

**QUANTUM CHEMISTRY, MACHINE LEARNING AND ATOMISTIC MONTE CARLO
TO STUDY MELTING-LIKE TRANSITIONS IN SMALL CLUSTERS**

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Abstract

This thesis develops computational methods for efficiently predicting melting-like transitions in clusters. Four criteria are introduced to characterize these transitions: (i) the width of the potential energy distribution (W_U), which broadens near the melting point; (ii) a dissimilarity measure relative to the ground-state configuration, defined from the ordered interatomic distances r_{ij} ; (iii) the effective count of r_{ij} values near the mean of the first two peaks of the pair distribution function; and (iv) the degree of non-uniformity in the r_{ij} distribution. Together with an artificial neural network classifier for estimating solid fractions, these measures identify melting transitions with two- to threefold reductions in computational effort compared to conventional heat-capacity-based ($C(T)$) analyses. Parallel Tempering Monte Carlo (PTMC) was combined with an $E(3)$ -equivariant neural network potential (Allegro) trained to reproduce density functional theory (DFT) energies. The framework was validated on sodium clusters and applied to aluminum clusters containing up to 16 atoms in both neutral and charged states. Predicted melting temperatures ranged from 305 K to above 1200 K , exhibiting size- and charge-dependent nonmonotonic variations consistent with experimental and theoretical data. The methodology was further extended to global optimization, where tens of millions of candidate geometries were screened using the neural network, refined through local optimization, and classified by topological fingerprints and bond-orientational order. This reduced computational cost by three to four orders of magnitude compared to DFT-based sampling while maintaining near-DFT accuracy. The same approach was applied to heteroatomic icosahedral clusters AB_2C_{10} chosen for their superatomic potential. Among them, $Zr_1Rb_2Au_{10}$ and Sn_3Y_{10} were prioritized based on atomization energies and electronic simplicity. Estimated melting

temperatures 1263 K and 2061 K, respectively, exceeded the weighted average of their elemental melting points. Overall, this work provides new insights into cluster melting, revealing size-dependent trends, enhanced thermal stability in superatomic systems, and non-melting behaviour in certain aluminum clusters. By integrating multiple indicators and scalable algorithms, it advances the understanding of phase-like transitions at the nanoscale.

Dedication

To my late Achaachan and Achamma

I know you both would be proud of me. I carry your blessings in my heart, always.

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Abbreviations and Symbols

$\mathbf{X}_n$	Cluster or nanoparticle of element X containing n atoms
CN	Coordination number
$\mathbf{T}_m$	Melting temperature
$\mathbf{T}_f$	Freezing (onset) temperature
$\mathbf{T}_c$	Characteristic temperature corresponding to a melting indicator peak
$\mathbf{T}_{\text{evap}}$	Evaporation temperature
LJ	Lennard-Jones potential
MLIP	Machine-learned interatomic potential
DFT	Density Functional Theory
NN	Neural network
ANN	Artificial neural network
FFANN	Feed-forward artificial neural network
CNN	Convolutional neural network
GNN	Graph neural network
DFT-NN	Density Functional theory- Neural Network Framework

ML	Machine learning
AI	Artificial intelligence
PES	Potential energy surface
MC	Monte Carlo simulation
PTMC	Parallel Tempering Monte Carlo
REMC	Replica Exchange Monte Carlo
AIMD	<i>Ab initio</i> molecular dynamics
AIMC	<i>Ab initio</i> Monte Carlo
BO	Born–Oppenheimer approximation
HF	Hartree–Fock approximation
HFS	Hartree–Fock–Slater approximation
HK	Hohenberg–Kohn theorems
KS	Kohn–Sham formulation of DFT
E_{xc}	Exchange–correlation functional
LDA	Local Density Approximation
GGA	Generalized Gradient Approximation
TPSS	Tao–Perdew–Staroverov–Scuseria meta-GGA functional
MP2	Møller–Plesset perturbation theory (second order)
MO	Molecular orbital
STO	Slater-type orbital

GTO	Gaussian-type orbital
CGTO	Contracted Gaussian-type orbital
ECP	Effective core potential
SDD	Stuttgart/Dresden pseudopotential
EAM	Embedded Atom Method
TB	Tight-binding potential
PCA	Principal Component Analysis
GM	Global minimum
C(T) / C_v	Heat capacity as a function of temperature
W_U	Potential energy distribution of atomic clusters
U_{LJ-V4}	Valence-saturated Lennard–Jones potential
f_U	Probability density function of energy
δ(T)	Structural dissimilarity parameter
dδ/dT	Derivative of the order parameter δ with respect to temperature
G	Geometric melting indicator
d²G/dT²	Second derivative of G with respect to temperature
h_p	Uniformity indicator of cluster ($p = 1\text{--}10$)
U_i	Potential energy of configuration i
F_s	Solid fraction of atomic configurations
LOWESS	Locally Weighted Scatterplot Smoothing

ROC	Receiver Operating Characteristic
AUC	Area Under the Curve
Ar_n	Argon cluster containing n atoms
Si_n	Silicon cluster containing n atoms
Ag_n	Silver cluster containing n atoms
Al_n	Aluminum cluster containing n atoms
Na_n	Sodium cluster containing n atoms
Zr_nRb_mAu_l	Zirconium–rubidium–gold heteroatomic cluster containing n , m , and l atoms
Sn_nY_m	Tin–yttrium heteroatomic cluster containing n and m atoms
$\bar{r}$	Mean distance of an atom to its neighbors
ZBL	Ziegler–Biersack–Littmark screened Coulomb potential
PCC	Pearson correlation coefficient
SVR	Support Vector Regression
MAE	Mean absolute error
QMC	Quantum Monte Carlo
COM	Center of mass
E_{DFT}	Density Functional Theory energy (single-point at fixed geometry)
E_{ML}	Machine-learned potential energy predicted by MLIP
E_{DFT/ML}	DFT energy evaluated at a machine-learned optimized geometry
IP/IE	Adiabatic ionization potential / ionization energy

VIE	Vertical ionization energy
EA	Electron affinity
LF	Lowest vibrational frequency
FES	Free energy surface
ZPE	Zero-point energy
E	Atomization energy of the system
$\mathbf{r}_{ij}$	Distance between atoms i and j
σ	Standard deviation

List of Publications

A. Krishnadas, M. Moshi, R. A. Miranda Quintana, and R. Fournier, “*Geometric Features and a Neural Network Classifier for Detecting Melting-Like Transitions in Clusters.*”, in review.

A. Krishnadas, N. Charron, and R. Fournier, “*Melting Transitions in Small Aluminum Clusters Simulated with Energies Approaching DFT Accuracy.*”, in review.

A. Krishnadas, N. Charron, and R. Fournier, “*DFT-Monte Carlo Driven Global Optimization of Geometric Structures in Neutral and Charged Aluminum Clusters*”, in preparation.

A. Krishnadas, and R. Fournier, “*Selection of AB_2C_{10} Superatom Candidates and Investigation of Their Melting Transitions*”, work in progress.

Chapter 1

Introduction

1.1 Clusters.

Cotton first used the word **cluster** while investigating low-valent polynuclear rhenium halides [3] that exhibit metallic bonding between a few atoms [4]. Later, the word cluster was also used for chemical species made of nonmetals and semimetallic elements. Nowadays, a cluster is generally understood to be a chemical species X_n where $n \lesssim 100$ and X is an atom or a small repeating unit (e.g., H_2O or Al_2O_3) that may be viewed as a fragment of a bulk material. The word **nanoparticle** is generally used for species X_n with $n \gtrsim 100$ and a diameter of 1 to 100 nm. Most clusters form three-dimensional structures and exhibit properties that diverge from those of their bulk counterparts. Atomic clusters and nanostructures have garnered interest due to their applications in catalysis [5], electronics [6], biodiagnostics [7], and specialized materials [8].

The properties of clusters can differ greatly from those of the corresponding bulk for many reasons. Clusters have a much higher molar surface area. Their surface atoms have a lower coordination number (CN) than those of a flat surface. The geometric arrangement of atoms in clusters differs from that of a crystal fragment. Due to their finite size and quantum confinement, clusters exhibit a HOMO–LUMO gap (often called a “band gap”) that is larger and more size-dependent than in the bulk. Additionally, clusters and nanoparticles often exhibit superior catalytic properties due to their high surface area and unique surface sites. For example, gold is catalytically inactive as a bulk solid, but gold clusters are effective catalysts for CO oxidation [9]. Metal nanoclusters with modified biocompatible surfaces have been used in biomedical applications. By controlling their size and surface chemistry, one can target specific tissues, while the photoabsorption properties of the inner metallic core can be utilized as a beacon for diagnosis or as a light-activated radiotherapy agent [10].

Clusters are being investigated as possible building blocks for new materials with favourable conductivity, magnetism, or light absorption properties [11]. Semiconductor quantum dots, in particular, are used in optoelectronics [12] and medical imaging [13]. Metal clusters are also considered for applications in energy storage systems where their large surface area and tunable features could boost charge storage capacity and ion transport [14].

1.2 Size evolution of cluster properties.

The properties of nanoparticles X_n evolve smoothly toward bulk properties when n is large. But when $n \lesssim 100$, cluster properties are non-monotonic functions of n and sometimes change abruptly with the addition of a single atom. The transition to monotonic behaviour occurs at different values of n depending on the property and a cluster's chemical composition. Interatomic distances are nearly converged already at $n \sim 50$, but experimental calorimetry measurements show that the melting temperature of aluminum clusters starts to vary monotonically only at $n \sim 150$ [15]. In contrast, the electronic structure and photoabsorption properties of gold clusters, as seen in both experimental and computational studies, begin to evolve monotonically toward bulk behaviour only at $n \sim 250$ [16].

Sodium clusters exhibit enhanced stability at certain electron counts called **magic numbers** [17] (2, 8, 18, 20, 34, 40, 54, ...) in a way similar to shell closings of noble gas atoms with 2, 8, 18, 32 valence electrons. The chemical reactivity of transition metal clusters can vary dramatically with size [18, 19]. Small metallic clusters show discrete, molecule-like electronic transitions while larger clusters and nanoparticles have plasmon resonances [20]. Small clusters of *Fe*, *Co*, *Ni* and *Rh* exhibit enhanced magnetic moments caused by the presence of many surface atoms with low coordination and higher spin polarization [21, 22, 23, 24, 25]. Gold clusters exhibit catalytic activity for *CO* oxidation at particular sizes attributed to quantum electronic effects and specific geometric features [26].

An interesting class of metal clusters, called **superatoms**, have stable quasispherical shapes and delocalized electrons in orbitals of *s*, *p*, *d*, *f* ... type that form shells resembling the electronic structure of atoms. The best-known superatom is the superhalogen Al_{13} . It has 39 valence electrons, one short of the magic number 40, with electronic configuration $1S^2 1P^6 1D^{10} 2S^2 1F^{14} 2P^5$ [26]. The high electron affinity of Al_{13} , relative stability of Al_{13}^- , and chemical reactivity of Al_{13} toward iodine atoms [27] all show superatomic characteristics. The monotonic evolution of cluster properties with size above a threshold n_0 that depends on the property and cluster composition, the abrupt changes of properties sometimes seen at $n < n_0$, and the distinct superatomic behaviour

found for a few specific clusters X_n , make for an interesting topic of study. The complexity in the size-dependent variation of cluster melting temperatures is especially relevant for this work. No simple theory predicts these melting points, and many details remain unknown. Experimental measurements are challenging because clusters exist at very low concentrations and have millisecond lifetimes [28]. Gas-phase measurements typically use ionization and mass spectrometry to select cluster sizes and compositions [29], but the ionization process and resulting charge states can modify the cluster's structure and shift its melting temperature compared to its neutral form. Even small perturbations, such as temperature fluctuations or adsorption, can change cluster structures and complicate melting measurements [30].

