Electronic Supplementary information

Understanding the cooperative atomic motion and shape change of ultrasmall Au nanoparticles below the premelting temperature

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Methodology

Radius of gyration R_g is described as

$$R_g^{\,2} = \frac{1}{N}\sum_i \left(r_i - r_{mass}\right)^2$$

where r_{mass} is the mass center for any given moment. It can be used to characterize the total shape change for the object. This quantity can be generalized by defining moments about different coordinate directions to define the R_g tensor.

The shape factors, R_g, λ_1, λ_2, λ_3, b, c, and k^2 are defined below:

$$R_g^{\,2} = \lambda_1^{\,2} + \lambda_2^{\,2} + \lambda_3^{\,2}$$

$$b = \lambda_1^{\,2} - \frac{1}{2}\left(\lambda_2^{\,2} + \lambda_3^{\,2}\right)$$

$$c = \lambda_2^{\,2} - \lambda_3^{\,2}$$

$$k^2 = \frac{b^2 + (3/4)c^2}{R_g^{\,4}}$$

Dynamic atomic position r is used to show the relative position of the specific atom as a fucntion of time, and can be rescaled by the initial spherical radius, r_0. For N55 Au NP, the initial radius is 0.53 nm. The relation is

$$\rho = \frac{1}{r_0}\left|r_i - r_{mass}\right|$$

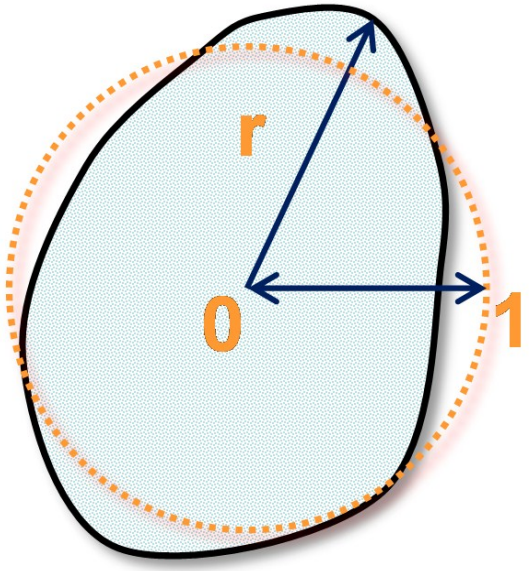
where r_i is the position of specified atom i, r_0 is the initial radius, and r_{mass} is the center of mass of the NP. If $\rho \to 0$, the i^{th} atom occupies the central position within the NP, while $\rho = 1$ indicates that this particle has emerged at the NP surface. See Scheme S1 for details.

The dynamic heterogeneity of the nanoparticle (NP) was quantified using the non-Gaussian parameter α_2. The peak position represented a characteristic time t^* meaning the cage effect gets the maximum. The expression for α_2 is

$$\alpha_2(\Delta t) = \frac{3\left\langle r^4(\Delta t)\right\rangle}{5\left\langle r^2(\Delta t)\right\rangle^2} - 1$$

The Van Hove function $G_s(r, t)$ gives the probability that a particle has moved a distance of r in a period of time t. The peaks at the successive nearest neighbour distances indicate a "hopping" motion, thus helping distinguish different kinds of atoms based on their movement. Substituting t^* derived in non-Gaussian parameter α_2 into $G_s(r, t)$, van Hove function becomes $G_s(r, t^*)$, which is essential for the definition of string-like cooperative motion. The mathematical formula for $G_s(r, t^*)$ is written as

$$G_s(r,t^*) = \frac{1}{N}\sum_k \left\langle \delta(\mathsf{r} - [\mathsf{r}_k(t^*) - \mathsf{r}_k(0)]) \right\rangle$$



Scheme S1. Sketch of the dynamic atomic position ρ (distance of the arrow).

