Supplemental Materials for "Vapour Condensed and Supercooled Glassy Nanoclusters"

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I. OVERVIEW

This work contains the supplemental material for our work exploring the supercooled or vapour condensation glassy Lennard-Jones clusters.

II. BOND ORDER PARAMETERS

To distinguish between amorphous and crystalline atoms in a nanocluster, we calculate the bond order parameter. A local six-fold complex vector $q_{l,m}(i)$ for atom i is defined as

$$q_{6,m}(i) = \frac{1}{nn(i)} \sum_{j=1}^{nn(i)} Y_{6,m}(\mathbf{r}_i j), \tag{1}$$

where $nn(i)$ is the number of nearest neighbors of atom i, $Y_{6,m}(\mathbf{r}_{ij})$ is the spherical harmonic function with $m \in [-6, 6]$ and $\mathbf{r}_{ij}$ is the vector from atom i to atom j. The number of crystalline bond for atom i is given by

$$n_c(i) = \sum_{j=1}^{nn(i)} H(u_6(i,j) - u_c), \tag{2}$$

where H is the Heaviside step function, $u_c = 0.7$ is a threshold value, and $u_6(i,j)$ is the correlation between the bond orientational order of atoms i and j defined as

$$u_6(i,j) = \frac{\sum_{m=-6}^{6} q_{6,m}(i) q^*_{6,m}(j)}{\left(\sum_{m=-6}^{6} |q_{6,m}(i)|^2\right)^{1/2} \left(\sum_{m=-6}^{6} |q_{6,m}(j)|^2\right)^{1/2}}. \tag{3}$$

In the glassy nanoclusers, amorphous atoms rarely have more than four crystalline bonds. The atoms that where identified as crystalline usually have more than nine bonds. Figure S1 shows a configuration in a supercooled glassy nanocluster at $T^* = 0.1$, containing two crystalline atoms with $n_c \leq 5$. In general, we find that no more than 5 atoms ($< 1\%$) are crystalline, which suggests all the nanoclusters studied here are glassy.

We also calculated the local bond order parameter or Steinhardt order parameter for atom i, which is defined as

$$q_6(i) = \sqrt{\frac{4\pi}{13} \sum_{m=-6}^{6} |q_{6,m}(i)|^2}. \tag{4}$$

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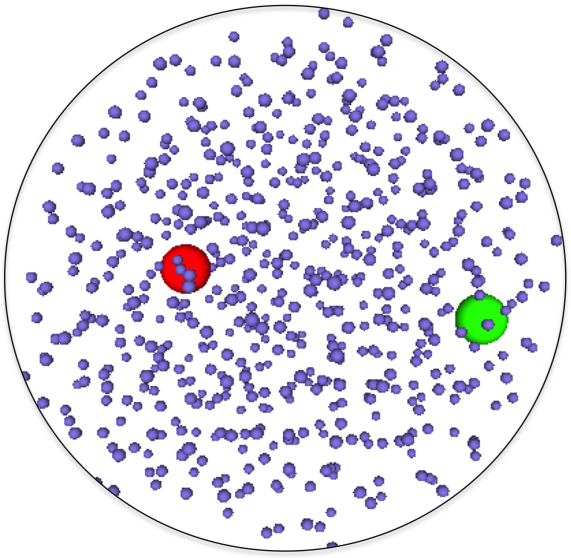

FIG. S1. A typical configuration for a supercooled glassy nanocluster prepared at temperature $T^* = 0.1$ with cooling rate 3.3×10^{-3}. Small atoms are amorphous atoms with $n_c < 5$ and large atoms are crystalline with $n_c = 5$ (red) and $n_c = 6$ (green).

Figure S2 shows the distribution of $q_6(i)$ for supercooled glassy nanoclusters (SCGN) prepared with a cooling rate of $\gamma = 3.3 \times 10^{-6}$ and vapour condensed glassy nanoclusters (VCGN) prepared with a cooling rate $\gamma = 3.3 \times 10^{-4}$ at temperature $T = 0.30$. There little or no difference between the distributions of q_6 for the two types of glassy nanoclusters. For all the atoms in the nanoclusters, the value of q_6 is smaller than 0.01. Again, this result indicates no crystallization has occurred in the glassy nanoclusters.

III. COORDINATION NUMBERS AND LOCAL POLYHEDRA

We analyse the number of nearest-neighbours around $B-$type atoms using Voronoi tessellation. Figure S3 shows the distribution of coordination numbers of $B-$type atoms for SCGN and VCGN at $T = 0.26$, which is similar to the results of bulk glass, with most of the $B-$type atoms having coordination numbers between 9 and 13. The favoured local structure for the bulk Kob-Andersen model is thought to be the bicapped square an-

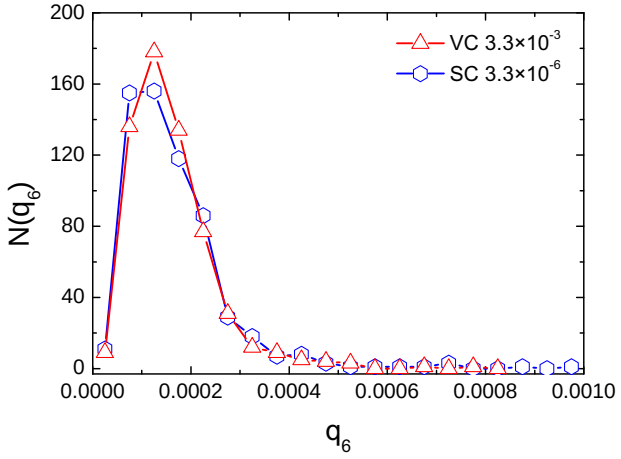

FIG. S2. Distribution of the q_6 Steinhardt order parameter for VCGN with cooling rate 3.3×10^-3 and SCGN with cooling rate 3.3×10^-6 at $T = 0.3$.

