods (Fig. 3h, j, k, n and Supplementary Fig. 20) and the columns of stacked triangular prisms (Fig. 3i, l, n, o and Supplementary Fig. 21)³¹. Both fit well to a simple model with harmonic NN springs (Fig. 3h, i and Supplementary Note 12). The columns of stacked prisms exhibit weaker interactions compared with the rods ($E_{\text{NN,m}} = -0.3 k_B T$ for columns versus $-2.3 k_B T$ for rods; Fig. 3h, i), resulting in decreases in phonon frequency and spring constants by over one order of magnitude (Table 1 and Supplementary Tables 4–6 and 9).

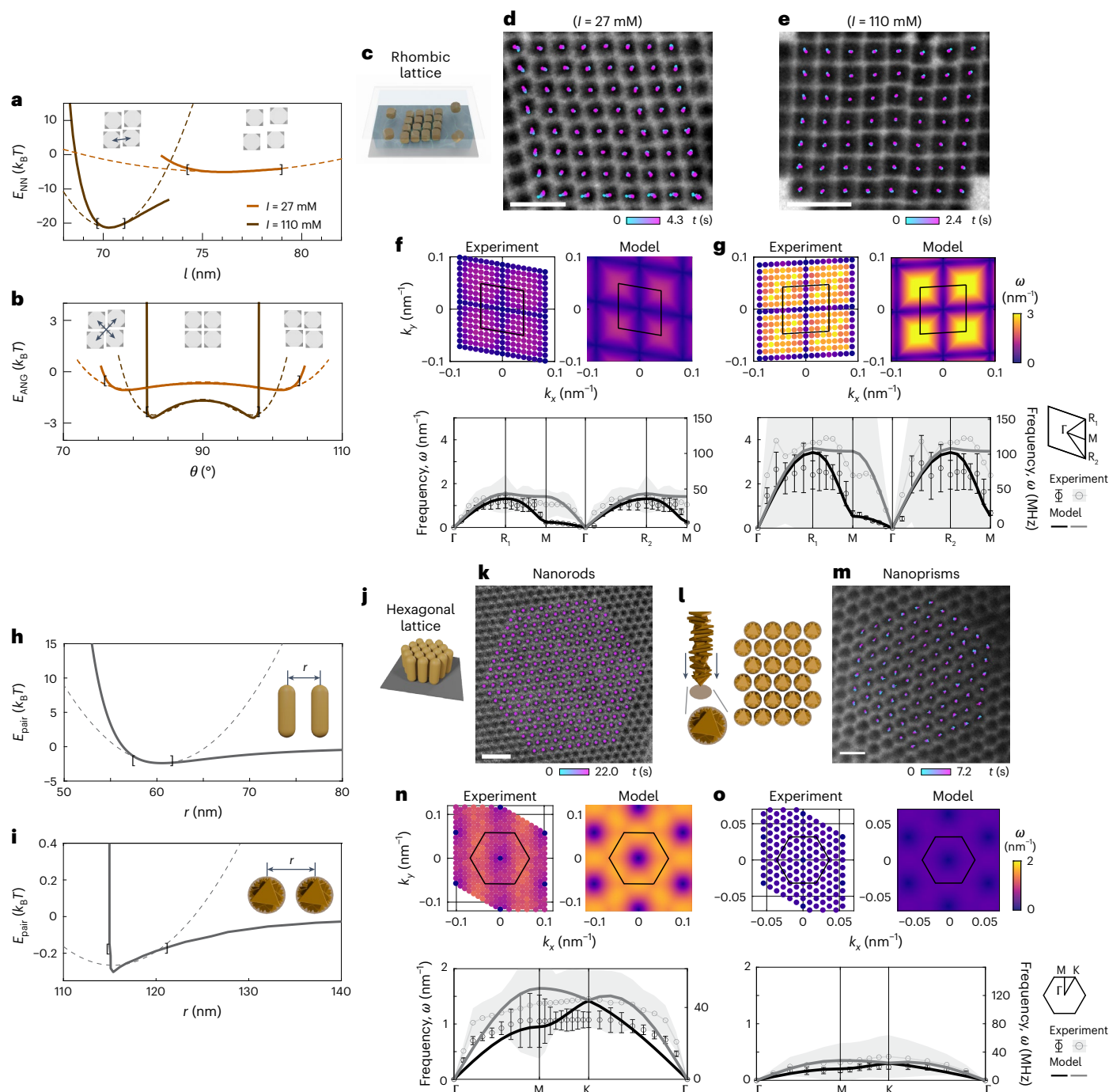


Fig. 3 | Effect of inter-NP interactions and lattice types on phonon band structures and spring constants. a,b, CG-modelled interaction energies of NN springs (E_{NN}) as a function of l (**a**) and of ANG springs (E_{ANG}) as a function of θ (**b**). The dashed lines are fits to the potential forms of the discrete mechanical models (equations (3) and (4)). The square brackets indicate the $(E_{NN,m}, E_{NN,m} + 1 k_B T)$ fitting range in **a** and the $(E_{ANG,m}, E_{ANG,m} + 1 k_B T)$ fitting range in **b**, where $E_{NN,m}$ is the minimum of the sum of interaction energies of all four NN pairs $E_{NN,i}$ and $E_{ANG,m}$ is the minimum of the sum of interaction energies of two diagonal pairs $E_{ANG,i}$ (insets and Supplementary Note 9). **c**, Schematic of the rhombic lattice self-assembled from gold nanocubes. **d,e**, Liquid-phase TEM images of the rhombic lattices at $l = 27$ mM (**d**, pixel size: 2.44 nm) and $l = 110$ mM (**e**, pixel size: 1.48 nm) overlaid with trajectories coloured to the elapsed time. Scale bars, 200 nm. **f,g**, Phonon frequencies and phonon band structures of rhombic lattices at $l = 27$ mM and electron dose rate = $10.9 e^- \text{\AA}^{-2} \text{s}^{-1}$ (**f**) and at $l = 110$ mM and electron