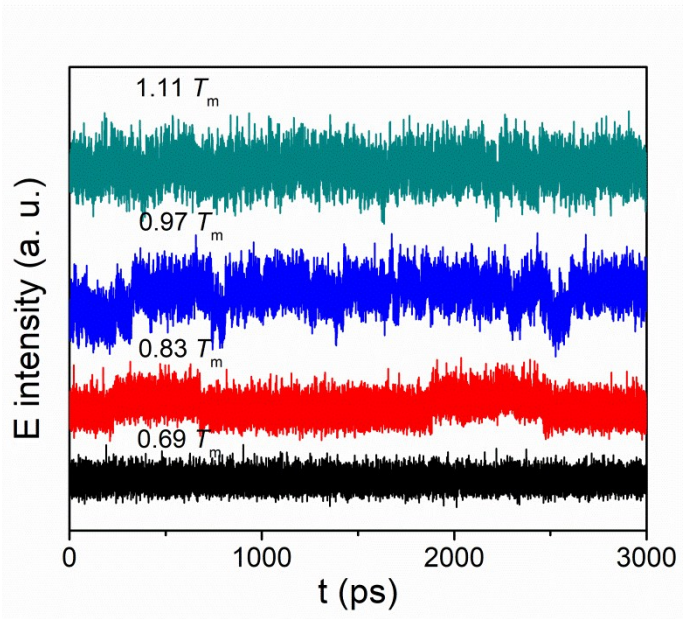


Figure S1. The variation of *E* as a function of time at different temperatures for N55 Au NP.

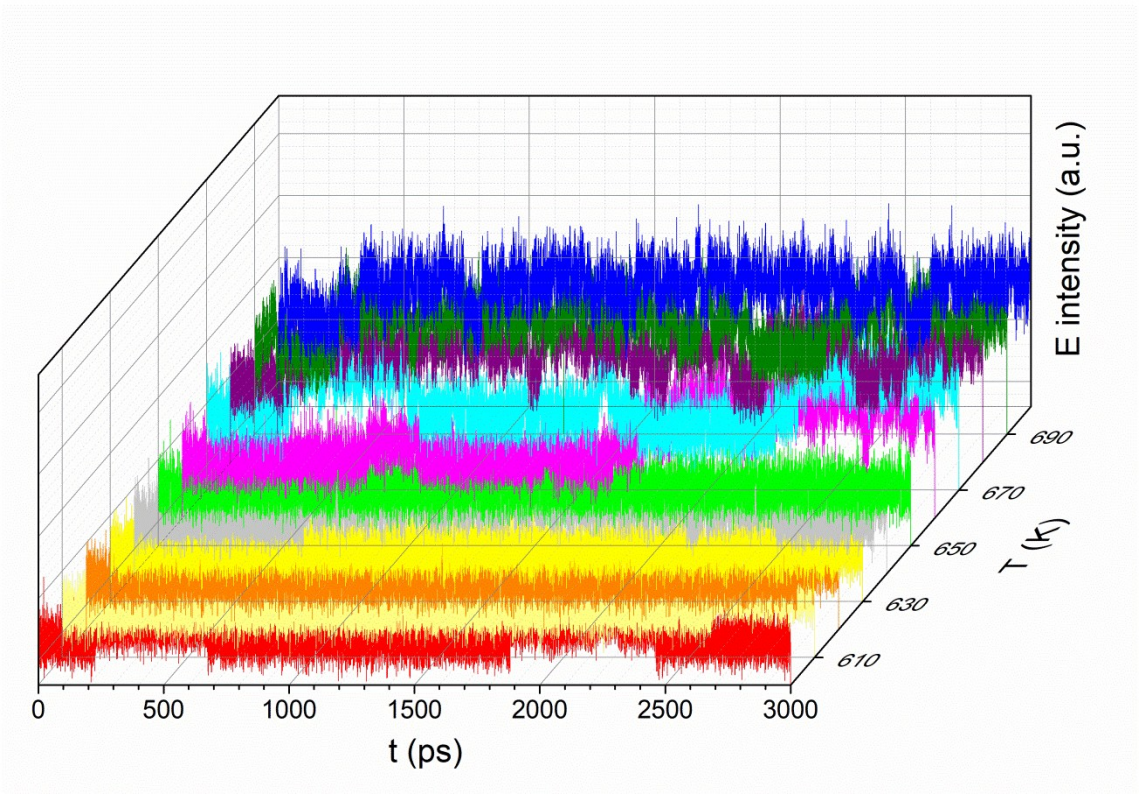


Figure S2. The variation of *E* as a function of time at different temperatures from 0.83 T_m to 0.97 T_m for N55 Au NP.