1.3 Size variations in melting points and other properties of clusters.

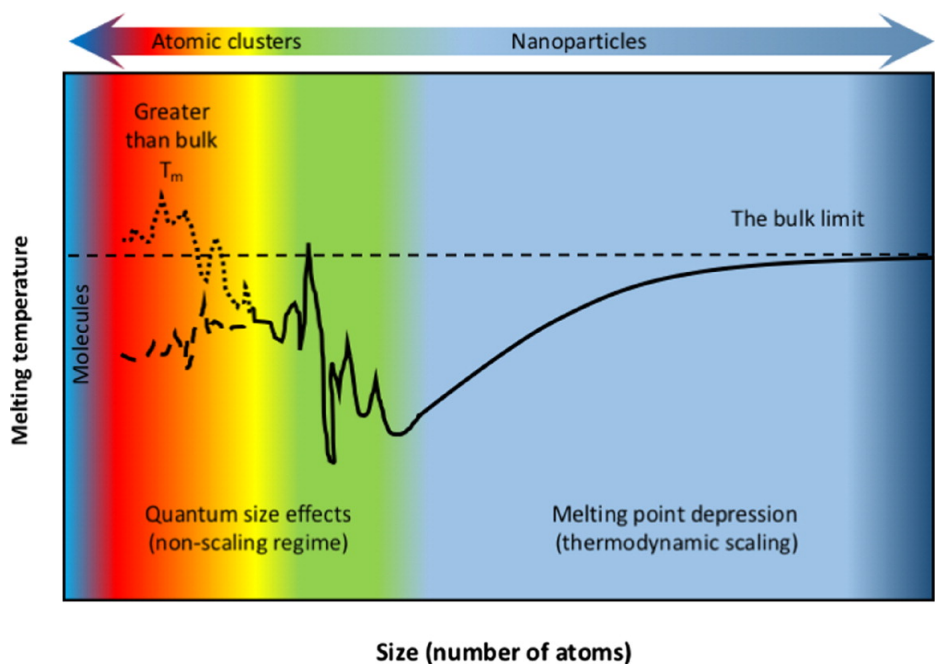


Figure 1.1: Schematic of size-dependent melting from scaling to non-scaling regimes as size decreases from nanoparticles to clusters. Transitional domains are shaded, with dashed lines indicating possible melting above bulk temperatures. Reproduced from Gaston *et al.* [1], distributed under the terms of the Creative Commons license.

Figure 1.1 highlights how the melting points of clusters deviate from the bulk limit. In the non-scaling regime ($n \lesssim 100$), cluster melting points can fluctuate strongly and even exceed the bulk value, before gradually converging toward thermodynamic scaling at larger n . These deviations arise largely from structural differences between clusters and bulk solids. Most atoms in a bulk metal are interior atoms with a CN close to 12, while surface atoms with CN = 8–9 form only a small minority. In clusters, by contrast, the majority of atoms are on the surface with much lower CN values, leading to reduced cohesive energy (the energy required to separate the n atoms of a cluster infinitely far from each other) and, in general, lower melting points than the bulk. For example, even the most compact 13-atom structure—the icosahedron—contains just a single interior atom with CN = 12, while the remaining 12 atoms are all surface atoms with CN = 6. In general, the fraction of surface atoms decreases with increasing n , but remains much larger than in bulk solids. It is $13/55 = 0.24$ for the most compact 55-atom structure (the Mackay icosahedron), and roughly $2/3$ for a compact n -atom cluster. The mean CN in compact clusters increases from ~ 6.5 at $n = 13$ to ~ 8.2 at $n = 55$ and ~ 9.3 at $n = 100$. This decrease in surface fraction with size explains why both cohesive energy and melting points generally decrease with n , a trend confirmed by numerous experiments and simulations [1, 30, 31]. For example, sodium clusters with $n \lesssim 100$ have melting points approximately 33% lower than bulk sodium (371 K) [31, 32, 33]. Similar behaviour has been observed for many other elements, although a few (such as tin [34], gallium [35], and possibly aluminum [15, 36]) deviate from this trend. The low CN of cluster atoms can also result in fluxional (non-rigid) behaviour, with rapid interconversion between isomers even at low temperatures.

High surface-to-volume ratio and low CN of surface atoms are also invoked to explain the relatively high chemical reactivity and catalytic activity of clusters. For example, Iron clusters have shown exceptional catalytic activity and improved durability in fuel cell applications [37]. But high surface area and low atomic CN are not the only reasons for the special properties of small clusters. Metal clusters activate small molecules like H_2 and N_2 , and the size dependence of this activation is related to variations in HOMO-LUMO gap and other *electronic* properties. Niobium clusters, in

particular, exhibit size-dependent reaction rates and mechanistic pathways [38].

Sharma *et al.* [39] emphasized that clusters with fewer than 100 atoms have discrete electronic energy levels, making them qualitatively different from bulk solids. The size evolution of frontier orbitals manifests itself in non-monotonic trends in reactivity, stability, and optical properties. The ionization potential (IP) of small clusters is usually higher than the work function ϕ of the metal and approaches ϕ with cluster size. This is seen, for instance, in aluminum clusters (Al_n , $n = 32\text{--}95$) [40]. Simple theories predict this trend [41], but not the details of the changes of IP with the number n of atoms.

1.4 Phase Transitions in Small Clusters

A solid melts at a characteristic temperature T_m that depends only on its chemical composition and the external pressure. For instance, at 1 atm, aluminum melts at 933.47 K. In the **thermodynamic limit** (i.e., for an infinite number of atoms), melting is a **first-order phase transition**: the heat capacity exhibits a discontinuous jump, reflecting the latent heat absorbed at constant temperature. At T_m , macroscopic properties change abruptly—crystals lose their sharp edges, phonon modes soften toward zero frequency, and atoms begin to diffuse as long-range order breaks down. For finite systems, such as atomic clusters, this sharp discontinuity is rounded: the transition extends over a finite temperature range rather than occurring at a single point. Hence, the concept of a true phase transition does not strictly apply to a cluster with, say, a hundred atoms. However, when clusters are heated, they undergo a transformation analogous to melting – a *melting-like transition*. Early studies of such transitions revealed important differences between the melting of bulk solids and clusters [42, 1]. First, in cluster melting, the heat capacity increases but remains finite, and the transition occurs over a *temperature range* from T_f to T_m , where solid-like and liquid-like configurations coexist for $T_f < T < T_m$. Second, the atomic diffusion coefficient increases more gradually than in bulk melting. Third, a cluster’s overall shape does not always change upon melting, and when it does, it does not necessarily become more spherical. Finally, the shape of

the heat capacity curve often indicates the presence of *multiple structural transitions* between the zero-kelvin solid and the fully liquid state. For instance, in some larger clusters, the surface melts before the core; in others, the core melts first.

The melting point depression of small particles was first observed by Pawlow [43]. This has since been confirmed in many studies, with clusters having fewer than 100 atoms [44, 45]. Melting-point depression has also been observed in thin films of bismuth, lead, and tin, as shown by electron-diffraction studies [46]. The melting of small particles of lead and indium [47], and gold [48], also showed melting point depression. Labastie et. al [49] did Monte Carlo simulations of Lennard-Jones (LJ) clusters. They found a broad peak in the heat capacity curve of a LJ_{13} cluster but a narrow peak for LJ_{147} . Figure 1.2 shows representative configurations of Ar_{13} (LJ) and its temperature-dependent structural evolution.

Schmidt *et al.* [50] discovered a counterintuitive phenomenon in a calorimetric study of Na_{147} : a *negative* microcanonical heat capacity. In simple terms, adding energy to the cluster causes its measured temperature to decrease, the opposite of what is expected in bulk systems. Such behaviour cannot occur in macroscopic solids or liquids, but it can appear in finite systems during a phase transition. One interpretation is that the system cannot separate into distinct solid and liquid regions in a partially melted cluster, as in the bulk. Instead, under the right conditions, it avoids coexistence by switching entirely to the liquid state, converting kinetic energy into potential energy and thereby lowering the temperature.

Generally, cluster melting temperatures decrease with the number of atoms n up to some n_c below which changes are non-monotonic and T_m may increase with diminishing n [51, 52, 53]. Some clusters undergo many melting-like transitions [54], others exhibit surface melting. Sebetci *et al.* [55] found melting of Pt_{15-19} clusters occurs in stages. Breaux *et al.* found that some Ga_n^+ ($n < 50$) clusters have melting temperatures hundreds of degrees above the bulk melting point (303 K). Ga_{17}^+ and Ga_{13}^+ were found to melt at 650 K and 1400 K, respectively [53]. Calculations confirm these findings. Chacko *et al.* performed density functional molecular dynamics simulations on Ga_{17} and Ga_{13} clusters. They found that their high melting temperatures are associated with

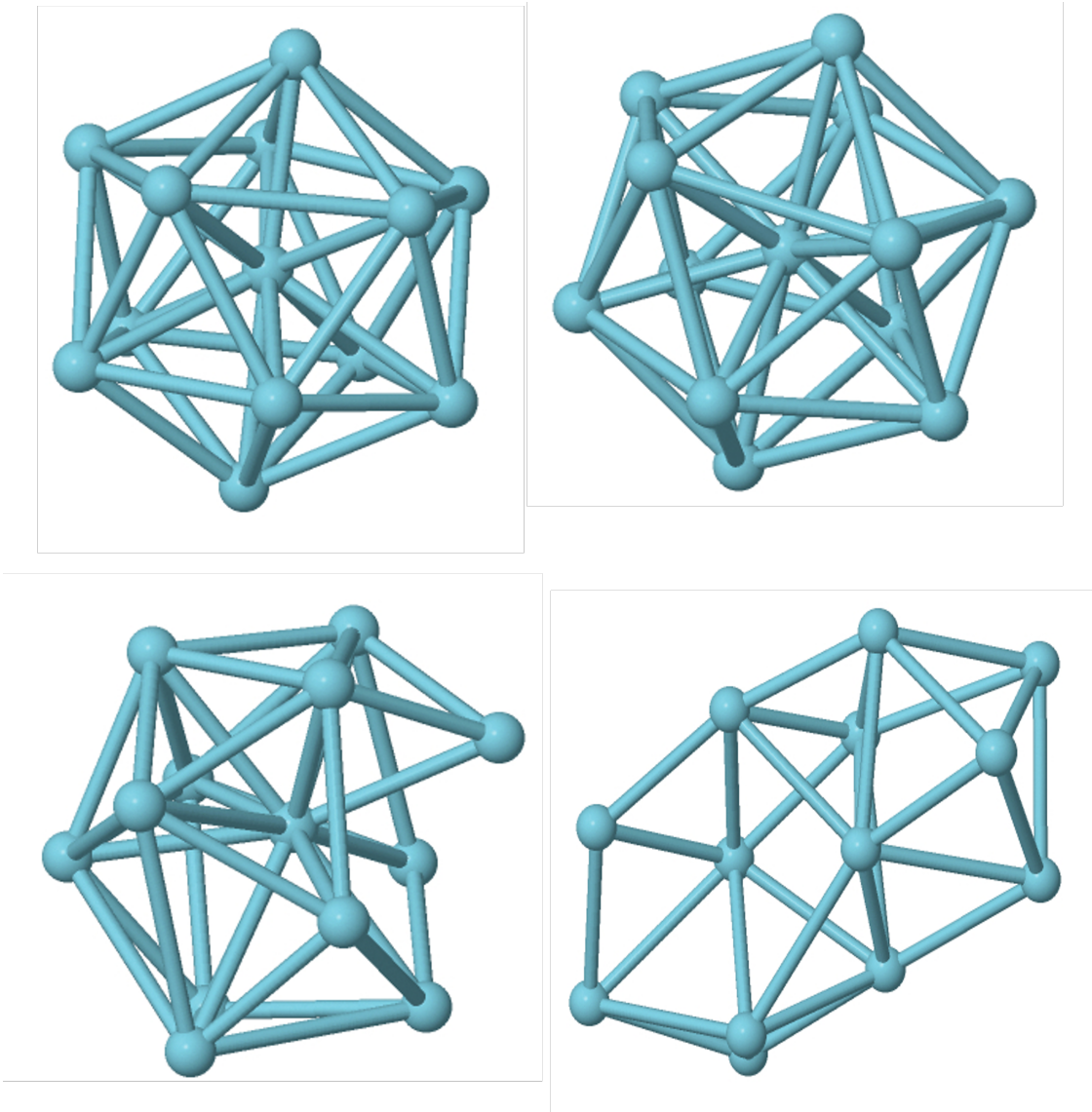


Figure 1.2: Representative configurations of the Ar_{13} LJ cluster at various temperatures: $4K$ (top left), $22K$ (top right), $40K$ (bottom left), and $50K$ (bottom right). The images illustrate the transition from a solid-like structure to a liquid-like state as temperature increases.

covalent bonding in these clusters, which is unlike the metallic bonding in bulk gallium [35]. The stronger directional bonds in these small clusters give them greater thermal stability. Pyfer *et al.* [56] showed that the melting temperatures of bigger gallium clusters go down with size and approach the bulk limit of around 95 atoms.