dose rate = $14.4 e^- \text{\AA}^{-2} \text{s}^{-1}$ (**g**). **h,i**, CG-modelled interaction energy (E_{pair}) of NN interactions of gold nanorods (**h** and inset) and columns of gold nanoprisms (**i** and inset). The dashed lines are fittings to the harmonic springs and the square brackets indicate the fitting range as detailed in Supplementary Note 12. **j,l**, Schematics of the hexagonal lattice self-assembled from gold nanorods ($l = 15$ mM, dose rate = $13.1 e^- \text{\AA}^{-2} \text{s}^{-1}$) (**j**) and gold triangular nanoprisms ($l = 35$ mM, dose rate = $8.9 e^- \text{\AA}^{-2} \text{s}^{-1}$) (**l**). **k,m**, Liquid-phase TEM images of the lattices of gold nanorods (**k**) and gold nanoprisms (**m**) overlaid with trajectories coloured to the elapsed time. Scale bars, 200 nm. **n,o**, Phonon frequencies and phonon band structures of the lattices of gold nanorods (**n**) and gold nanoprisms (**o**). The solid lines in the phonon band structures (**f,g,n** and **o**) are the fitting lines based on discrete mechanical modelling. In **f** and **g**, the same colour map is shared for the phonon frequency curves, as is also the case in **n** and **o**. For pixel size and errors of tracking, see Supplementary Tables 4 and 5.

Table 1 | Comparison of spring stiffness derived from PMN and CG model for different NP-assembled lattices

Sample	$k_{NN} (k_B T \text{nm}^{-2})$		$k'_{ANG} (k_B T \text{nm}^{-2})$	
	PMN	CG model	PMN	CG model
Cubes ($l=27 \text{mM}$)	0.50 ± 0.03	0.219 ± 0.017	0.0037 ± 0.0007	0.0044 ± 0.0002
Cubes ($l=110 \text{mM}$)	3.07 ± 0.15	4.18 ± 0.47	0.013 ± 0.002	0.0259 ± 0.0008
Rods	0.45 ± 0.01	0.21 ± 0.01	—	—
Prisms	0.021 ± 0.004	0.0071 ± 0.0003	—	—