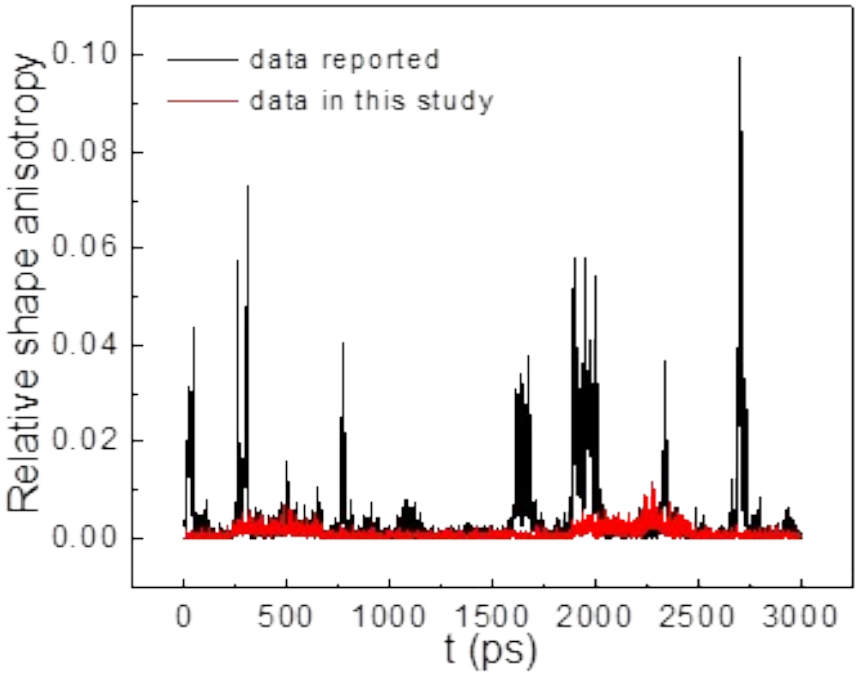


Figure S3. A comparison of the relative shape anisotropy of N55 Au NP at $T<T_w$ and the previously reported N55 Ni NP at $T>T_w$ in ref. 25.

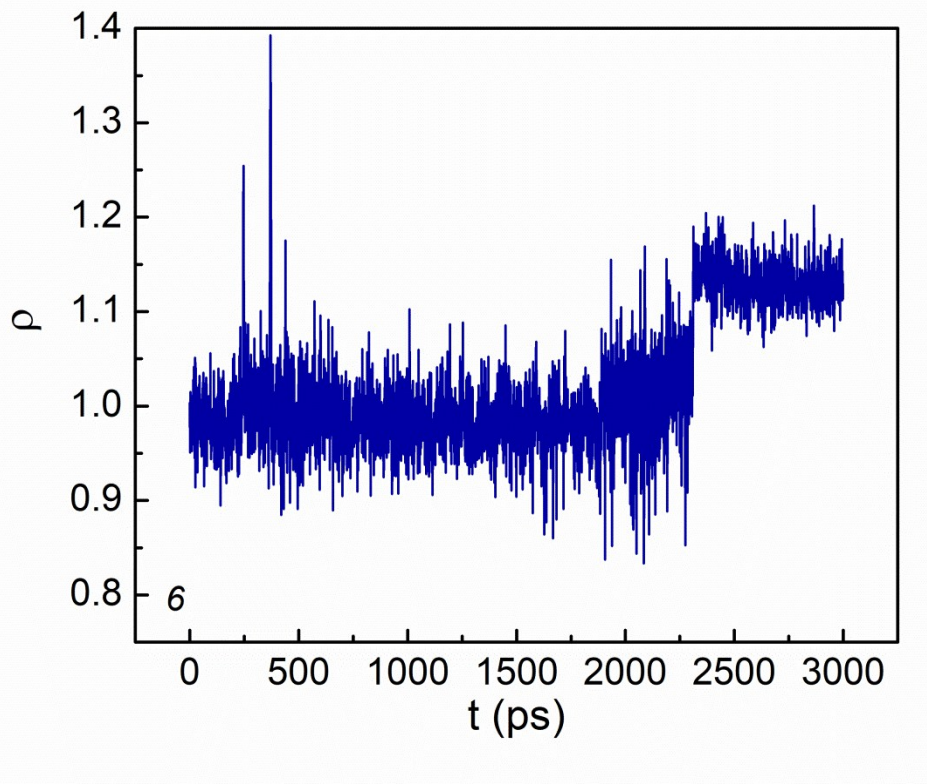


Figure S4. The variation of ρ as a function of time for atom 6, indicating the outward movement of this outer atom.

