Final Report

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The original objective of this project was to measure the melting point of copper as a function of cluster size. Finding the melting point of copper as a function of cluster size is useful as a check for the validity/usefulness of inter-atomic potentials found using machine learning methods. The author has failed in this respect, however, this project has measured the melting point of copper for three spherical clusters of differing sizes. This project consists of using LAMMPS software to run molecular dynamics (MD) simulations that model the thermal behavior of spherical copper clusters under the influence of different fixed temperatures. The fixed temperatures were achieved using the NVT thermostat command in LAMMPS, and by fixing the net velocity of particles in the cluster as a Gaussian distribution such that the temperatures were achieved. The thermal behavior of a cluster was determined by performing calculations based on data regarding the positions of each atom at a given time, and on data regarding the inter-atomic forces experienced by each atom at a given time. The inter-atomic forces were calculated with LAMMPS using Deep-MD machine learning data provided by the CSI lab at Princeton University. The spherical clusters were created using LAMMPS software also. The spherical clusters were created at a temperature of 50 degrees Kelvin. The three spherical clusters are of size N = 19, N = 627 and N = 2093 copper molecules.

The melting point of a cluster is determined roughly by measuring the temperature at which a phase transition occurs. A phase transition in this instance is characterized by the diffusion of the particles as their positions change significantly over time. The presence of diffusion or a phase transition can be detected by analyzing the time averaged net displacement of any atom with respect to all other atoms for a given MD simulation run.

The local Lindemann index q_i, assigned to atom i, is used to for measuring the net displacement of atom i with respect to other particles, and is defined as

$$q_i = \frac{1}{N-1} \sum_{j \neq i} \frac{\sqrt{\langle r_{ij}^2 \rangle_{\mathrm{MD}} - \langle r_{ij} \rangle_{\mathrm{MD}}^2}}{\langle r_{ij} \rangle_{\mathrm{MD}}}$$

where N equals the number of atoms and r_{ij} represents the displacement between atom i and distinct particle j. The angled brackets denote the time average over the course of the MD simulation.

The global Lindemann index $\langle q \rangle$ for the system is defined as the the system average over all the q_i. For given cluster of size N, the global Lindemann index was computed for a series of temperatures ranging from 50 K to 1400 K with an interval ΔT of 50 K.

It is known [1] that a plot of $\langle q \rangle(T)$ for a given cluster of size N is approximately linear for temperatures lower than the melting point before then experiencing a sudden "jump" for temperatures within a certain range of the melting point after which approximate linearity returns. Thus, the melting point of cluster of size N is determined by fitting a sigmoid function of the form

$$\langle q(T) \rangle \approx \frac{x_1}{1 + e^{-x_2(T - T_m)}} + x_3$$

to a plot of $\langle q \rangle(T)$ with parameters x_1,x_2,x_3 and the parameter T_m, the turning point of the function, is defined to be the melting point. The curve fitting was done using a Python script provided by Jiayan Xu of the CSI lab at Princeton University.

Figure 1 plots the global Lindemann indexes as a function of temperature. As seen in the figure, the indexes exhibit approximate linear behavior at lower temperatures before their slope changes drastically in the region surrounding the estimated melting point. A point of concern: the sigmoid function used to fit the data assumes that the slope of $\langle q \rangle(T)$ should approach zero for temperatures above the