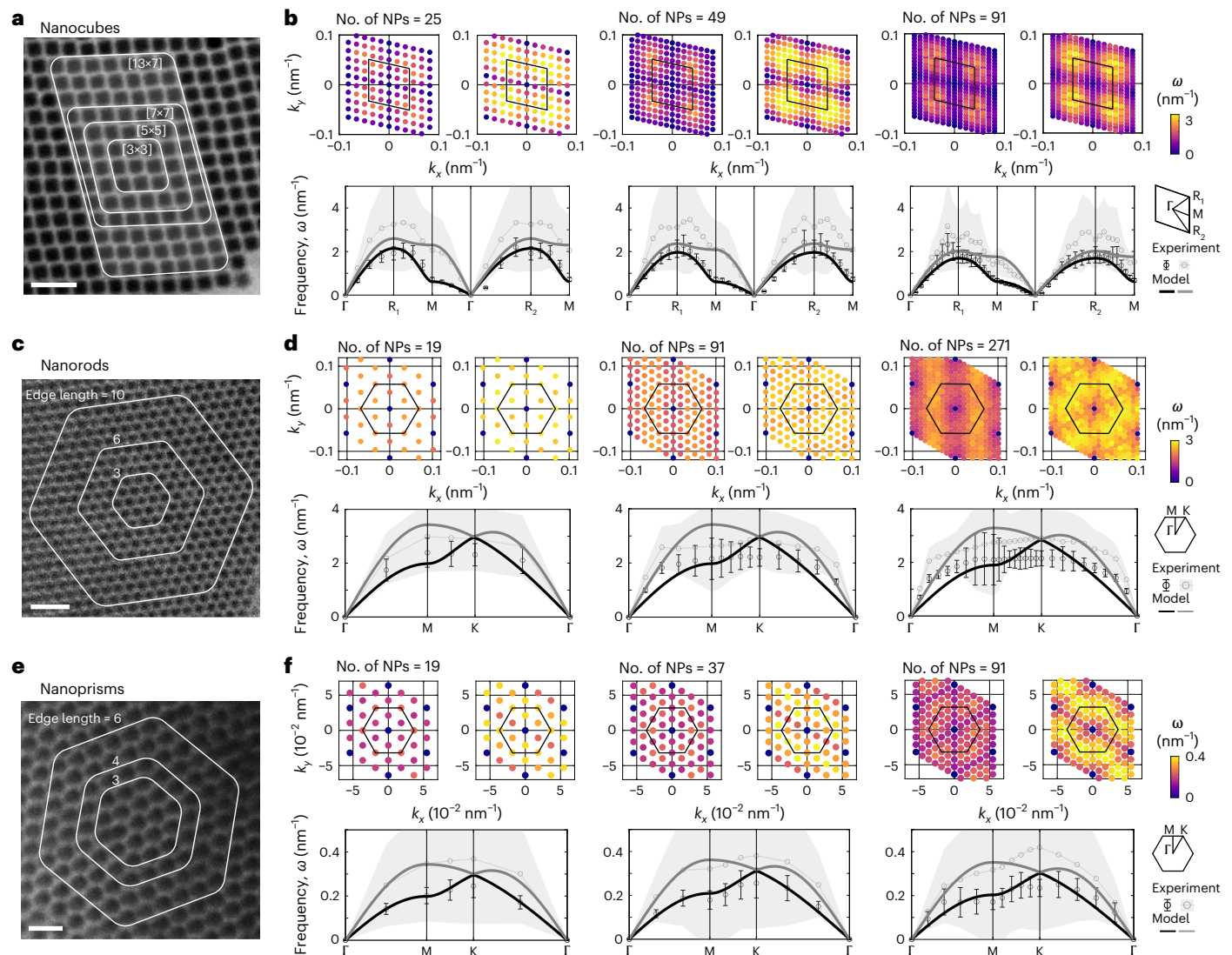


Fig. 4 | PMN analysis of differently sized sublattices to show the fast convergence of phonon band structure and spring constant measurement at small systems. a, c, e, Schematics of the local sublattices for nanocubes (a), nanorods (c) and nanoprisms (e) boxed in the liquid-phase TEM image of NP-assembled lattices. Scale bars, 200 nm. **b, d, f,** Examples of phonon frequencies

(top left, lower branch; top right, upper branch) and phonon band structure (bottom) along high-symmetry paths of sublattices for nanocubes (b), nanorods (d) and nanoprisms (f) of varying sizes. 'No. of NPs' denotes the number of NPs in the sublattice.

Whereas a large lattice adds more wave vector points in the phonon band structures, we find that the phonon band structures measured via PMN converge at rather small systems (Supplementary Note 9.2), that is, those containing fewer than 100 NPs or an area smaller than $1 \mu\text{m}^2$ (Fig. 4, Supplementary Figs. 22–26, Supplementary Tables 10–14 and Supplementary Note 10.2). This observation enables spatially resolved mapping of local phonon band structures (Supplementary Figs. 23–26 and Supplementary Tables 11 and 12), characterizing inhomogeneity

and potential topological states (Supplementary Note 1.3). In Maxwell lattices, the sublattice positioned close to the corner of the large lattice has a less constrained local environment, exhibiting a smaller k_{NN} , and is floppier than that at the centre region. Note that in our control lattice deliberately pushed out of equilibrium, the lattice undergoes contraction, displaying non-Gaussian NP displacement statistics and unphysical phonon modes (Supplementary Figs. 27 and 28 and Supplementary Notes 2.2 and 4.2).