Experimental studies of cluster melting are challenging [57], and there have been only a limited number of such studies. Measuring the caloric curve is difficult, but it gives the most

direct way to characterize the melting transition. Schmidt and Haberland studied sodium clusters with this approach and observed melting and solid–liquid coexistence [58]. Neal *et al.* did a calorimetric study and found melting transitions in Al_n^+ [57]. Ion mobility measurements detect melting indirectly and can be used mainly for clusters, like Si_n and Sn_n , with highly non-spherical ground state structures. A sudden increase, at temperature T_m , in the mobility of a cluster drifting through a buffer gas indicates that its shape changed from non-spherical (prolate or oblate) to quasi-spherical [53]. This is taken as indicative of the liquid state. Jarrold and collaborators found that aluminum clusters show an increase in chemical reactivity upon melting. The melting of Al_{100}^+ clusters at 620–660 K triggers a remarkable catalytic effect: the clusters become highly active for the **dissociative adsorption** of N_2 , leading to the formation of Al–N species on the cluster surface and a 10^8 -fold increase in reaction rate [59]. A molecular dynamics study by Mottet *et al.* [60] found that substituting the central atom of icosahedral Ag_{55} with Ni or Cu increases the melting temperature by up to 70 K . Atomic and electronic shell closings have been shown to impart extra stability and relatively higher melting points in clusters like Ar_{13} and Ar_{55} (closed atomic shells), Na_{40} (closed electronic shell), and Al_{13}^- (closed atomic *and* electronic shells, see Chapter 4).

1.5 Outline, Motivation and Scope of the thesis

Understanding melting-like transitions in atomic clusters is still an open problem. These transitions differ from bulk melting because size, atomic structure, and composition affect their behaviour. Predicting these effects is essential for developing nanomaterials with reliable thermal properties. It is not clear whether classical thermodynamics, developed for macroscopic systems, can describe phase-like behaviour in small clusters. For clusters with up to 100 atoms, defining and predicting melting (T_m) and freezing (T_f) temperatures remains challenging. Earlier simulations employed approximate energy models and inefficient sampling methods. Recent machine-learned interatomic potentials (MLIPs) have improved energy accuracy; however, sampling methods for clusters still require improvement. Direct heat capacity calculations using DFT are too expensive because they

require many costly energy evaluations.

This thesis addresses this concern with a hybrid computational strategy that combines first-principles calculations (Density Functional Theory (DFT)), MLIPs, and Monte Carlo sampling. This approach improves efficiency while maintaining accuracy in estimating melting temperatures and characterizing structural transitions in small clusters.

The thesis goals are:

1. Develop geometric indicators to identify melting transitions, as an alternative to traditional heat capacity analysis.
2. Train a MLIP and combine it with Monte Carlo sampling to estimate melting temperatures with DFT-like accuracy and affordable computational cost.
3. Build an active-learning search framework for global optimization of clusters, and then use first-principles calculations to analyze their electronic properties.

Key contributions:

1. Structural descriptors, including interatomic distance patterns and potential energy distribution functions, were developed as an alternative to heat capacity analysis for identifying melting transitions in clusters. These descriptors, when combined with a neural network classifier, enabled the efficient identification of solid-like and liquid-like states, thereby reducing simulation time. Details are in **chapter 3** and a manuscript currently under review:

A. Krishnadas, M. Moshi, R. A. Miranda Quintana, and R. Fournier, “*Geometric Features and a Neural Network Classifier for Detecting Melting-Like Transitions in Clusters.*” [61], in review.

2. Developed a DFT–NN framework combining neural network potentials with parallel tempering Monte Carlo, enabling > 40 million energy evaluations at DFT accuracy within days. Applied to Na_{20} and Al clusters: Al^{+}_{9-16} , $\text{Al}^{0/-}_{12-14}$, for melting analysis, with results benchmarked against experiment and theory. The same pipeline was used for global structure

search; global minima were identified using the framework and subsequently refined with Gaussian 16 [2] to obtain isomer energetics, atomization energies, and ionization potentials. See **Chapters 4, 5**; associated manuscripts are listed below.

A. Krishnadas, N. Charron, and R. Fournier, “*Melting Transitions in Small Aluminum Clusters Simulated with Energies Approaching DFT Accuracy*.” [62], in review.

A. Krishnadas, N. Charron, and R. Fournier, “*A Machine-Learned DFT-Based Global Optimization Framework for Atomic Clusters: Application to Neutral and Charged Aluminum Clusters*” [63], in preparation.

3. A selection of AB_2C_{10} heteroatomic superatom candidates containing transition elements was investigated using the DFT-NN framework. Their melting curves, HOMO–LUMO energies, and electronic properties were analyzed. This ongoing work is described in **chapter 6**.

A. Krishnadas and R. Fournier, “*Selection of AB_2C_{10} Superatom Candidates and Investigation of Their Melting Transitions*” [64], work in progress.

Thesis Structure:

- **Chapter 1** introduces the fundamental concepts of cluster science, highlighting the unique thermodynamic and structural behaviour of finite systems.
- **Chapter 2** outlines the computational methodologies employed in this work, including DFT, MLIPs, and parallel-tempering Monte Carlo (PTMC) sampling techniques.
- **Chapters 3, 4, and 5** present original research contributions in manuscript-style format. Each chapter is self-contained, with its abstract, introduction, and results. This structure is designed to enhance readability and allow each contribution to stand independently while maintaining a cohesive narrative throughout the thesis.

- **Chapter 6** is a work in progress and provides early insights and motivation for ongoing research that builds upon the foundations established in the earlier chapters.
- **Chapter 7** concludes the thesis with a synthesis of findings and directions for future research.

Chapter 2

Theory

2.1 Electronic Structure Theory

The simulations of cluster melting that we report are done in the Born-Oppenheimer approximation, see **section 2.1.2**. The key quantity in these simulations is the energy of n interacting atoms. It is obtained by finding approximate solutions to the Schrödinger equation for N electrons moving in the potential of the n nuclei. There are many approximate theories and methods for doing this. They are briefly reviewed in the following sections. Density Functional Theory (DFT) is our method of choice because it gives a good compromise between accuracy and speed of computation. The energy for one configuration of a 20-atom cluster can be calculated in 10 minutes. But simulations typically require 40 million energy calculations that would be far too costly if done directly with DFT. The approach we take is to calculate the DFT energy for thousands of configurations of a cluster, and fit those energies to a tight-binding model or a machine-learned potential. The concepts and methods behind these fits are explained in **sections 2.3 and 2.4**. The simulations are done in configuration space (atomic velocities are ignored) with the Parallel Tempering Monte Carlo (PTMC) method described in **section 2.5**.

2.1.1 The Schrödinger Equation

The non-relativistic time-independent Schrödinger equation is used as the starting point for describing n -atom molecules and clusters. Relativistic effects are neglected for the lighter elements and are treated approximately for heavier elements with effective core potentials and scalar relativistic corrections. With these caveats, the non-relativistic time-independent Schrödinger equation provides a complete formulation of quantum mechanics for many-atom systems.

$$\hat{H}\Psi(\vec{r}_1, \dots, \vec{r}_N; \vec{R}_1, \dots, \vec{R}_M) = E\Psi(\vec{r}_1, \dots, \vec{r}_N; \vec{R}_1, \dots, \vec{R}_M), \quad (2.1)$$

The symbol $\hat{H}$ denotes the Hamiltonian operator, E is the energy, and Ψ is the many-body wavefunction that depends on the positions of all electrons $\vec{r}_i$ ($i = 1, \dots, N$) and nuclei $\vec{R}_I$

($I = 1, \dots, M$). The Hamiltonian $\hat{H}$, in atomic units (*i.e.*, $\hbar = 1$ and $m_e = 1$), is

$$\hat{H} = \underbrace{-\sum_{i=1}^N \frac{\nabla_i^2}{2}}_{\text{Electron kinetic energy}} - \underbrace{\sum_{I=1}^M \frac{\nabla_I^2}{2M_I}}_{\text{Nuclear kinetic energy}} - \underbrace{\sum_{i=1}^N \sum_{I=1}^M \frac{Z_I}{|\vec{r}_i - \vec{R}_I|}}_{\text{Electron-nucleus attraction}} + \underbrace{\sum_{i=1}^N \sum_{j>i}^N \frac{1}{|\vec{r}_i - \vec{r}_j|}}_{\text{Electron-electron repulsion}} + \underbrace{\sum_{I=1}^M \sum_{J>I}^M \frac{Z_I Z_J}{|\vec{R}_I - \vec{R}_J|}}_{\text{Nucleus-nucleus repulsion}} \quad (2.2)$$

The terms in Eqn. (2.2) include kinetic and potential energy contributions from all particles:

- The first term represents the kinetic energy of the N electrons, ∇_i^2 is the Laplacian with respect to the position of the i^{th} electron.
- The second term accounts for the kinetic energy of the M nuclei.
- The third term describes the Coulomb attraction between electrons and nuclei, where Z_I is the atomic number of nucleus I .
- The fourth term is the Coulomb repulsion between pairs of electrons.
- The fifth term is the repulsive interaction between pairs of nuclei.

The Laplacian operator ∇_p^2 , used in the kinetic energy terms, is defined as the sum of second-order partial derivatives with respect to the Cartesian coordinates of particle p :

$$\nabla_p^2 = \frac{\partial^2}{\partial x_p^2} + \frac{\partial^2}{\partial y_p^2} + \frac{\partial^2}{\partial z_p^2}. \quad (2.3)$$

Exact solutions to Eqn. (2.1) can be obtained only for one-electron atoms and atomic ions (H , ^2H , He^+ , Li^{2+} , $\dots$). For all other systems, approximate solutions can be obtained with variational methods (section 2.1.3) or by perturbation theory. The computational cost for solving Eqn. (2.1) with a useful degree of accuracy (*e.g.*, a few percent errors on bond lengths and bond energies) increases rapidly with the number of particles. The antisymmetry requirement on the electronic part of the wavefunction is a source of great difficulty. Approximate methods are essential to make quantum mechanical modelling possible. These methods are a crucial component of electronic structure theory. They are described briefly in the next sections.

2.1.2 The Born-Oppenheimer Approximation

The Born–Oppenheimer (BO) approximation is one of the most widely used approximations in molecular quantum mechanics. It exploits the significant mass disparity between nuclei and electrons: even the lightest nucleus is approximately 1836 times heavier than an electron. As a result, nuclei move much more slowly than electrons, allowing the assumption that electrons adjust instantaneously to changes in nuclear positions. This permits a separation of nuclear and electronic motion.