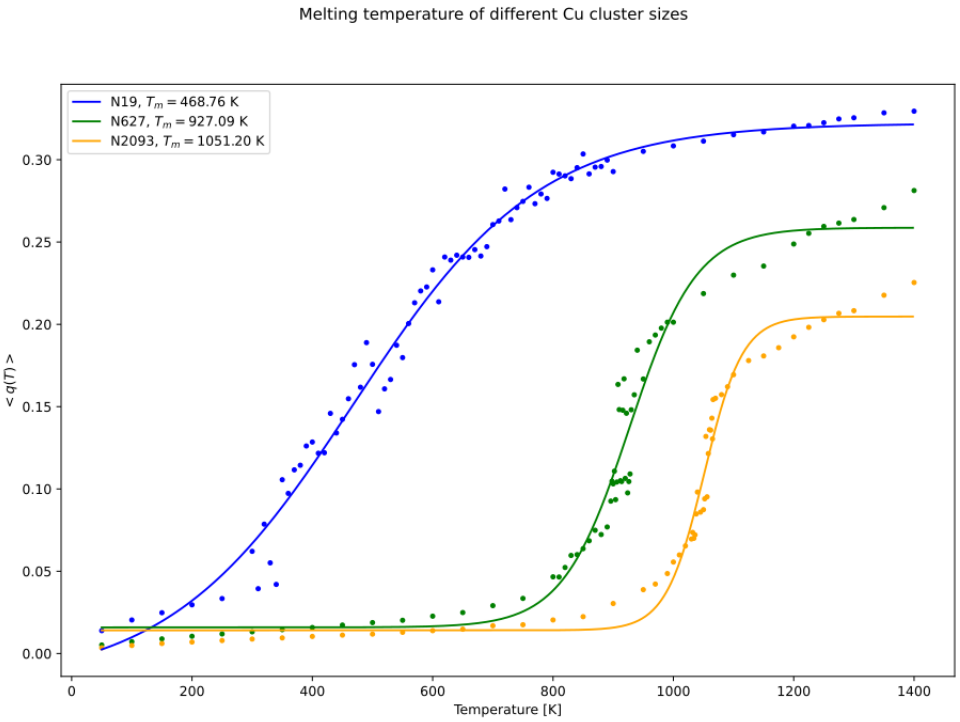


Figure 1: $\langle q \rangle$ as a function of temperature for different values of N