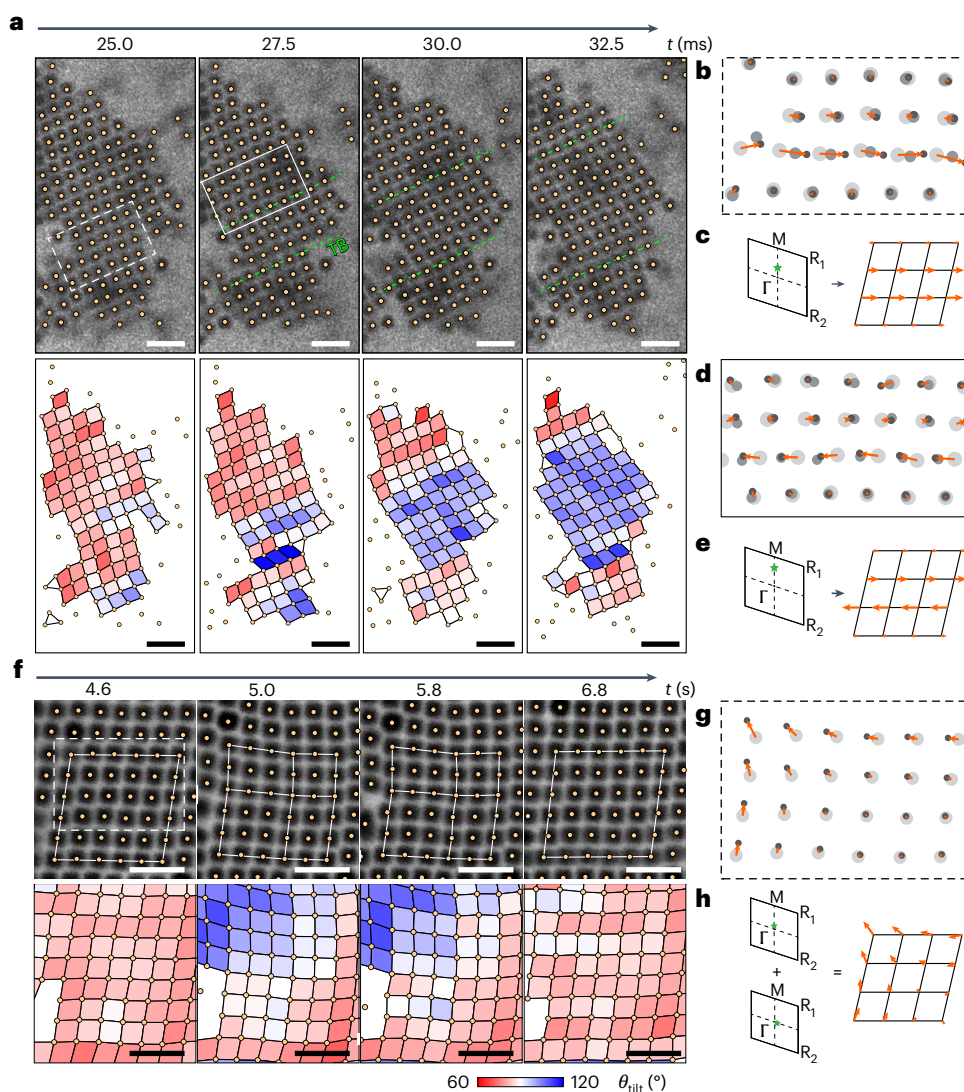


Fig. 5 | Collective deformation paths of Maxwell lattices upon thermal agitation. a, f, Time-lapse liquid-phase TEM images overlaid with tracked NP centroid positions (top) and rhombuses coloured according to θ_{tilt} (bottom). The migration process of the TB (a, labelled as a green dashed line) is captured by the direct electron detector at a frame rate of 400 frames per s (f.p.s.) ($I = 22$ mM, dose rate = $10.2 \text{ e}^- \text{ \AA}^{-2} \text{ s}^{-1}$). The quadruple-junction formation and annealing process (f) is captured at $I = 22$ mM, dose rate = $10.9 \text{ e}^- \text{ \AA}^{-2} \text{ s}^{-1}$. Scale

bars, 200 nm. **b, d,** Expanded view of NP motions in the dashed (b) and solid (d) boxes in a, highlighting gliding. **c, e,** Schematics of the first Brillouin zone and one of the phonon modes corresponding to the positions marked by the green stars according to the dashed (b) and solid (d) boxes in a. **g,** Expanded view of NP motions in the dashed box in f, highlighting quadruple-junction formation. **h,** Schematic of the first Brillouin zone and superposition of the phonon modes corresponding to the positions marked by the green stars.

Nonlinear lattice reconfiguration

The floppy modes in Maxwell lattices are easily excited to large amplitudes, leading to collective nonlinear lattice deformation paths. As shown in Fig. 5a, f, the low kinetic barrier for a rhombus to distort (Fig. 1g) underpins ‘layer gliding’ where one row (or subrow) of cubes glides concertedly. Gliding creates a contact twin, which can be dynamically driven by thermal fluctuations at the twin boundary (TB). Subsequent reorientations of other rhombus rows push the migration of the TB (Fig. 5a, Supplementary Fig. 29c–e and Supplementary Video 5). Such spatially localized TB shifting starts from a linear combination of the floppy modes along the Γ and M points (Fig. 5b–e) and continues to the nonlinear regime. Although twinning has been found in minerals or metals⁴⁵, such as deformation twinning upon stress⁴⁶, we observe twinning dynamics in NP-assembled lattices. These deformation paths are also modulated by inter-NP interactions (for example, ionic strengths for charged NPs; Supplementary Figs. 30 and 31 and Supplementary Note 13).

When multiple layers glide together, large-scale collective twinning (Supplementary Fig. 29a, b) or quadruple-junction formation are observed. Figure 5f shows the formation and annealing of a quadruple junction where twins intercept and pin. This leads to polysynthetic twinning⁴⁷, which has been discussed in previous simulations of a DNA-coated colloidal lattice⁴⁸. This lattice relaxation to linear order corresponds to transverse motions (Fig. 5g, h), contrasting with the stable relaxation dynamics limited to the lattice surface or local defect observed in previous studies³¹. Conventionally in metal systems⁴⁹, the generation and migration of the TB can effectively soften the material, whereas the TB can also strengthen the material by acting as pinning points that impede dislocation propagation. Our observation of the quadruple junction may suggest that the TB strengthening mechanism does not hold for the nanoscale Maxwell lattices.

Such structural transitions driven by floppy modes in lattices hold promise for intriguing topologically polarized elasticity. NP assembly provides the opportunity to create topological metamaterials

with a large number of unit cells, in contrast to current capabilities of manufacturing of approximately ten unit cells in one direction (Supplementary Note 1.3).

Outlook

Phonon mode structures are essential for controlling the properties and topological states in mechanical metamaterials. Our work to measure them and effective NN or beyond-NN interactions for NP-assembled lattices is thoroughly validated by our discrete mechanical and CG models, and is therefore the foundation for realizing the full potential of NP-based mechanical metamaterials. The beyond-NN interactions are found to be crucial for realizing Maxwell and potentially other open lattices, influencing defect propagation and phase transitions. We demonstrate the tunability of phonon bands through NP shape, inter-NP interaction, lattice structure and local geometry. This insight can enable phonon engineering: factors such as the types of NP, their size-defined properties, self-assembly structure, inter-NP interactions and their combinations offer essentially unlimited opportunities for NP-based self-assembled mechanical metamaterials. The PMN method and discrete mechanical model developed here can be applied to other nanoscale systems such as protein transformation⁵⁰ (Supplementary Note 14).

Our Maxwell lattices in liquids exhibit structural reconfigurability and a frequency range of 0–117 MHz (~ultrasound), with floppy mode features at 20 MHz (Supplementary Note 9.2), a frequency range of interest for applications such as non-invasive imaging, acoustic waveguides, diodes for sonar cloaking, mechano-logic and memory. These systems respond to stimuli such as temperature or pH, and even in the dry state, their phonon features remain predictable through a frequency scaling (Supplementary Notes 1.2 and 1.4). NP-based mechanical frames thus offer a rich platform beyond atomic or macroscopic systems.

Online content

Any methods, additional references, Nature Portfolio reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at <https://doi.org/10.1038/s41563-025-02253-3>.