In the first part of the BO approximation, nuclei are treated as fixed point charges dropping their kinetic energy (the second term in Eqn.(2.2)). The nuclear–nuclear repulsion (the fifth term) is considered constant for a given set of nuclear positions. The resulting *electronic Hamiltonian* is

$$\hat{H}_e = - \sum_{i=1}^N \frac{\nabla_i^2}{2} - \sum_{i=1}^N \sum_{I=1}^M \frac{Z_I}{|\vec{r}_i - \vec{R}_I|} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{|\vec{r}_i - \vec{r}_j|}. \quad (2.4)$$

The full time-independent Schrödinger equation (Eqn.(2.1)) is thereby reduced to the electronic Schrödinger equation:

$$\hat{H}_e \Psi_e(\vec{r}_1, \dots, \vec{r}_N; \vec{R}_1, \dots, \vec{R}_M) = E_{el.,j}(\vec{R}_1, \dots, \vec{R}_M) \Psi_e(\vec{r}_1, \dots, \vec{r}_N; \vec{R}_1, \dots, \vec{R}_M), \quad (2.5)$$

yielding the electronic energies $E_{el.,j}(\vec{R})$ as functions of the nuclear coordinates. The second part of the BO approximation then defines an interaction potential between atoms, corresponding to a given electronic state j :

$$U_j(\vec{R}) = E_{el.,j}(\vec{R}) + E_n(\vec{R}), \quad (2.6)$$

where E_n is the classical nucleus–nucleus repulsion energy. In an n -atom system, each electronic state gives rise to a distinct Potential Energy Surface (PES). In our simulations, we are interested only in the PES of the ground electronic state, treating the nuclei classically and ignoring their

kinetic energy in a configuration-space Monte Carlo approach.

2.1.3 Variational Principle

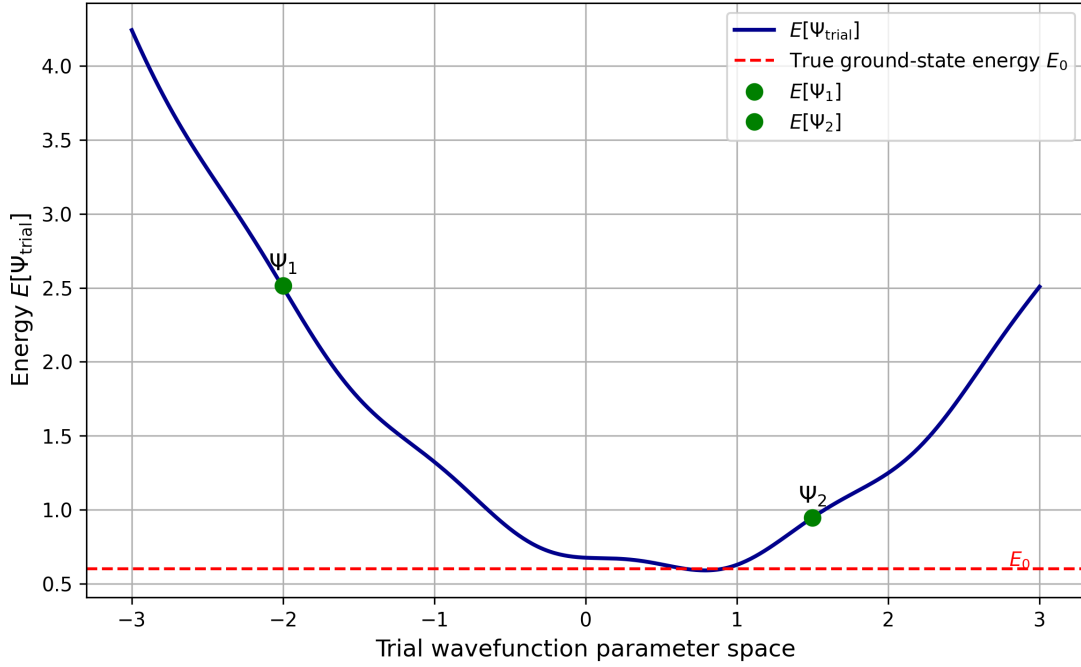


Figure 2.1: Schematic illustration of the variational principle showing how the expectation value of the energy depends on different trial wavefunctions.

With the BO approximation, we obtain Eqn. (2.4), whose exact solutions exist only for the simplest systems. The Variational Principle provides a way to approximate ground-state energies. In quantum mechanics, all physically acceptable wavefunctions Ψ are normalized, satisfying

$$\langle \Psi | \Psi \rangle = \int \Psi^*(\mathbf{r}_1, \dots, \mathbf{r}_N) \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) d\tau = 1. \quad (2.7)$$

This normalization ensures the expectation value of the Hamiltonian has a physical meaning; equivalently, it implies that the sum of the probabilities of observing the system across all possible states is unity. According to the variational principle, for any normalized trial wavefunction, the

expectation value of the Hamiltonian is an upper bound on the exact ground-state energy E_0 :

$$E[\Psi_{\text{trial}}] = \langle \Psi_{\text{trial}} | \hat{H} | \Psi_{\text{trial}} \rangle \geq E_0. \quad (2.8)$$

By building a class of trial wavefunctions with variational parameters, one can optimize these parameters ($\alpha_1, \alpha_2, \dots$) which often relate to orbital shapes or basis functions — to minimize the energy (Fig. 2.1):

$$\frac{\partial E[\Psi_{\text{trial}}(\alpha_1, \alpha_2, \dots)]}{\partial \alpha_i} = 0.$$

One of the most common applications of this principle is the **Hartree-Fock method**, which uses a single Slater determinant made of orthonormal molecular orbitals. Minimizing the energy with respect to these orbitals under orthonormality conditions leads to the self-consistent field equations.

2.1.4 The Hartree-Fock Approximation (HF).

As discussed with the variational principle, the exact electronic wavefunction Ψ of a many-electron system is generally unknown, so it is approximated by a trial function Ψ_{trial} . One of the most widely used approximations is the **Hartree-Fock (HF) method** [65], developed by Douglas Hartree and Vladimir Fock, which represents the wavefunction as a single Slater determinant built from one-electron spin orbitals.

In HF theory, the electronic energy is minimized with respect to the spin orbitals, keeping them orthonormal. The resulting equations are solved self-consistently, refining both the one-electron Hamiltonian and the orbitals. The HF wavefunction is

$$\Psi_{\text{HF}}(\vec{r}_1, \dots, \vec{r}_N) = \Phi_{\text{SD}} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\vec{x}_1) & \dots & \chi_N(\vec{x}_1) \\ \vdots & \ddots & \vdots \\ \chi_1(\vec{x}_N) & \dots & \chi_N(\vec{x}_N) \end{vmatrix}, \quad (2.9)$$

with spin orbitals

$$\chi_i(\vec{x}) = \phi_i(\vec{r}) \omega(s), \quad (2.10)$$

where $\omega(s)$ is a spin function. This guarantees antisymmetry and satisfies Pauli's principle. The HF energy is the expectation value of the Hamiltonian:

$$E_{\text{HF}} = \langle \Phi_{\text{SD}} | \hat{H} | \Phi_{\text{SD}} \rangle, \quad (2.11)$$

which separates into one-electron and two-electron parts:

$$E_{\text{HF}} = \sum_i \langle \chi_i | \hat{h} | \chi_i \rangle + \frac{1}{2} \sum_{i,j} (J_{ij} - K_{ij}), \quad (2.12)$$

where

$$\langle \chi_i | \hat{h} | \chi_i \rangle = \int \chi_i^*(\vec{x}_1) \left[-\frac{1}{2} \nabla^2 - \sum_I \frac{Z_I}{|\vec{r}_1 - \vec{R}_I|} \right] \chi_i(\vec{x}_1) d\vec{x}_1, \quad (2.13)$$

and the Coulomb and exchange integrals are

$$J_{ij} = \iint \chi_i^*(\vec{x}_1) \chi_j^*(\vec{x}_2) \frac{1}{r_{12}} \chi_i(\vec{x}_1) \chi_j(\vec{x}_2) d\vec{x}_1 d\vec{x}_2, \quad (2.14)$$

$$K_{ij} = \iint \chi_i^*(\vec{x}_1) \chi_j^*(\vec{x}_2) \frac{1}{r_{12}} \chi_j(\vec{x}_1) \chi_i(\vec{x}_2) d\vec{x}_1 d\vec{x}_2. \quad (2.15)$$

Orthonormality of the spin orbitals is enforced using Lagrange multipliers λ_{ij} . Upon diagonalization of the Lagrange-multiplier matrix, these reduce to orbital energies ε_i , leading to the definition of the **Fock operator**, $\hat{F}$:

$$\hat{F} = \hat{h} + \sum_j \left(\hat{J}_j - \hat{K}_j \right), \quad (2.16)$$

where the second term is the Hartree-Fock potential. The HF equations are

$$\hat{F} \chi_i = \varepsilon_i \chi_i, \quad (2.17)$$

which are solved iteratively in the **self-consistent field (SCF)** method. While it captures the average repulsion between electrons, it cannot describe dynamic or static correlation. Still, the HF solution

is an eigenfunction of an effective one-electron Hamiltonian:

$$\sum_i \hat{F}_i \Phi_{\text{SD}} = \sum_i \varepsilon_i \Phi_{\text{SD}}. \quad (2.18)$$

HF provides a baseline treatment of many-electron systems, with **Restricted Hartree-Fock** for closed-shell and **Unrestricted Hartree-Fock** for open-shell cases [66]. These still miss correlation effects. To improve, **post-Hartree-Fock methods** such as second-order Møller–Plesset perturbation theory [67], configuration interaction [68], or coupled-cluster [69] theory include electron correlation, albeit at higher computational cost. Another approach is **Density Functional Theory (DFT)**, which reformulates the problem using the electron density, a function of only three variables, giving an efficient way to treat correlation. The following section provides a detailed discussion of DFT.

2.1.5 Density Functional Theory (DFT)

DFT [70] reformulates the many-electron problem of Eqn. (2.5) in terms of the electron density $\rho(\vec{r})$. In principle, this simplifies things a lot as the electron density is a function of only 3 variables (and spin), whereas an electronic wavefunction $\Psi(\vec{r}_1, \dots, \vec{r}_N)$ depends on $3N$ variables (and N spin variables). The electron density is defined as

$$\rho(\vec{r}) = N \int |\Psi(\vec{r}, \vec{r}_2, \dots, \vec{r}_N)|^2 d\vec{r}_2 \dots d\vec{r}_N, \quad (2.19)$$

The electron density, $\rho(x, y, z)dx dy dz$, is the the probability of finding an electron in a volume element $dx dy dz$ centered at point (x, y, z) . It is an observable, non-negative function that vanishes at infinity and integrates to N . Figure 2.2 shows an electron density isosurface for the ammonia molecule (NH_3). The *pair density* $\rho(\vec{r}_1, \vec{r}_2)$ also plays an important role in conceptual DFT. It is associated with the probability of simultaneously finding one electron in the vicinity of $\vec{r}_1$ and

another electron near $\vec{r}_2$. It is given by:

$$\rho(\vec{r}_1, \vec{r}_2) = \frac{1}{2}N(N-1) \int |\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_N)|^2 d\vec{r}_3 \dots d\vec{r}_N, \quad (2.20)$$

Integrating the pair density over the coordinates of electron 2 gives $(N-1)/2$ times the electron density, and integrating again over the coordinates of electron 1 gives the number of electron pairs, $N(N-1)/2$.