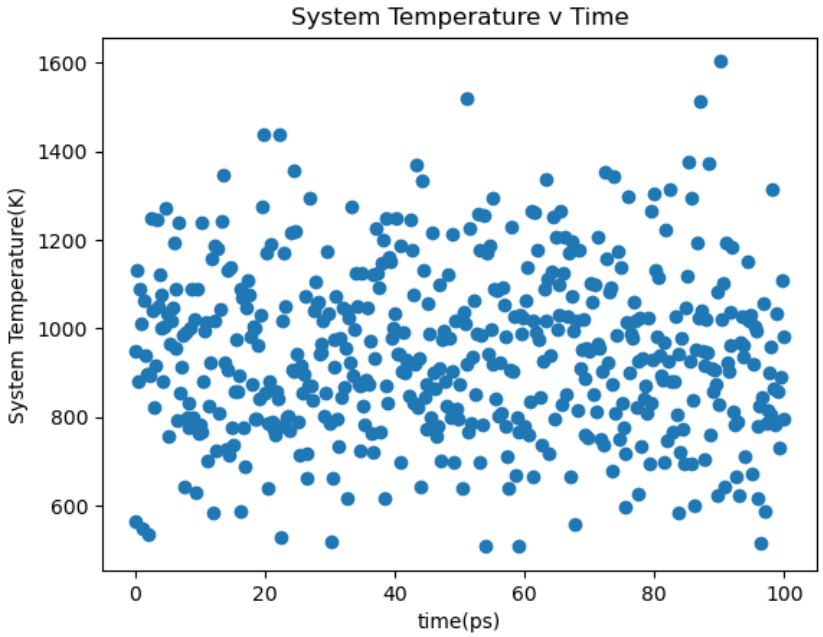


Figure 2: System temperature as a function of time for N = 19, $T_s = 950$ K

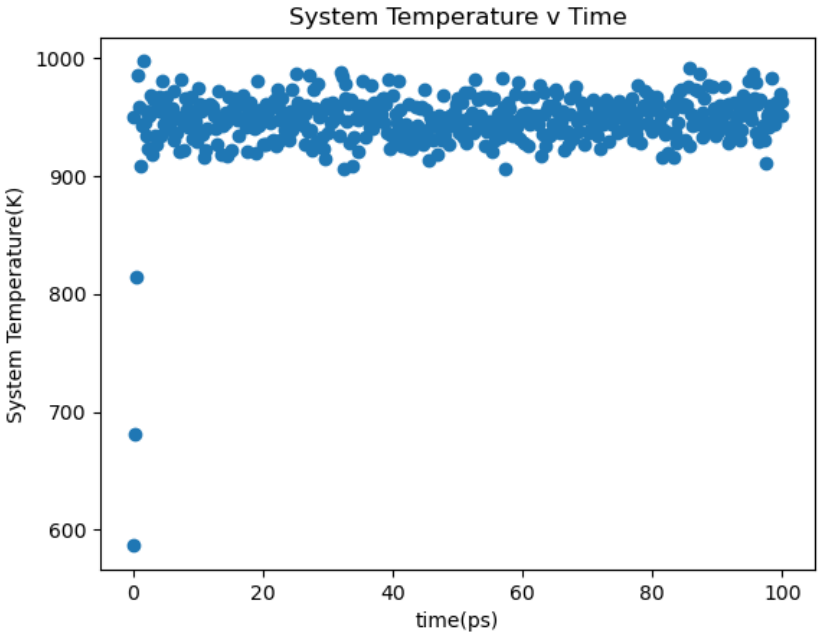


Figure 3: System temperature as a function of time for N = 2093, $T_s = 950$ K

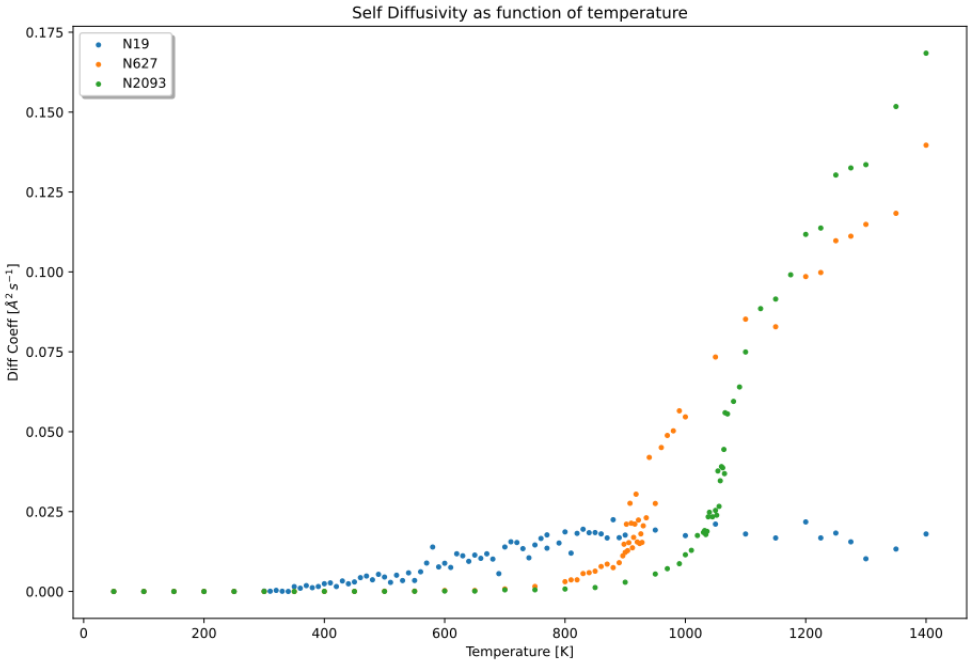


Figure 4: Self diffusivity as a function of temperature

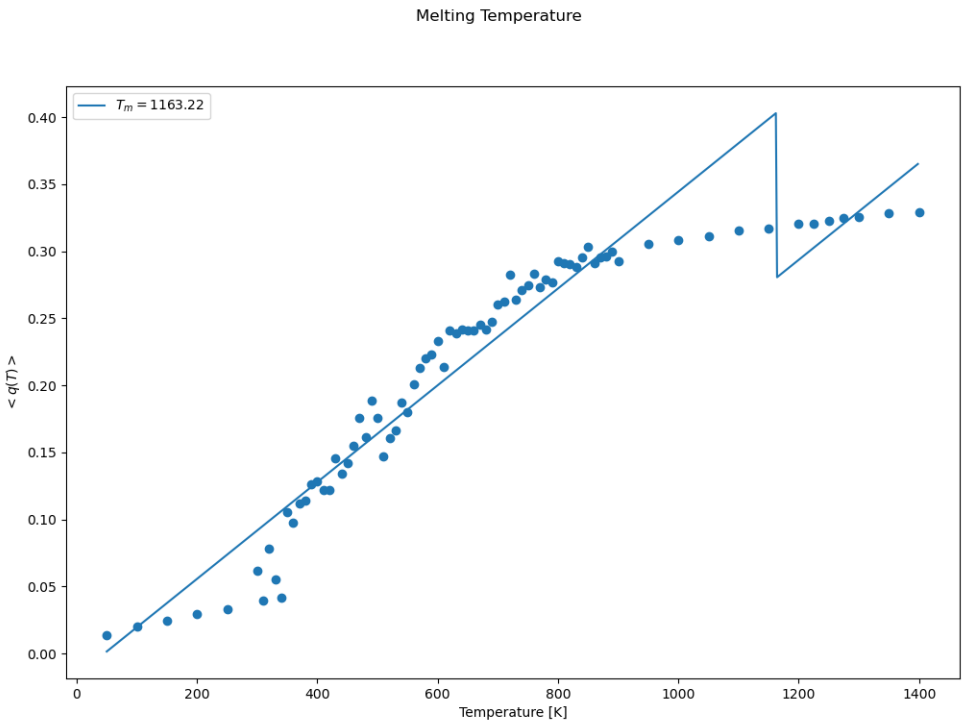


Figure 5: $\langle q \rangle(T)$ for N = 19, fitted with alternative sigmoid function