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Methods

Chemicals

Sodium borohydride (NaBH_4) (99%, Sigma-Aldrich), silver nitrate (AgNO_3) ($\geq 99.0\%$, Sigma-Aldrich), L-ascorbic acid (BioXtra, $\geq 99.0\%$, Sigma-Aldrich), hexadecyltrimethylammonium bromide (CTAB) (BioXtra, $\geq 99\%$, Sigma-Aldrich), gold(III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) ($\geq 99.9\%$, Sigma-Aldrich), hexadecylpyridinium chloride monohydrate (CPC) ($>98.0\%$, TCI), sodium phosphate monobasic monohydrate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$) (99.0–102.0%, EMD Millipore), sodium phosphate dibasic anhydrous (Na_2HPO_4) (99+%, Acros), potassium bromide (KBr) (99.999%, Acros), hydrochloric acid (HCl) (99.999%, Alfa Aesar), sodium oleate ($>97\%$, TCI) and 2-[2-[2-[2-[2-[2-(1-sulfanylundecoxy)ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]acetic acid ($\text{HS}(\text{CH}_2)_{11}(\text{OC}_2\text{H}_4)_6\text{OCH}_2\text{COOH}$) ($\geq 95\%$, Prochimia Surfaces) were used as purchased without further purification. All glassware was treated with aqua regia (a mixture of HCl and HNO_3 at a volume ratio of 3:1), thoroughly rinsed with water and dried before use. Nanopure water (with a resistivity of $18.2 \text{ M}\Omega \text{ cm}$ at 25°C) purified by a Milli-Q Advantage A10 system was used in this work.

Synthesis of gold NPs

Synthesis of gold nanocubes. Gold nanocubes were synthesized with adaptations to a universal seeded growth method⁵². The synthesis includes three steps: (1) preparation of gold nanorods, (2) preparation of monodisperse spherical seeds from the gold nanorods via iterative etching and regrowth and (3) growth of the gold nanocubes from the monodisperse spherical seeds.

First, a seed solution was prepared by rapidly mixing aqueous solutions of CTAB (100 mM, 5 ml), HAuCl_4 (10 mM, 125 μl) and freshly prepared ice-cold NaBH_4 solution (10 mM, 300 μl) in a 20 ml vial in sequence, with stirring at 1,150 revolutions per min (r.p.m.) for 1 min. The addition of NaBH_4 should be fast to obtain small and monodisperse gold seeds. The solution was then incubated at 30°C in a water bath for 30 min. Next, gold nanorods were synthesized by adding aqueous solutions of CTAB (100 mM, 200 ml), HAuCl_4 (10 mM, 10 ml), AgNO_3 (10 mM, 1.8 ml) and ascorbic acid (100 mM, 1.14 ml) to the as-synthesized seed solution (240 μl) in sequence to a 250 ml Erlenmeyer flask under stirring at 400 r.p.m. and 30°C . After 2 h of growth without stirring, the solution was collected and centrifuged twice (Eppendorf Centrifuge 5804, $7,200 \times g$, 15 min each). After the first centrifugation, the remaining sediment in each tube was redispersed in CTAB (20 ml, 50 mM). We kept $\sim 100 \mu\text{l}$ sediments after each centrifugation unless otherwise stated. After the second centrifugation, the remaining sediment was diluted in 50 mM CTAB to achieve a final gold nanorod concentration with a peak extinction intensity value of two at 700–800 nm in the ultraviolet-visible (UV-vis) spectrum (Scinco S-4100 PDA spectrophotometer).

Next, the high-monodispersity spherical seeds were synthesized by etching the gold nanorods, followed by reductive growth and oxidative etching. The first etching was performed by adding an aqueous solution of HAuCl_4 (10 mM) to the gold nanorod solution in a 250 ml Erlenmeyer flask with stirring at 200 r.p.m. and at 40°C . The volumes of the HAuCl_4 added were optimized on a small-scale test reaction according to ref. 52, which is typically 6–8 μl per millilitre of nanorod solution. The etching proceeded for 4 h, and the sediments were collected via two rounds of centrifugation ($8,400 \times g$, 45 min; $8,400 \times g$, 30 min). The remaining sediment was redispersed in 100 mM CPC to achieve a concentration with an extinction intensity of unity at the peak wavelength of 525 nm in the UV-vis spectrum of the solution. Then, aqueous solutions of CPC (10 mM, 40 ml), HAuCl_4 (10 mM, 700 μl) and ascorbic acid (100 mM, 9 ml) and the gold NP solution (6 ml) obtained above were added in sequence to a 125 ml Erlenmeyer flask with stirring at 300 r.p.m. and 40°C . The growth of the spherical seeds proceeded for 15 min with no stirring, and the solution was collected and centrifuged twice ($7,636 \times g$, 10 min each). The sediment of reductively grown NPs

was redispersed with 50 mM CTAB to achieve the concentration with a peak extinction intensity of unity at 530–540 nm in the UV-vis extinction spectrum. The next round of oxidative etching was performed by adding aqueous HAuCl_4 solution (10 mM) to the grown NP solution in a 250 ml Erlenmeyer flask. The volume of the HAuCl_4 solution added was 6 μl per millilitre of the grown NP solution. The solution was then stirred at 200 r.p.m. and 40°C for 4 h. The improved spherical seeds were obtained by centrifuging the reaction solution twice ($8,400 \times g$, 30 min each) and dispersing the sediment in 100 mM CPC to achieve the desired spherical seed concentration with a peak extinction intensity of unity at 525 nm in the UV-vis extinction spectrum.