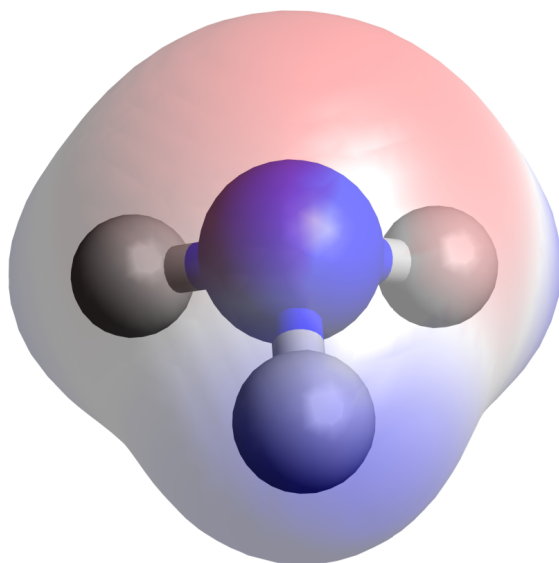


Figure 2.2: Electron density surface for NH_3 calculated using Gaussian 16. [2]

A key result of DFT, shown in section 2.1.7, is that the ground-state energy is uniquely determined by $\rho(\vec{r})$. In principle, we only need to know $\rho(\vec{r})$ to calculate $E_{el.}$. This has profound implications. One could ignore $3N$ -dimensional wavefunctions and work instead with the much simpler 3-dimensional electron density. However, the functional relation between the density and energy, $E_{el.}[\rho(\vec{r})]$, is not known, and developing a model or approximation for it is quite difficult. It requires an accurate modeling of quantum mechanical effects, including:

- the **exchange interaction**, arising from the antisymmetry of the electronic wavefunction;
- the **correlation energy**, an energy lowering that comes when we go from a mean-field description of electron interactions to a model with instantaneous electron–electron repulsion;

- the **kinetic energy** of electrons, which is easily calculated given a wavefunction, but has an unknown dependence on electron density.

These effects are collectively described by an *exchange–correlation functional*, $E_{xc}[\rho(\vec{r})]$. Before this concept was formalized, in the early days of DFT, many models were proposed, most notably the Thomas–Fermi and Slater approximations, to calculate energy directly from the density.

2.1.6 The early models of Thomas–Fermi, Dirac, and Slater.

The first attempt to describe a quantum many-electron system using only the electron density was made independently by Thomas and Fermi in 1927 [71, 72]. The Thomas–Fermi model approximates the kinetic energy of the electrons with a local functional of the density:

$$T_{\text{TF}}[\rho] = \frac{3}{10}(3\pi^2)^{2/3} \int \rho(\vec{r})^{5/3} d\vec{r}. \quad (2.21)$$

The nuclear-electron attraction and electron-electron repulsion energy terms are modelled as classical electrostatic interactions between a gas of electrons of density $\rho(\vec{r})$ and point charges for the nuclei. The result is the Thomas-Fermi total energy functional. For a single nucleus of charge Z , it is

$$E_{\text{TF}}[\rho] = T_{\text{TF}}[\rho] - Z \int \frac{\rho(\vec{r})}{r} d\vec{r} + \frac{1}{2} \iint \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r} d\vec{r}_2. \quad (2.22)$$

To account for exchange interactions, Dirac [73] later introduced a term based on the uniform electron gas.

$$E_{\text{x}}^{\text{Dirac}}[\rho] = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int \rho(\vec{r})^{4/3} d\vec{r}. \quad (2.23)$$

The resulting Thomas-Fermi-Dirac energy functional becomes:

$$E_{\text{TFD}}[\rho] = E_{\text{TF}}[\rho] + E_{\text{x}}^{\text{Dirac}}[\rho] \quad (2.24)$$

Building upon HF theory and Dirac’s exchange expression, Slater [74] replaced the nonlocal Hartree–Fock exchange operator by a local approximation obtained by averaging exchange interactions over the occupied orbitals in a uniform electron gas. This yielded a convenient exchange potential expressed directly in terms of the electron density:

$$v_x^{\text{Slater}}(\vec{r}) = -\frac{3}{2} \left(\frac{3}{\pi} \rho(\vec{r}) \right)^{1/3}. \quad (2.25)$$

This expression differs from Dirac’s original form by a numerical prefactor of $3/2$. It became the basis for the widely used $\mathbf{X}\alpha$ method, also known as *Hartree–Fock–Slater (HFS)*, where the exchange potential is multiplied by an empirical parameter α .

$$v_x^{\mathbf{X}\alpha}(\vec{r}) = -\alpha \frac{3}{2} \left(\frac{3}{\pi} \rho(\vec{r}) \right)^{1/3}, \quad \text{typically } \alpha \approx 0.7. \quad (2.26)$$

Slater used this potential in Hartree-like equations for orbitals and for calculating the total energy $E_{el.}$. The HFS method was initially developed as a convenient approximation to HF theory. However, calculations showed that, in many ways, HFS gives better results than HF, especially in regard to ionization energies and energy levels of metallic solids and metal complexes. This was a puzzle that had eluded many for years.

Although approximate and lacking explicit treatment of correlation effects, the early density-based models of Thomas–Fermi and Dirac, and the density-based exchange of Slater, laid the groundwork for modern DFT. However, the Thomas-Fermi-Dirac model has severe deficiencies: it fails to reproduce the shell structure in atoms, and cannot describe chemical bonding in molecules. The HFS method could not describe electron correlation in inhomogeneous systems and was unreliable for bond energies. The work of Hohenberg and Kohn (1964) put DFT on a strong formal basis and marked the start of modern DFT.

2.1.7 Hohenberg-Kohn theorem

The Hohenberg-Kohn (HK) theorems [75] (1964) showed that the ground-state properties of a many-electron system are uniquely determined by its electron density $\rho(\vec{r})$, shifting the focus from the $3N$ -dimensional wavefunction Ψ to the three-dimensional density.

The first HK theorem states that the external potential $V_{\text{ext}}(\vec{r})$ acting on the system is uniquely determined, up to a constant, by the ground-state density $\rho_0(\vec{r})$. As a result, all ground-state observables, including energy and wavefunction, are functionals of $\rho_0(\vec{r})$. The proof proceeds by contradiction. Suppose two different external potentials, $V_a(\vec{r})$ and $V_b(\vec{r})$, produce the same non-degenerate ground-state density $\rho(\vec{r})$, with Hamiltonians H_a , H_b , and ground states Ψ_a , Ψ_b . The variational principle gives

$$E_{0,a} < \langle \Psi_b | H_a | \Psi_b \rangle, \quad (2.27)$$

which expands to

$$E_{0,a} < E_{0,b} + \int [V_a(\vec{r}) - V_b(\vec{r})] \rho(\vec{r}) d\vec{r}. \quad (2.28)$$

By symmetry,

$$E_{0,b} < E_{0,a} + \int [V_b(\vec{r}) - V_a(\vec{r})] \rho(\vec{r}) d\vec{r}. \quad (2.29)$$

Adding Equation (2.28, 2.29) leads to a contradiction.

$$E_{0,a} + E_{0,b} < E_{0,a} + E_{0,b}, \quad (2.30)$$

Therefore, no two different external potentials can give the same ground-state density, and the density uniquely determines the potential (up to a constant).

The second HK theorem establishes a variational principle: for any trial density $\rho(\vec{r})$ integrating to N , the energy functional

$$E[\rho] = F_{\text{HK}}[\rho] + \int V_{\text{ext}}(\vec{r}) \rho(\vec{r}) d\vec{r} \quad (2.31)$$

is minimized by the true ground-state density $\rho_0(\vec{r})$, giving the exact ground-state energy E_0 .

The universal HK functional (F_{HK}) is

$$F_{\text{HK}}[\rho] = T[\rho] + U[\rho], \quad (2.32)$$

where

- $T[\rho]$ is the exact kinetic energy,
- $U[\rho]$ is the total electron–electron interaction energy.

The interaction energy can be written as

$$U[\rho] = J[\rho] + E_{\text{xc}}[\rho], \quad (2.33)$$

with

- $J[\rho] = \frac{1}{2} \iint \frac{\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}'$ the classical Coulomb energy,
- $E_{\text{xc}}[\rho]$ the exchange-correlation energy, which includes non-classical effects: Pauli exchange and dynamic correlation.

Hence

$$F_{\text{HK}}[\rho] = T[\rho] + J[\rho] + E_{\text{xc}}[\rho]. \quad (2.34)$$

In principle, one could find the exact ground-state density and energy by minimizing $E[\rho]$ over all densities ρ integrating to N . This is the *constrained-search approach*, which searches over all N -representable densities from antisymmetric wavefunctions. However, this is unfeasible because explicit forms of $T[\rho]$ and $E_{\text{xc}}[\rho]$ are unknown for interacting systems. To address this, Kohn and Sham proposed a practical framework, which is discussed in the next section.

2.1.8 Kohn-Sham Equations

The Kohn-Sham (KS) formulation [76] introduces a fictitious system of non-interacting electrons that exactly reproduces the interacting ground-state density $\rho(\vec{r})$, avoiding the need to minimize the unknown Hohenberg-Kohn functional directly.

In this non-interacting reference system, electrons are governed by an effective one-electron potential $V_{\text{eff}}(\vec{r})$ chosen. Hence, the resulting density matches the true ground-state density. The non-interacting kinetic energy is

$$T_s[\rho] = -\frac{1}{2} \sum_{i=1}^N \langle \chi_i | \nabla^2 | \chi_i \rangle, \quad (2.35)$$

where $\{\chi_i\}$ are the KS orbitals, forming a Slater determinant consistent with non-interacting fermions. The remaining unknown energy contributions are collected in the exchange-correlation functional:

$$E_{\text{xc}}[\rho] = \Delta T[\rho] + \Delta E_{\text{ee}}[\rho], \quad (2.36)$$

where

- $\Delta T[\rho]$ is the difference between the true and non-interacting kinetic energies,
- $\Delta E_{\text{ee}}[\rho]$ contains all non-classical electron–electron interactions, including exchange and correlation.

The total KS energy functional is

$$E[\rho] = T_s[\rho] + E_{\text{ne}}[\rho] + J[\rho] + E_{\text{xc}}[\rho], \quad (2.37)$$

where

$$E_{\text{ne}}[\rho] = \int V_{\text{ext}}(\vec{r}) \rho(\vec{r}) d\vec{r},$$

is the nuclear attraction, and

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}'$$

is the classical Coulomb repulsion.

The electron density is reconstructed from the KS orbitals:

$$\rho(\vec{r}) = \sum_{i=1}^N |\chi_i(\vec{r})|^2, \quad (2.38)$$

allowing the energy functional to be expressed fully in terms of these orbitals.

The KS orbitals are determined by minimizing $E[\rho]$ with respect to $\{\chi_i\}$, subject to orthonormality, leading to the KS equation:

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{ext}}(\vec{r}) + V_{\text{H}}(\vec{r}) + V_{\text{xc}}(\vec{r}) \right] \chi_i(\vec{r}) = \varepsilon_i \chi_i(\vec{r}), \quad (2.39)$$

where

$$V_{\text{H}}(\vec{r}) = \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'$$

is the Hartree potential, and

$$V_{\text{xc}}(\vec{r}) = \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(\vec{r})}$$

is the exchange-correlation potential. Because V_{eff} depends on ρ , which depends on the orbitals, these equations must be solved self-consistently. One starts from an initial density, builds V_{eff} , solves for new orbitals, updates the density, and repeats until convergence.

Once converged, the total ground-state energy is evaluated as

$$E[\rho] = T_s[\rho] + \int V_{\text{ext}}(\vec{r})\rho(\vec{r}) d\vec{r} + J[\rho] + E_{\text{xc}}[\rho]. \quad (2.40)$$

While the KS scheme formally separates known and unknown energy components, the exact form of $E_{\text{xc}}[\rho]$ is unknown. In practice, approximations to $E_{\text{xc}}[\rho]$ are essential and strongly affect the accuracy of DFT. The following section provides a detailed discussion of these approximations.