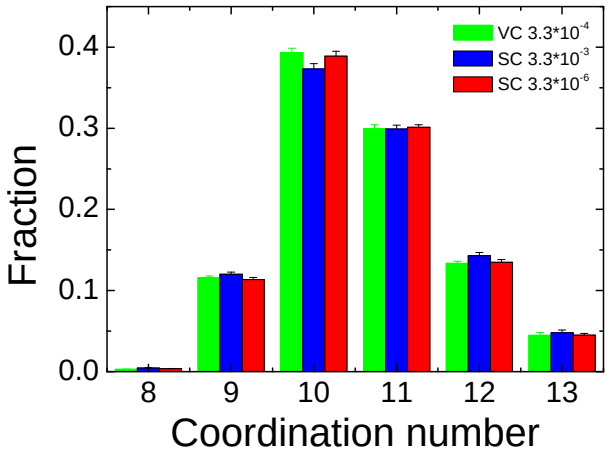

FIG. S3. Distribution of coordination numbers for SCGN and VCGN prepared at temperature $T = 0.26$ with cooling rates as marked. The error bars represent the standard deviation for data obtained from ten independent runs.

tiprism, which is a polyhedra with one central $B-$type atom surrounded by ten neighbours. This is consistent with our results. There are no significant differences between the coordination numbers of the SCGN prepared with cooling rate of $\gamma = 3.3 \times 10^{-6}$ and the VCGN prepared with cooling rate of $\gamma = 3.3 \times 10^{-4}$, where the inherent structure energy for both glassy nanoclusters is very close. However, there are less atoms with a coordination number of ten in the SCGN prepared with $\gamma = 3.3 \times 10^{-3}$, suggesting it may be less stable than the other two glassy nanoclusters.

The local polyhedral structure of the $B-$type atoms can also be characterized by their Voronoi index $\langle n_3, n_4, n_5, n_6 \rangle$. The ultrastable glasses formed through vapour deposition onto a surface are characterized by an excess of regular polyhedra of the types, $\langle 0, 2, 8, 0 \rangle$, $\langle 0, 2, 8, 1 \rangle$, $\langle 0, 0, 12, 0 \rangle$, and a decrease in irregular polyhedra, $\langle 0, 2, 8, 2 \rangle$ and $\langle 1, 2, 7, 1 \rangle$. Based on the Voronoi analyses, we calculated the fraction of polyhedra $P(N_p) = N_p/N_B$, where N_p is number of one type of polyhedra and N_B is number of $B-$type atoms. The main text shows that the fraction of $\langle 0, 2, 8, 0 \rangle$ polyhedra, which includes the bicapped square antiprism, is significantly increased in the nanocluster systems. However, the nanoclusters see a decrease in the number of $\langle 0, 2, 8, 1 \rangle$ polyhedra and icosahedra, denoted $\langle 0, 0, 12, 0 \rangle$, are completely eliminated by $T \approx 0.35$. Figure S4 also shows that the fraction of $\langle 0, 2, 8, 2 \rangle$ polyhedra tend to decrease with T, but there are significant fluctuations below the glass transition temperature.

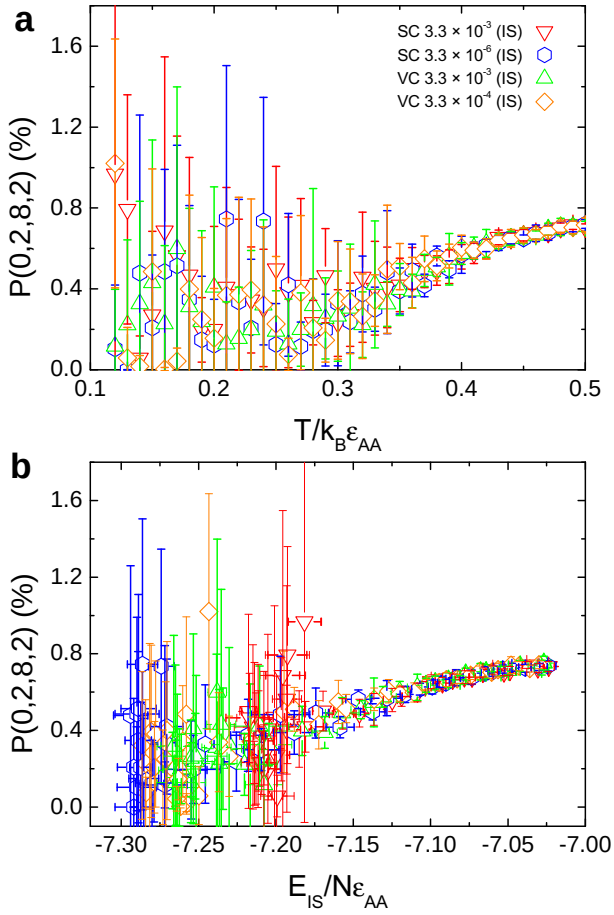

FIG. S4. Fraction of $\langle 0, 2, 8, 2 \rangle$ as a function of temperature (a) and inherent structure energy (b) in the inherent structures of SCGN and VCGN with cooling rate as labeled.