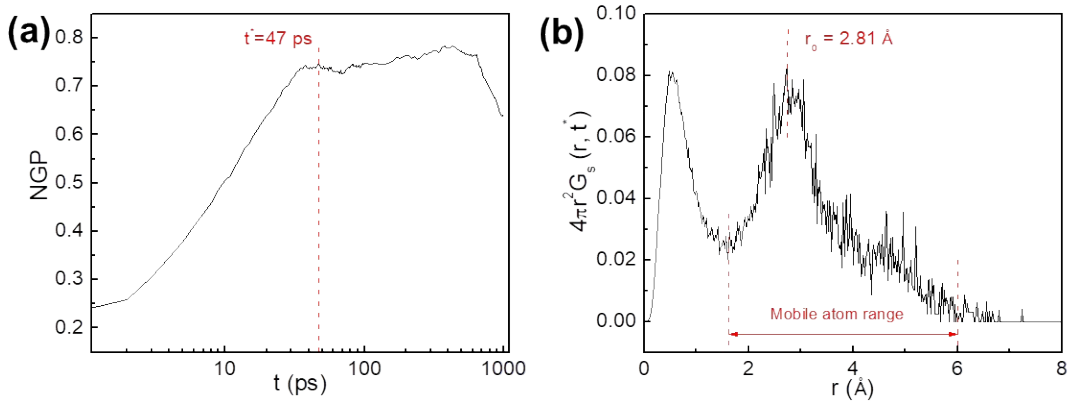


Figure 5. The plot of (a) Non-Gaussian parameter α_2 and (b) van Hove function *Gs (r, t*)* at $0.83T_m$ for N55 Au NP.

α_2 reached the peak position at t* = 47 ps, indicating the cage effect came to the maximum. Substituting t* into Gs (r, t) yielded the typical "hopping" peak at 2.81 Å, evidencing the heterogeneity of the dynamic motions of atoms. The "mobile" atom cut-off range is shown by the dashed line, from $0.58r_0$ to $2.14r_0$.

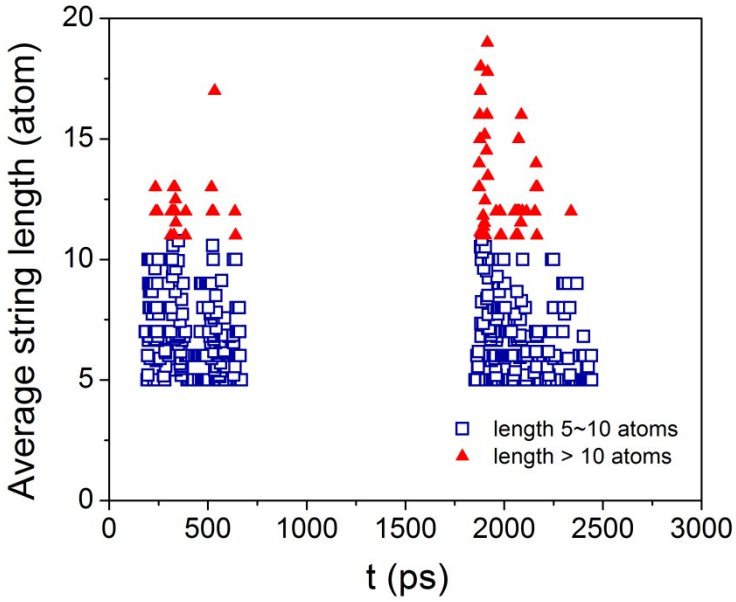


Figure 6. The plot of strings with the length >5 atoms for N55 Au NP at $0.83T_m$.