2.1.9 Climbing Jacob’s Ladder: Exchange–Correlation Approximations

The need for accurate exchange–correlation approximations naturally arises in the Kohn–Sham framework. Since the exact form of the exchange–correlation functional $E_{xc}[\rho]$ is unknown, its quality directly determines DFT accuracy. To organize their development, Perdew and collaborators introduced *Jacob’s Ladder* [77], a metaphorical hierarchy of density functionals (see Fig. 2.3). Each rung improves accuracy while increasing computational cost, ranging from local to more nonlocal approximations. The ladder represents a climb from simple models toward ”chemical accuracy”.

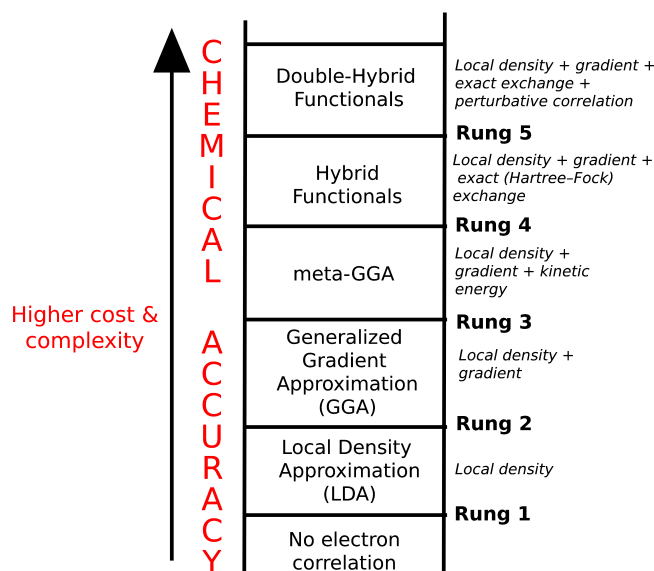


Figure 2.3: Jacob’s Ladder of exchange–correlation approximations in Kohn–Sham DFT. Each rung increases complexity and accuracy at a higher computational cost.

The first three rungs describe *semilocal* approximations, built on progressively more information about the density. The **Local Density Approximation (LDA)** [78] is the first rung, assuming the exchange–correlation energy at a point depends only on the local electron density as if it were a uniform electron gas:

$$E_{xc}^{\text{LDA}}[\rho] = \int \rho(\vec{r}) \varepsilon_{xc}^{\text{HEG}}(\rho(\vec{r})) d\vec{r}. \quad (2.41)$$

LDA performs well for metals and bulk solids but struggles for molecules or strongly inhomogeneous systems. Its extension to spin systems, the Local Spin Density Approximation, includes spin-polarized densities. The second rung, **Generalized Gradient Approximation (GGA)**, uses both

the local density and its gradient:

$$E_{\text{xc}}^{\text{GGA}}[\rho] = \int f(\rho(\vec{r}), \nabla\rho(\vec{r})) d\vec{r}, \quad (2.42)$$

Improving accuracy for molecular systems. Popular GGAs include PW91 [79], PBE [80], and BLYP [81, 82], which strike a balance between accuracy and modest computational effort. The third rung, **meta-GGA**, adds the kinetic energy density

$$\tau(\vec{r}) = \frac{1}{2} \sum_i |\nabla\chi_i(\vec{r})|^2 \quad (2.43)$$

or the Laplacian of the density, giving functionals of the form

$$E_{\text{xc}}^{\text{meta-GGA}}[\rho] = \int f(\rho, \nabla\rho, \tau) d\vec{r}. \quad (2.44)$$

These capture finer bonding effects, improving accuracy across covalent, metallic, and noncovalent systems. Among meta-GGAs, TPSS [83] is a widely used nonempirical choice, and SCAN [84] enforces many exact constraints. M06-L [85] is a semi-empirical option optimized for thermochemistry. The fourth rung, **hybrid functionals**, incorporate a fraction of exact Hartree-Fock exchange:

$$E_{\text{xc}}^{\text{hybrid}} = aE_x^{\text{HF}} + (1 - a)E_x^{\text{DFA}} + E_c^{\text{DFA}}, \quad (2.45)$$

with mixing parameter a . The best-known hybrid, B3LYP [86], combines exact exchange with GGA components and empirical fitting, yielding good performance for organic and main-group systems.

Finally, the fifth and highest rung of Jacob’s Ladder, the **double-hybrid** functionals, incorporate perturbative correlation—typically from second-order Møller–Plesset (MP2) theory—on top of hybrid exchange-correlation functionals. These methods blend both wavefunction-based and

density-based components to enhance accuracy:

$$E_{xc}^{DH} = a_x E_x^{HF} + (1 - a_x) E_x^{DFA} + a_c E_c^{MP2} + (1 - a_c) E_c^{DFA}, \quad (2.46)$$

where a_x and a_c are empirical or semi-empirical parameters controlling the fractions of HF exchange and MP2 correlation. The remaining components, E_x^{DFA} and E_c^{DFA} , are provided by a density functional approximation (DFA), typically a GGA or meta-GGA, such as BLYP or PBE.

Examples of widely used double-hybrid functionals include B2PLYP [87] and DSD-BLYP [88], both of which demonstrate improved thermochemical and kinetic accuracy across benchmark datasets, albeit at increased computational cost. These functionals exemplify the trend toward combining physical rigour with data-driven tuning.

Hybrid and double-hybrid functionals have significantly advanced the predictive power of density functional theory by achieving a better balance between empirical fitting and formal constraints. Nevertheless, the choice of functional often remains system-dependent, reflecting a trade-off between computational cost, accuracy, and transferability to the chemical or physical system of interest.

2.1.10 Basis Sets

Different exchange-correlation functionals, E_{xc} , imply different physical models of electronic structure, and their choice directly impacts accuracy. In principle, any complete basis set could be used, whether built from Gaussian or exponential functions centred on nuclei, plane waves, or other expansions. However, a complete basis set would require infinite computational resources, so in practice, one selects a basis set that balances accuracy and computational cost.

In quantum chemistry, basis sets typically consist of nonorthogonal functions centered on nuclei. Linear combinations of these basis functions produce the molecular orbitals (MOs) of Kohn-Sham theory. There are two principal types of basis functions. Slater-type orbitals (STOs) [89] resemble the solutions of hydrogen-like atoms, exhibiting exponential decay and the correct nuclear cusp

behavior. They can be expressed as

$$\phi_{nlm}^{\text{STO}}(r, \theta, \phi) = N r^{n-1} e^{-\zeta r} Y_{\ell}^m(\theta, \phi) \quad (2.47)$$

where n, ℓ, m are quantum numbers, N is a normalization constant, ζ controls the radial decay, and Y_{ℓ}^m is a spherical harmonic. Although STOs are physically well justified, exact analytical evaluation of multi-center integrals with STOs is extremely challenging. Consequently, STOs are often tabulated for approximate matrix elements, or more commonly replaced altogether by Gaussian-type orbitals (GTOs) [90].

GTOs employ Gaussian radial decay instead of exponential decay, which greatly facilitates analytic evaluation of integrals through the Gaussian product theorem. This makes them computationally far more efficient. However, GTOs lack a nuclear cusp and decay too rapidly at long range. To compensate, contracted Gaussian-type orbitals (CGTOs) are employed, where several primitive GTOs are linearly combined to approximate the behavior of STOs near the nucleus [91]. These CGTOs form the basis of many widely used sets, offering controllable accuracy at reasonable cost.

The quality of a basis set is primarily defined by the number and types of CGTOs assigned to each atomic orbital. A minimal basis set, such as STO-3G, uses a single CGTO per atomic orbital in the ground-state configuration. Double-zeta, triple-zeta, and higher-zeta basis sets employ two, three, or more CGTOs per orbital to improve flexibility systematically. Split-valence basis sets allocate more CGTOs to valence orbitals while keeping a minimal description for core orbitals. Further refinements include polarization functions of higher angular momentum (d, f, g, etc.) and diffuse functions with higher principal quantum numbers, which are especially important for describing anions or long-range interactions [92].

For heavy elements, it is advantageous to use effective core potentials (ECPs), which replace core electrons with a pseudopotential while retaining explicit valence treatment. This substantially reduces computational cost with minimal loss of accuracy. We employed the Stuttgart/Dresden (SDD) ECP and associated basis set, which incorporates scalar relativistic corrections and models

the core–valence interaction using Gaussian-type potentials. A typical term in the SDD basis set has the form

$$V_{\text{ECP}}(r) = \sum_l \sum_i C_{l,i} r^n e^{-\alpha_{l,i} r^2} P_l \quad (2.48)$$

where $C_{l,i}$ and $\alpha_{l,i}$ are fitted coefficients and exponents, and P_l denotes angular-momentum projection operators. This combination has been extensively validated for transition metal systems and provides an effective trade-off between efficiency and chemical accuracy [93].

In solid-state physics, where periodic systems extend infinitely, atom-centred basis sets are impractical. Instead, plane-wave basis sets are commonly employed, as implemented in codes such as VASP [94] and Quantum Espresso [95]. Plane waves naturally respect periodic boundary conditions and converge systematically as the kinetic energy cutoff increases.

For this work, we adopted the TPSS meta-GGA functional, for three reasons: (i) it is theoretically superior to GGA functionals, lying one rung higher on Jacob’s ladder (Fig. 2.3); (ii) it is free of empirical parameters; and (iii) it has been thoroughly benchmarked on both molecules and solids, offering robust and consistent performance even if not the absolute most accurate in every scenario.

2.1.11 Software Used for This Work

All quantum chemical calculations in this thesis were performed with **Gaussian 16** [2], a widely used electronic structure program supporting HF, DFT, post-HF, and coupled-cluster methods. It was used primarily for geometry optimizations, single-point energy calculations, and vibrational frequency analyses within DFT. A representative input file for a single-point TPSS/SDD calculation is shown below, with coordinates omitted for clarity:

```
# TPSSTPSS/SDD SP
Single-point calculation for the test molecule

0 1 <- charge and multiplicity
Sn x y z
Sn x y z
Sn x y z
Y x y z
Y x y z
```

Similar settings were applied elsewhere, with adjustments as needed.

2.2 The Potential Energy Surface

The behaviour of atomic and molecular systems, whether in equilibrium or during transitions like melting, is fundamentally governed by the **Potential Energy Surface** (PES). The PES is a $(3n - 6)$ -dimensional hypersurface (for n atoms), excluding translational and rotational degrees of freedom (or $3n - 5$ for linear molecules). This reduction arises because overall translations and rigid rotations do not change internal energy. Each point on the PES corresponds to a specific nuclear configuration, with a potential energy often calculated by solving the time-independent Schrödinger equation within the BO approximation. In this framework, the separation of electronic and nuclear motion allows to calculate a point of the PES, with fixed nuclear coordinates, as follows.

$$E(x) = E_{\text{elec}} + E_{\text{nn}}, \quad (2.49)$$

where E_{elec} is the electronic energy and E_{nn} is the nuclear–nuclear repulsion, both evaluated at nuclear configuration U [96]. In practice, every single-point calculation with Gaussian or another electronic structure method provides the value of $E(U)$ at one location of this hypersurface.