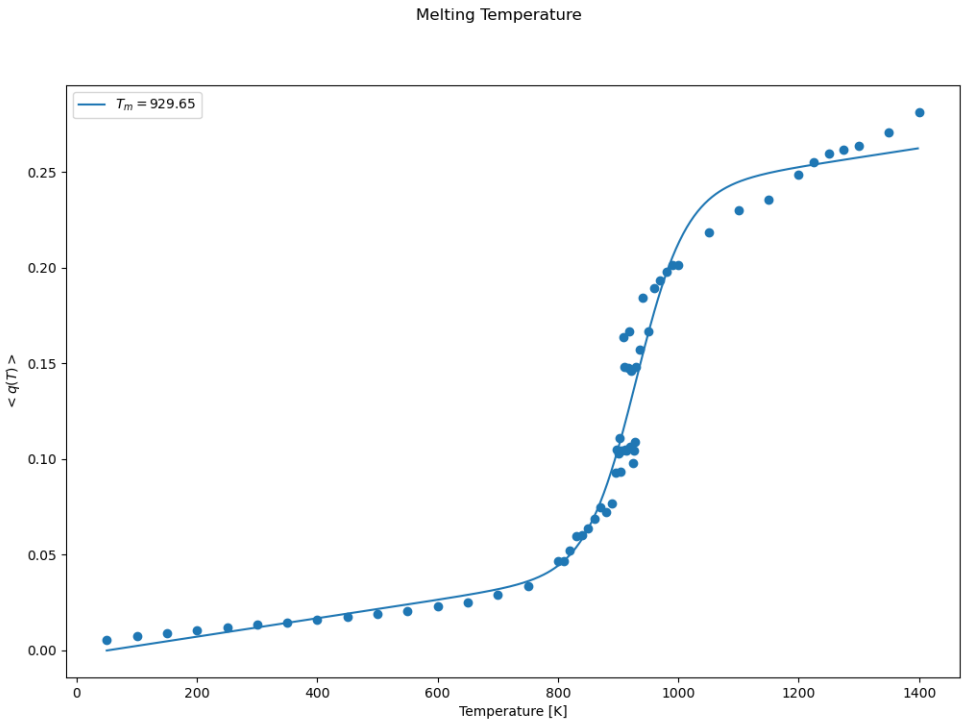


Figure 6: $\langle q \rangle(T)$ for N = 627, fitted with alternative sigmoid function