Finally, gold nanocubes were grown from the spherical seeds prepared above. Aqueous solutions of CPC (100 mM, 5 ml), KBr (100 mM, 500 μl), HAuCl_4 (10 mM, 100 μl) and ascorbic acid (100 mM, 150 μl) and the spherical seed solution (200 μl) were added in sequence to a 20 ml vial at room temperature. The reaction was left undisturbed for 1 h and then the solution was centrifuged twice ($4,770 \times g$, 5 min; $3,600 \times g$, 5 min). The gold nanocubes were obtained by redispersing the sediment in 50 mM CTAB for long-term storage.

Synthesis of gold nanorods. Gold nanorods were synthesized following a seeded growth method⁵³. First, a seed solution was prepared by mixing ice-cold NaBH_4 (1.0 ml, 6 mM) with an aqueous solution of HAuCl_4 (5 ml, 0.5 mM) and CTAB (5 ml, 0.2 M) in a 20 ml scintillation vial under vigorous stirring (1,150 r.p.m.). The seed solution was incubated at room temperature for 30 min. Next, CTAB (3.6 g) and sodium oleate (0.49 g) were dissolved in warm water (200 ml, -50°C) in a 500 ml Erlenmeyer flask. The solution was allowed to cool before adding AgNO_3 (3.84 ml, 10 mM). The mixture was kept at 30°C for 15 min, then HAuCl_4 solution (10 ml, 10 mM) was added under stirring at 700 r.p.m. for 90 min. Afterwards, HCl (1.6 ml, 12.1 M) was added, and the solution was stirred for another 15 min at 400 r.p.m. Ascorbic acid (0.5 ml, 10 mM) was then added under vigorous stirring for 30 s. Finally, the as-prepared seed solution (40 μl) was injected into the solution, which was stirred for 30 s and then left undisturbed at 30°C for 12 h to allow nanorod growth. The gold nanorods were collected via centrifugation at $6,300 \times g$ for 30 min and redispersed in 50 mM CTAB for later use. The rods are $154.2 \pm 2.8 \text{ nm}$ in length and $45.1 \pm 2.5 \text{ nm}$ in width.

Synthesis of gold nanoprisms. Gold nanoprisms were synthesized following the procedures in ref. 31. First, a gold NP seed solution was prepared by rapidly mixing ice-cold NaBH_4 (300 μl , 10 mM) with an aqueous solution of HAuCl_4 (250 μl , 10 mM), sodium citrate (500 μl , 10 mM) and water (18.95 ml) in a 50 ml Erlenmeyer flask under stirring at 1,150 r.p.m. for 1 min. The seed solution was then incubated at $40\text{--}45^\circ\text{C}$ for 15 min and was allowed to cool to room temperature before use. Next, aqueous solutions of HAuCl_4 (250 μl , 10 mM), NaOH (50 μl , 100 mM) and ascorbic acid (50 μl , 100 mM) and the as-synthesized gold seed solution (22 μl) were added sequentially to a 9 ml volume of 50 mM CTAB containing 50 μM NaI in a 20 ml scintillation vial. After each addition, the solution was shaken by hand for 1 s, and the mixture was left to react for 30 min. The formation of triangular nanoprisms was indicated by the gradual colour change from clear to purple. For purification of the product, the purple solution was transferred to a 15 ml centrifuge tube, and an aqueous solution of NaCl (0.9 ml, 2 M) was added. After thorough mixing, the solution was left undisturbed for 2 h and then centrifuged twice (first round: $4,410 \times g$ for 30 s; second round: $1,215 \times g$ for 5 s). Following each centrifugation, as much of the supernatant as possible was removed using a micropipette. After the second centrifugation, several drops of water were first added to the sediment to redisperse the product back to individual prisms in solution, before CTAB (9 ml, 50 mM) was added to the solution for later use of the sample. The synthesized triangular prisms are $100.5 \pm 9.5 \text{ nm}$ in edge length and $7.5 \pm 0.3 \text{ nm}$ in thickness.

Surface modification of gold NPs

The gold NPs (gold nanocubes, gold nanorods and gold nanoprisms) obtained above were coated with CTAB ligands. The ligands were exchanged with carboxylate-terminated thiols ($\text{HS}(\text{CH}_2)_{11}(\text{OC}_2\text{H}_4)_6\text{OCH}_2\text{COOH}$) following the modified procedure in ref. 31, to improve the stability of the NPs in solution.

For surface modification of the gold nanocubes, firstly, two rounds of centrifugation were carried out to decrease the concentration of CTAB ($4,770 \times g$, 5 min; $3,600 \times g$, 5 min). After the first round of centrifugation, the supernatant was removed, and the remaining solution with sediments ($\sim 50 \mu\text{l}$) were redispersed in water (4.95 ml). After the second round of centrifugation, the remaining sediments ($\sim 50 \mu\text{l}$) were mixed with water (3.00 ml). Next, an aqueous solution of thiols (7.93 mM, $44.26 \mu\text{l}$) was added to the gold nanocube solution. The mixture was first left undisturbed for 30 min and then sonicated for 5 s, and PBS solution (0.344 ml, 1 M; pH = 8, composed of 70 mM $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ and 930 mM Na_2HPO_4) was gently added to the mixture and left undisturbed overnight. The final solution contains thiol molecules (100 μM) and 0.1 M PBS, where the PBS solution was present to screen the electrostatic repulsion of deprotonated thiol ligands and to facilitate efficient thiol coating of the gold NP surface. During the incubation, the gold NPs were not only fully covered by thiols but also began to assemble and form into a black sediment. The sediment (12 μl) was pipetted out and redispersed in water (100 μl) to give a reddish solution, indicative of dispersed gold NPs. This red solution was left undisturbed for a few days for sedimentation, and the colourless upper solution (92 μl) was removed to further concentrate the gold nanocubes. This final concentrated solution was used for liquid-phase TEM imaging.