Figure 2.4 illustrates a simple PES for a three-atom LJ cluster. In general, the key features of a PES are its critical points, especially the minima and saddle points, and steepest descent

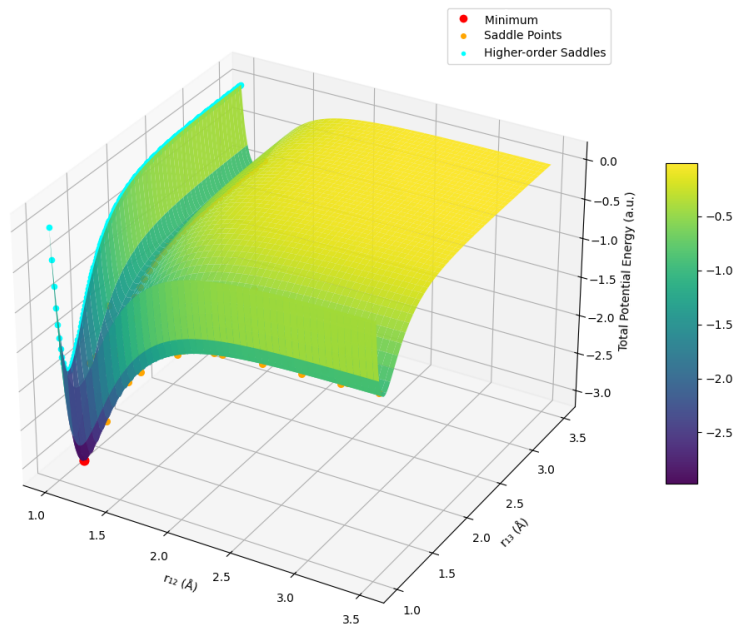


Figure 2.4: Schematic PES of a 3-atom LJ cluster with r_{12} and r_{13} on the axes and energy on the vertical. The minimum is marked in red, first-order saddles in yellow, and higher-order saddles in cyan.

paths connecting them. Stationary points are classified by the eigenvalues of the Hessian (matrix of second derivatives of E): minima have all positive eigenvalues (vibrationally stable isomers), first-order saddles have one negative eigenvalue, and critical points of order $n > 1$ are maxima along n directions and minima along all other directions. Physically, minima represent metastable structures (isomers), while first-order saddles often correspond to *transition states* that connect neighbouring minima along the minimum-energy pathways of the potential energy surface. The minima, saddle points, and steepest descent lines connecting them make up what might be called an energy network.

The PES may be viewed as an energy landscape in $3n-6$ dimensions. The energy gradient is non-zero at every point other than critical points. From any point x other than a critical point, one could follow a line of steepest descent through a series of small steps in the negative gradient direction and reach a minimum M_k . So every point x where the gradient is non-zero can be mapped to one of the minima M_k . Therefore, the PES consists of valleys (sometimes called basins). A broad valley that leads to a deep minimum is sometimes called a funnel. A funnelled landscape

facilitates equilibration into the global minimum, while a rugged landscape with competing funnels leads to trapping, frustration, and glassy dynamics.

The PES also governs the dynamical behaviour of clusters. At low total energy, a cluster vibrates near a single minimum. As the energy increases, intramolecular fluctuations allow the system to cross barriers and visit other minima [97]. In the microcanonical ensemble, this process is driven by the redistribution of kinetic and potential energy at fixed total energy E . Formally, the number of accessible configurations at energy E is given by the density of states

$$\Omega(E) = \int \delta(E - E(x)) dU, \quad (2.50)$$

from which one defines the entropy

$$S(E) = k_B \ln \Omega(E), \quad (2.51)$$

and the microcanonical temperature

$$T(E) = \left(\frac{\partial S}{\partial E} \right)^{-1}. \quad (2.52)$$

The curvature of $S(E)$ further determines the microcanonical heat capacity,

$$C(E) = - \frac{(\partial S / \partial E)^2}{\partial^2 S / \partial E^2}. \quad (2.53)$$

This formalism clarifies why finite clusters can exhibit unusual effects, such as negative heat capacity. In regions where $S(E)$ is locally convex, the slope $T(E)$ decreases with increasing E , reflecting the inability of small systems to separate coexisting phases spatially. Instead of forming an equilibrium mixture with spatially separated phases, clusters undergo sudden transitions between solid-like and liquid-like regimes as they explore different basins of the PES, over time.

Accurate PES modelling is therefore essential for describing the structure, dynamics, and ther-

modynamics of atomic clusters. The quality of the PES depends on the underlying electronic structure method: from quantum chemical approaches (HF, DFT) to empirical interatomic potentials (Lennard-Jones, Morse, Embedded atom model), and, more recently, machine learning models. Direct mapping of the PES at a high level is computationally prohibitive for large n , motivating the use of approximate yet accurate models. Modern machine-learned interatomic potentials (MLIPs) provide a continuous and near-DFT-accurate representation of the PES across broad configuration spaces, enabling microcanonical sampling and thermodynamic analysis with accuracy. Once built, the PES provides the essential link between quantum mechanics and observable behaviour, describing the multidimensional landscape over which atomic rearrangements, phase transitions, and chemical transformations occur. Descriptions of dynamics without invoking the Born-Oppenheimer approximation, and quantum treatments of nuclei motion by solving the nuclear Schrodinger equation, are much more difficult and normally done only for small systems. We will not discuss them.

The following sections discuss how PES are constructed and explored using both classical potentials and machine-learned models.

2.3 Empirical Interatomic Potentials

Calculating the electronic structure by solving the Schrödinger equation at each configuration to map the PES is computationally expensive, especially for large systems. Empirical interatomic potentials offer a faster alternative by approximating the PES with analytical functions that model atom-atom interactions without explicitly treating electrons. These potentials enable efficient simulations of atomic clusters, biomolecules, and extended materials. Widely used models include the Lennard-Jones (LJ), Morse, Embedded Atom Method (EAM), and tight-binding (TB) potentials, applied to study the structure, energetics, and phase transitions of small atomic clusters [98, 99, 100, 101, 102].

One of the simplest and most common is the 6-12 LJ potential, describing van der Waals

interactions:

$$U_{\text{LJ}} = 4\epsilon \sum_{i=2}^n \sum_{j=1}^{i-1} \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right], \quad (2.54)$$

where ϵ is the well depth and σ the distance at which the potential is zero. The r^{-12} term models the repulsive Pauli exclusion effect, while the r^{-6} term models dispersion (attractive van der Waals) interactions. Figure 2.5 shows its shape, with a minimum at the equilibrium separation. For argon, typical parameters are $\epsilon = 0.238$ kcal/mol and $\sigma = 3.405$ Å, giving $r_m \approx 3.822$ Å. Although efficient, the LJ potential's pairwise form and lack of directionality limit its accuracy and its use in studies of rare gases and quasi-spherical closed-shell molecules.

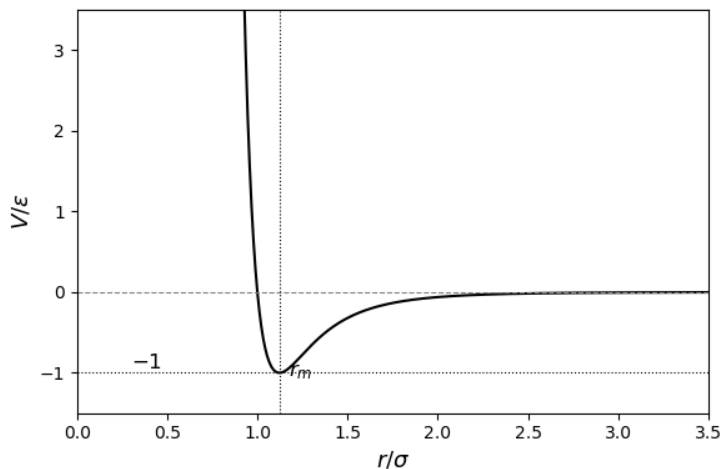


Figure 2.5: Dimensionless Lennard-Jones potential, $V(r)/\epsilon$, as a function of reduced distance r/σ . The minimum at $r/\sigma = 2^{1/6} \approx 1.122$ marks the equilibrium separation.

Metallic clusters, with delocalized electrons, are better described by the EAM [103], which combines a pair potential with a non-additive embedding function dependent on the local electron density. This many-body formulation captures cohesive energies in metallic environments and is widely used for bulk metals. However, its transferability to low-coordination or surface-dominated systems, such as clusters, can be limited, motivating the need for parameter refitting [104]. Moreover, EAM fails to model the details of electronic structure and can not (or can not easily) capture the effect on energy of shell closing, spin subshell closing, magnetism, atomic charges and long-range Coulombic forces, the Jahn-Teller effect, and many more.

The TB method originates from the quantum-mechanical description of electrons in solids using the *linear combination of atomic orbitals* approach. In this framework, the electronic wavefunction is expressed as a linear combination of localized atomic orbitals:

$$\Psi_n(\mathbf{r}) = \sum_i c_i^{(n)} \phi_i(\mathbf{r}), \quad (2.55)$$

where ϕ_i are atomic orbitals centered on each atom, and $c_i^{(n)}$ are coefficients describing the contribution of each orbital to the n^{th} electronic state.

Substituting Eqn. (2.55) into the electronic Schrödinger equation yields a matrix eigenvalue problem:

$$\sum_j H_{ij} c_j^{(n)} = E_n \sum_j S_{ij} c_j^{(n)}, \quad (2.56)$$

where $H_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle$ are Hamiltonian matrix elements and $S_{ij} = \langle \phi_i | \phi_j \rangle$ are overlap integrals. In the orthogonal TB approximation, $S_{ij} = \delta_{ij}$, simplifying the problem to

$$\sum_j H_{ij} c_j^{(n)} = E_n c_i^{(n)}. \quad (2.57)$$

In TB, unlike ab initio electronic structure methods, the matrix elements H_{ij} are not calculated from first principles; they are parameterized with on-site energies ϵ_i and hopping integrals t_{ij} between neighboring atoms:

$$H_{ij} = \begin{cases} \epsilon_i, & i = j, \\ t_{ij}, & i \neq j. \end{cases} \quad (2.58)$$

The total electronic energy is obtained by summing over occupied electronic states, and a short-range repulsive potential is added to account for the ionic core repulsion:

$$E_{\text{tot}} = \sum_n^{\text{occ}} E_n + E_{\text{rep}}. \quad (2.59)$$

TB models thus bridge the classical and quantum descriptions by introducing a parameterized

Hamiltonian that approximates the band structure, along with a short-range repulsive term. They capture many-body and directional effects, making them suitable for different modes of bonding, and have been successfully applied to small clusters, such as Cu and Al [105, 106]. However, they are more demanding computationally and require careful parameterization for each system. In Chapter 3, a TB model was fitted on approximately 600–700 DFT energy-configuration data of Ag clusters. The model employed 6–7 fitting parameters per cluster size and was designed to reproduce the DFT PES with reasonable accuracy.

While classical empirical potentials, such as LJ, EAM, and TB, offer speed and reasonable accuracy within their respective domains, they lack transferability across different bonding types. They are constrained by the analytic form chosen a priori, meaning new chemistry cannot be captured without introducing new parameters. This motivates the rise of machine learning interatomic potentials (MLIPs), which aim for near-first-principles accuracy at modest computational cost. MLIPs do not impose a fixed analytical functional form, but instead learn the mapping from atomic coordinates to energies and forces directly from data, retaining more of the quantum-mechanical information embedded in their training set. They are particularly promising for modelling complex cluster PES, as discussed in the next section.

2.4 Machine Learning Approaches and Neural Network Potentials

2.4.1 Machine Learning for Atomistic Modelling

Machine learning (ML) refers to algorithms that learn functional relationships directly from data, rather than being prescribed by explicit analytical equations. In atomistic physics, the most important regression task is, arguably, to approximate the high-dimensional potential energy surface $E(\mathbf{R})$ and its gradients $-\nabla_{\mathbf{R}}E(\mathbf{R})$ (forces) using examples generated from quantum-chemical calculations.

Machine learning approaches are generally categorized into three broad classes: **(i) Supervised learning**, which uses labelled pairs $(\mathbf{x}_i, y_i)$ to train a model for prediction tasks such as regression (e.g., energy or force estimation) and classification (e.g., solid-like vs. liquid-like states differentiation). In this thesis, a supervised classification approach is employed to label and differentiate configurations within the solid–liquid coexistence region, and a supervised regression task is key to how we construct MLIPs and evaluate energies during simulations. **(ii) Unsupervised learning**, which identifies underlying patterns or clusters in data without prior labels. In this thesis, we use Principal Component Analysis (PCA) to project configuration descriptors onto a small subspace of orthogonal coordinates, revealing structural organization; details are provided in Section 2.4.2. **(iii) Reinforcement learning**, which optimizes sequential decisions through a system of rewards and penalties. Although not used in this work, it is mentioned here for completeness: the model learns by receiving rewards for desirable actions and penalties for undesirable ones, gradually improving its policy.