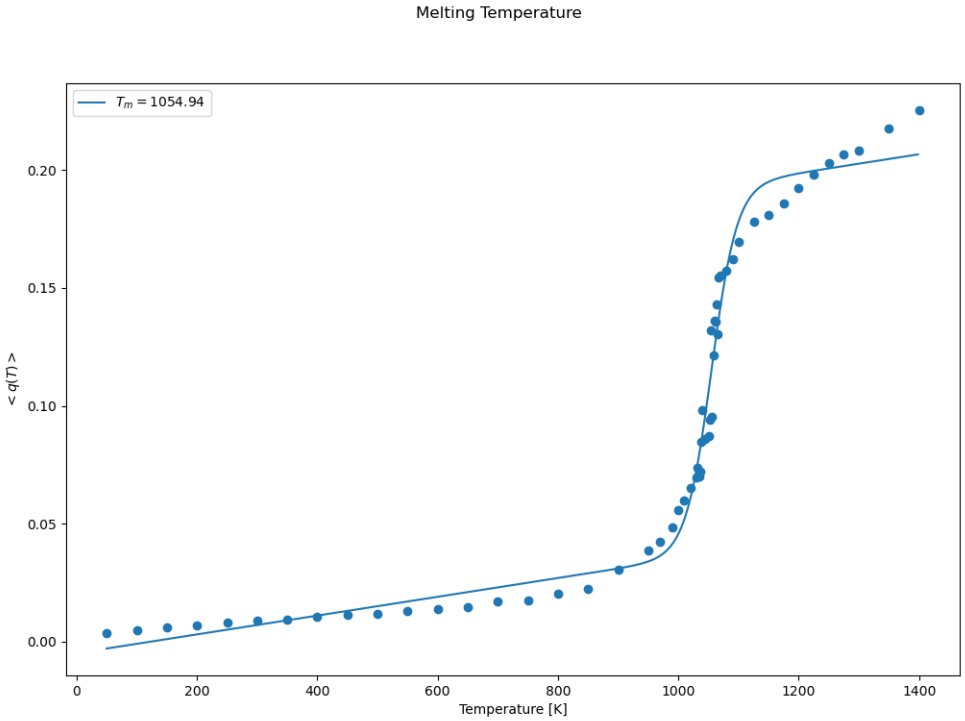


Figure 7: $\langle q \rangle(T)$ for N = 2093, fitted with alternative sigmoid function

melting point; the data points for the clusters, particularly for the larger sized clusters, do not fit well with this assumption - it is clear that their slopes are positive. It would be best to sample temperatures above 1400 K to observe if the slope flattens or gets closer to zero at these higher temperatures. It is possible, however, that there is a source of error in the collection of data that accounts for this discrepancy. Perhaps an inappropriate run time for the MD simulations was chosen. A time-step of 0.002 pico-seconds was chosen, the MD simulations were run for 50,000 time-steps. Perhaps 500,000 time-steps would have been best, albeit computationally intensive. This may be particularly true for the smaller N = 19 cluster as a plot of system temperature vs time (seen in figure 2) for a larger T_s - input temperatures set by NVT thermostatting in LAMMPS - shows large fluctuations throughout, indicative of an absence of thermal equilibrium. However, while this may be the case for the smaller cluster, this is not true for the larger N = 2093(figure 3) or N = 627 (plot not shown) clusters. The system temperature vs time plot for the larger cluster suggests that thermal equilibrium is reached well within the timescales chosen, and that the run time of 50,000 time-steps was appropriate. Another potential source of error is an inadequate sampling of data points: calculations for the local Lindemann indexes of atoms in an N-sized cluster may have included a significant amount of positional data (of the atoms) while the system was still not in thermal equilibrium. Another possibility is that the sigmoid function used for fitting inadequate. Fitting with an alternative sigmoid function, modified with an extra linear term to account for the non-zero positive slopes at the extreme end of sampled temperatures,

$$\langle q(T) \rangle \approx \frac{x_1}{1 + e^{-x_2(T - T_m)}} + x_3 T + x_4$$

yielded mixed results. Figure 5 shows that the alternative sigmoid function gives a very different estimate of the melting point for N = 19, and the curve fitting does not resemble a sigmoid function at all. The alternative sigmoid function is not adequate for the purpose of finding the melting point. Figure 6 shows that the alternative sigmoid function fit gives a very similar estimate as the original sigmoid function for the melting temperature of N = 627, and the curve fit seems adequate, although the same concerns can be said about the fit at higher temperatures; the same can be said for N = 2093 (figure 7). The alternative sigmoid function does not give substantially different results for the larger sized clusters, and it is inadequate for the smaller cluster, so it appears that the original sigmoid

function given is best.

The self diffusivity vs temperature plot (figure 4) is equally, if not more, troubling than the Lindemann index plot. Again, the diffusion coefficients are stable at lower temperatures before suddenly increasing for temperatures approaching the estimated melting point. This is expected behavior, however, the self diffusivity continues to increase with temperature and does not flatten out. The slope of the plots at higher temperatures suggest a possible levelling off, but like the Lindemann plots, more temperatures need to be sampled.

In all, the melting point of the copper clusters definitively increases with the size of the cluster. Fitting with a sigmoid function shows promise as being appropriate for the estimation of the melting points of copper, although data at higher temperatures needs to be collected for the three cluster sizes. Future work would require that more copper clusters of different sizes be used instead of using just three different copper cluster sizes. Using a greater variety of cluster sizes would also allow for an estimate of the melting point of bulk copper to be obtained; comparison of this estimate with the known melting point of bulk copper would serve as a check for the veracity of the methods used in obtaining the melting points of the different sized copper clusters.

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References

[1] Jan Weinreich, Anton Römer, Martín Leandro Paleico, and Jörg Behler. Properties of -brass nanoparticles. 1. neural network potential energy surface. *The Journal of Physical Chemistry C*, 124(23):12682–12695, 2020.