For the gold nanorods, the nanorod solution (9 ml) was centrifuged twice, at $4,500 \times g$ for 5 min each time. The sediment was redispersed in water (3 ml), into which aqueous thiol solution ($44.26 \mu\text{l}$, 7.93 mM) was added. This sample was incubated for 30 min to start the ligand exchange. Next, the solution was sonicated for 5 s. Then, PBS solution (0.344 ml, 1 M) was added and the sample was left undisturbed overnight to complete the ligand exchange. During this process, the nanorods formed a sediment at the bottom of the container. The sediment was then diluted with water as the stock solution for liquid-phase TEM imaging (12 μl sediment diluted with 80 μl water).

For the gold nanoprisms, nanoprism solution (9 ml) was centrifuged twice, at $7,920 \times g$ for 8 min and at $5,940 \times g$ for 8 min. The sediment was redispersed in water (3 ml), then aqueous thiol solution ($44.26 \mu\text{l}$, 7.93 mM) was added and the sample was incubated for 30 min to start the ligand exchange. Next, the solution was sonicated for 5 s, before PBS solution (0.538 ml, 1 M) was added and the sample was left undisturbed overnight to complete the ligand exchange. During this process, the nanoprisms formed a sediment at the bottom of the container. The sediment was then diluted with water as the stock solution for liquid-phase TEM imaging (12 μl sediment diluted with 52 μl water).

Characterization of NP size, shape and surface charge

Characterization of the shape and size of the gold NPs was carried out using scanning electron microscopy (SEM; Hitachi S4800, for the gold nanocubes in Supplementary Figs. 2e and 3b) and TEM (JEOL 2100 Cryo TEM). UV-vis spectra were measured using the Scinco S-4100 PDA spectrophotometer with a quartz cuvette (path length = 1 cm). The surface charge density (ρ_s) of the thiol-coated NPs was measured using a Malvern zetasizer following the method reported in ref. 31.

Liquid-phase TEM sample preparation and imaging

For gold nanocubes and gold nanorods, liquid-phase TEM imaging was performed using a Hitachi 9500 TEM microscope with a LaB_6 emitter at 200 kV and an electrochemical liquid-flow TEM holder (Hummingbird Scientific). The SiN_x microchips used in our experiments were purchased from Hummingbird Scientific (200 nm spacer microchip with a window size of $50 \mu\text{m} \times 200 \mu\text{m} \times 50 \text{nm}$; rectangular top microchip

with a window size of $30 \mu\text{m} \times 650 \mu\text{m} \times 50 \text{nm}$). Immediately before the microchip assembly, the flow tubing was wetted with water, and the microchips were treated with oxygen plasma (Harrick Plasma Cleaner PDC-23G) at a low radio frequency level for 27 s to clean their surfaces and render them hydrophilic. The liquid-phase TEM videos (Supplementary Videos 1, 3 and 4) were captured using a Gatan Orius fibre-optically coupled charge-coupled device (CCD) camera with an exposure time of 0.1 s per frame at a rate of 10 f.p.s. Supplementary Video 5 was captured using a K2 direct detection camera in IS mode at a high frame rate of 400 f.p.s. with an exposure time of 2.5 ms per frame. For most scans, a spot size of Micro1 was used for direct imaging. The liquid-phase TEM chamber provides a liquid volume of $1 \text{cm} \times 5 \text{mm} \times (-1 \mu\text{m})$ between the chips and a larger liquid reservoir in the TEM holder, with the lateral area exceeding the size of most NP-assembled lattices. Factors such as surface tension are not a concern.

To observe the gold nanocube assembly, immediately before loading the liquid sample of nanocubes onto the microchip, PBS solution (1.36 μl ; 150 mM, pH = 8) was added to the gold nanocube stock solution (5 μl) to achieve a final PBS concentration of 40 mM. Next, the particle solution ($\sim 0.1 \mu\text{l}$) was immediately pipetted onto the bottom SiN_x microchip and covered with the top SiN_x microchip to prepare the liquid chamber. After assembly of the microchip, 40 mM PBS solution was flowed into the liquid chamber for 2 h at a speed of $5 \mu\text{l min}^{-1}$. This step ensures an accurate PBS concentration (40 mM) in the sample to account for possible solvent evaporation during microchip assembly and assembly of the nanocubes into lattices. After flowing of the PBS, we directly observed the particle vibrations and structural relaxation of rhombic lattices at an electron dose rate of $14.4 \text{e}^- \text{\AA}^{-2} \text{s}^{-1}$ (Supplementary Video 4, $I = 110 \text{mM}$).

To observe the assembly of dispersed nanocubes into rhombic lattices, we next flowed water at $5 \mu\text{l min}^{-1}$ for about 12 min. During this step, the originally assembled nanocubes were disassembled into dispersed nanocubes due to decreased ionic strength, whereas within the beam-illuminated area, the ions generated via radiolysis increased the ionic strength³¹ to assemble the cubes into the rhombic lattice. We imaged this process using a dose rate of $10.9 \text{e}^- \text{\AA}^{-2} \text{s}^{-1}$ for Supplementary Videos 1, 3 and 4 ($I = 27 \text{mM}$), and a dose rate of $10.2 \text{e}^- \text{\AA}^{-2} \text{s}^{-1}$ for Supplementary Video 5.

To observe the gold nanorod assembly, the stock solution of gold nanorods was first loaded into the liquid chamber following similar procedure to that of the gold nanocubes, except that the final PBS concentration of the loaded gold nanorod solution was 50 mM to induce self-assembly. To observe the assembly of dispersed nanorods into a hexagonal lattice, we first flowed water at $5 \mu\text{l min}^{-1}$ for about 40 min to disperse the originally assembled nanorods due to decreased ionic strength. Then 15 mM PBS was flowed at $5 \mu\text{l min}^{-1}$ for about 30 min before we observed the hexagonal lattice of gold nanorods. A dose rate of $13.1 \text{e}^- \text{\AA}^{-2} \text{s}^{-1}$ was used for imaging the lattice used for PMN analysis (Fig. 3k).

In our experiments at $I = 15 \text{mM}$, nanorods favour side-by-side packing to maximize the van der Waals attraction, as shown in our CG modelling (Fig. 3h). This packing motif can lead to two assembly configurations in liquid-phase TEM: with the rods lying parallel to the substrate, usually stacked up to ~ 5 layers in the z direction given the limit of the chamber thickness, and with the rods standing to form a hexagonal lattice viewed from the top (Supplementary Fig. 20). The standing rods in the hexagonal lattices can be more favourable as more than 90% of the rods are not at the boundary and have the maximized coordination number of six (only ~ 30 rods at the boundary in lattices consisting of >300 NPs in Supplementary Fig. 20d). By comparison, the rods lying parallel to the substrate mostly have a coordination number lower than six. Indeed, under the experimental conditions where the gain in attraction energy of one side-by-side rod pair is large, such as at high ionic strength, standing hexagonal lattices are favoured and

observed with extended areas and over an extended time (22 s), which is ideal for phonon mode calculations.

For gold nanoprisms, the liquid-phase TEM imaging was performed as detailed in our previous work³¹ using the JEOL 2100 Cryo TEM instrument with a LaB₆ emitter at 200 kV using a Protochips Poseidon 210 liquid flow holder. The SiN_x chips were purchased from Protochips (150 nm spacer chip with a window size of 550 × 20 μm; top chip with a window size of 550 × 20 μm) and were treated with oxygen plasma at a medium radio frequency level for 45 s before use. The liquid-phase TEM video (Fig. 3m and Fig. 4e) was captured using a Gatan UltraScan 1000 CCD camera with a 0.1 s exposure time per frame at a rate of 1.3 f.p.s. A spot size of 3 was used for imaging. In a typical experiment, an aliquot of nanoprism stock solution was micropipetted onto the spacer chip, before assembly with the top chip in the liquid TEM holder. We captured the relaxation and vibration of hexagonal-packed nanoprism columns with a low dose rate of 8.9 e[−] Å^{−2} s^{−1} (Fig. 3m).

Processing of TEM images and single-NP tracking

For all of the TEM and SEM images presented in this work, we adjusted the brightness and contrast using ImageJ⁵⁴ or Matlab. For gold nanocubes and nanorods, a customized ML-based tracking algorithm with a customized pre-trained U-Net neural network⁵⁵ was used to track the motions of NPs following our previous work⁵⁶. Using one frame of Supplementary Video 1 as an example (Supplementary Fig. 7d), the raw TEM images (1,412 × 1,412 pixels) were cropped to 512 × 512 pixel blocks as input to the U-Net. The prediction results were further combined into a binarized image for each frame. A customized Matlab code was used to identify the contour and centroid positions of the nanocubes from the processed image using built-in Matlab functions of watershed.m and regionprops.m. Occasionally, multiple nanocubes were recognized as one feature due to motion blurring, which was manually corrected. See Supplementary Note 3 for the details of NP tracking and estimation of the tracking error.

To track the orientation of the nanocubes, we applied a rectangle fitting algorithm to each contour of nanocubes, following a rotational bounding box algorithm. A set of rectangular bounding boxes that enclose a nanocube, with orientations ranging from 0 to 90° at 1° intervals, were first suggested. Then the rectangle of the smallest area was chosen as the fitting of a nanocube. The orientations of the cubes were found to be mostly parallel to their neighbours (Supplementary Fig. 17). As shown in Supplementary Fig. 17d, the cube orientation ϕ has a narrow distribution, with a standard deviation of 2.6°.

For the liquid-phase TEM data used for the PMN analysis, tracking errors were estimated using simulated TEM images with well-defined ground truth generated following our previous work⁵⁶ (Supplementary Fig. 7) as the averaged distance (error in tracking position) and rotated angles (error in tracking orientation) between those of tracked particles and those of the ground truth over 20 images. See the details in Supplementary Note 3 and Supplementary Tables 4 and 5 for details of the tracking error estimation for different datasets.

Data availability

The data that support the findings of this study are available via GitHub at <https://github.com/chenlabUIUC/Phonon-mapping-nanoscopy>.

Code availability

The codes for the PMN analysis and BD simulations developed in this study are available via GitHub at <https://github.com/chenlabUIUC/Phonon-mapping-nanoscopy>.

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Author contributions

C.Q. and Q.C. designed the experiments. C.Q. and B.L. performed the experiments. C.Q., L.Y., C.L. and Q.C. carried out the CG modelling and single-particle tracking analysis. E.S. and X.M. developed the discrete mechanical model and theory. C.Q., J.L., P.P. and E.S. performed the PMN analysis. Z.M. and W.P. performed the BD simulations with ML-based inter-NP interaction modelling. C.Q. and Q.C. wrote the first draft of the paper. All authors contributed to the writing of the paper. Q.C., X.M. and W.P. supervised the work.

Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to Wenxiao Pan, Xiaoming Mao or Qian Chen.

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