The advent of ML has led to the development of various **neural network (NN)** architectures, including feed-forward neural networks (FFANNs), convolutional neural networks (CNNs), and graph neural networks (GNNs). In this thesis, we employ FFANNs for supervised classification and GNNs for constructing machine-learned interatomic potentials (MLIPs), discussed in detail in Section 2.4.3. FFANNs are universal function approximators defined by

$$z_j^{(\ell)} = \sigma \left(\sum_i w_{ij}^{(\ell)} x_i^{(\ell-1)} + b_j^{(\ell)} \right), \quad (2.60)$$

where $w_{ij}^{(\ell)}$ and $b_j^{(\ell)}$ are the weights and biases of layer ℓ , and σ is a nonlinear activation function.

In PES learning, the NN maps symmetry-preserving representations of local atomic environments to atomic energy contributions, with forces obtained as analytic gradients to ensure energy–force consistency. More broadly, ML has become an indispensable tool in modern physics and chemistry, enabling the exploration of complex, high-dimensional systems that were previously beyond reach. Its applications now span from molecular dynamics and electronic-structure pre-

diction to materials discovery and phase-transition analysis, underscoring its transformative role in data-driven scientific research.

2.4.2 Principal Component Analysis

Principal Component Analysis (PCA) is employed to analyze ensembles of atomic configurations by projecting high-dimensional structural descriptors onto orthogonal directions of maximal variance. Conceptually, PCA identifies the directions in which the data vary the most—analogueous to determining the principal moments of inertia for objects of different shapes, where each principal axis captures a dominant geometric mode.

Mathematically, given a set of mean-centred feature vectors $\{\mathbf{x}_i\}_{i=1}^M \subset \mathbb{R}^d$ (e.g., interatomic distances, angular descriptors, or bond-order metrics), the sample covariance matrix is

$$C = \frac{1}{M} \sum_{i=1}^M (\mathbf{x}_i - \bar{\mathbf{x}})(\mathbf{x}_i - \bar{\mathbf{x}})^\top. \quad (2.61)$$

PCA seeks orthonormal eigenvectors $\mathbf{v}_k$ and corresponding eigenvalues λ_k satisfying

$$C\mathbf{v}_k = \lambda_k \mathbf{v}_k, \quad (2.62)$$

where λ_k quantifies the variance captured along direction $\mathbf{v}_k$. In matrix form, this corresponds to diagonalizing $C = V\Lambda V^\top$, or equivalently computing eigenvectors of $A^\top A$ if the data matrix A is constructed by stacking the feature vectors row-wise. The transformed coordinates (or scores) are

$$\mathbf{s}_i = V^\top (\mathbf{x}_i - \bar{\mathbf{x}}), \quad (2.63)$$

and the explained-variance ratio $\lambda_k / \sum_j \lambda_j$ quantifies the fraction of information retained in each component.

In the context of this thesis, PCA reduces the structural complexity of samples of cluster configurations visited in simulations to a few dominant modes. Typically, the first principal

component (PC1) captures the largest structural variance—often linked to collective distortions or shape fluctuations—while the second (PC2) highlights secondary rearrangements. Plotting configurations in the (PC1, PC2) space provides a low-dimensional representation of the free-energy landscape. In this projection, densely populated regions correspond to energetically favourable geometries near the global minimum, while sparsely populated or diffuse regions represent higher energy configurations. Distinct clusters indicate the presence of structural isomers, whereas the progressive spreading of points with increasing temperature reflects melting-like transitions and clusters exploring larger regions in configuration space. This analysis is utilized in Chapter 5.

2.4.3 Machine-Learned Interatomic Potentials

Mapping the BO potential energy surface (PES) of even moderately sized clusters requires millions of energy evaluations, making direct *ab initio* simulations impractical. Machine-learned interatomic potentials (MLIPs) offer a practical alternative by achieving near first-principles accuracy at a fraction of the computational cost. Unlike classical empirical potentials, which rely on fixed functional forms and extensive parameter fitting, MLIPs learn flexible, high-dimensional representations of local atomic environments from quantum-mechanical reference data. This allows them to capture complex many-body effects and generalize across diverse structural motifs, although their extrapolation beyond the training domain remains an active area of research [107]. A comparative overview of DFT, empirical potentials, and MLIPs is summarized in Table 2.1, highlighting their respective accuracy, cost, and transferability trade-offs.

The objective of an MLIP is to construct a surrogate model of the BO PES such that

$$E(\mathbf{R}) \approx \sum_i E_i(\mathcal{N}(i)), \quad \mathbf{F}(\mathbf{R}) = -\nabla_{\mathbf{R}} E(\mathbf{R}), \quad (2.64)$$

where $\mathcal{N}(i)$ represents the neighborhood of atom i within a finite cutoff. This atomic decomposition ensures locality and enables linear scaling with system size. The model inputs must preserve translational, rotational, and permutational symmetries to remain physically meaningful. Two gen-

	DFT	Empirical Potentials	MLIPs
Physics represented	Electrons (density/orbitals); exchange-correlation functional	Analytic few-/many-body forms; no explicit electrons	Many-body correlations from data; no explicit electrons
Primary task	First-principles prediction	Fast surrogate with fixed form	Data-driven surrogate with learned form
Accuracy	High (functional dependent)	Low-moderate; system-specific	High in-domain ($\sim$ DFT)
Computational cost & scaling	Very high ($\sim N^3$)	Very low ($\sim N$)	Moderate (linear in N)
Transferability	Broad	Narrow; requires refits	Moderate; limited out of distribution
Predictable quantities	Energies, forces, electronic properties	Energies, forces (within fit)	Energies, forces (trained targets)
Limitations	Expensive	Poor transfer; rigid forms	Extrapolation risk; data bias; black-box nature

Table 2.1: Comparison of interatomic modelling frameworks: DFT, empirical potentials, and MLIPs.

eral strategies exist: handcrafted descriptors, such as Behler-Parrinello symmetry functions [108] and Smooth Overlap of Atomic Positions (SOAP) kernels [109], or learned descriptors generated within equivariant graph neural networks. The former explicitly encodes invariance through analytical functions, while the latter learn representations that transform correctly under symmetry operations.

MLIPs are typically trained on DFT-calculated reference data, $\{E^{\text{DFT}}, \mathbf{F}^{\text{DFT}}\}$, by minimizing a combined loss function,

$$\mathcal{L} = \alpha |E^{\text{ML}} - E^{\text{DFT}}|^2 + \beta \frac{1}{3N} \sum_{a=1}^{3N} |F_a^{\text{ML}} - F_a^{\text{DFT}}|^2, \quad (2.65)$$

which balances the energy and force terms. Including forces greatly improves sample efficiency

and the dynamical stability of molecular simulations.

Early MLIPs, such as the Behler-Parrinello neural network [108], decomposed the total energy into atomic contributions evaluated through symmetry functions, while the gaussian approximation potential used Gaussian process regression on SOAP descriptors and successfully reproduced melting behaviour in sodium clusters [110]. These descriptor-based models are efficient and transferable but rely on fixed functional forms that limit flexibility. More recent graph neural network models, including SchNet [111], DimeNet [112], NequIP [113], and MACE [114], embed geometric symmetries directly and use message passing to exchange information between neighbouring atoms. In this framework, each atom is treated as a node in a graph, and messages—functions of interatomic distances, atomic features, and geometric information are iteratively aggregated from neighbouring nodes to update the representation of each atom. This process enables the network to capture many-body correlations and the influence of the local chemical environment without requiring predefined functional forms. MACE, in particular, extends the atomic cluster expansion to include high-order equivariant interactions while maintaining efficiency through a minimal number of message-passing steps. These models do not enforce electronic antisymmetry explicitly but learn an effective potential energy surface consistent with quantum-mechanical data. By contrast, neural wavefunction models, such as PauliNet [115], represent the electronic wavefunction directly and incorporate fermionic antisymmetry; however, such approaches are beyond the scope of this work.

Allegro [116] represents a further development in this hierarchy by removing iterative message passing altogether. It constructs the total energy from pairwise-local equivariant tensors built using spherical-harmonic features and learnable weights:

$$E = \sum_i \sum_{j \in \mathcal{N}(i)} \tilde{E}_{ij}(\mathbf{h}_i^{(0)}, \mathbf{h}_j^{(0)}, \dots), \quad (2.66)$$

where $\mathbf{h}_i^{(0)}$ are atom-wise embeddings and $\mathcal{N}(i)$ defines the local neighborhood. The local tensors

are updated through bilinear tensor products,

$$\mathbf{V}_{ij}^{(L)} = \mathbf{V}_{ij}^{(L-1)} \otimes \left(\sum_{k \in \mathcal{N}(i)} w_{ik}^{(L)} \mathbf{Y}_{ik} \right), \quad (2.67)$$

where $\mathbf{Y}_{ik}$ denotes spherical harmonics and $w_{ik}^{(L)}$ are learnable weights. This architecture preserves rotational equivariance while remaining computationally efficient, making it well-suited for large-scale GPU acceleration.

In this thesis, Allegro was trained on DFT single-point energy calculations for *Al* and *Na* clusters and coupled with PTMC to investigate melting transitions. The Allegro models achieved mean absolute errors below 10 meV/atom on validation datasets and demonstrated good transferability to out-of-distribution geometries. These results highlight Allegro’s effectiveness for accurate and efficient potential-energy exploration in finite metallic systems.

Overall, the development of MLIPs—from early descriptor-based models to modern equivariant neural networks has transformed atomistic modelling by bridging the gap between DFT accuracy and molecular-mechanics efficiency. While current approaches deliver impressive precision, challenges remain regarding extrapolation, uncertainty quantification, and data diversity. Addressing these will be crucial for extending MLIP methodologies to increasingly complex, multicomponent, and reactive systems.

2.5 Monte Carlo Sampling and Parallel Tempering

The goal of the simulations we carry out here is to generate a sample of cluster configurations (i.e., sets of atomic coordinates) that is representative of the equilibrium at some temperature T . Statistical averages of properties can then be calculated for this cluster at that temperature. In the canonical ensemble, the probability of a configuration x_i is proportional to the Boltzmann factor $e^{-U_i/k_B T}$. The Metropolis-Hastings algorithm [117] is a practical realization of this principle: it performs a random walk in configuration (phase) space that satisfies the condition of detailed

balance, ensuring convergence to the canonical equilibrium distribution. The potential energy U_0 is calculated for the cluster at some initial configuration x_0 . This is followed by N simulation steps. At step k , a small change is made to configuration x_{k-1} and the potential energy is calculated for the new configuration x_k . If $U_k < U_{k-1}$, the new configuration is accepted. Otherwise, a random number r is drawn from the uniform distribution $[0, 1]$: if $r \geq e^{-(U_k - U_{k-1})/k_B T}$ configuration x_k is accepted; if $r < e^{-(U_k - U_{k-1})/k_B T}$ configuration x_k is rejected and replaced by x_{k-1} . After n_e equilibration steps, sums are updated at every step to compute statistical averages such as $\bar{U}$ or $\bar{U}^2$.

A serious problem with Metropolis-Hastings MC simulations is that the number of steps n needed to correctly sample the equilibrium distribution is sometimes extremely large, and impossible to reach in practice. The problem arises when two very different configurations x_a, x_b have energies U_a, U_b that are both within few times $k_B T$ of the global energy minimum, and are separated by a barrier that is many times $k_B T$, say, $100k_B T$. A simulation that starts near x_a has a negligibly small probability of visiting configurations near x_b in a small (say $n \sim 10^6$) number of steps. The sample would have no configuration near x_b and statistical averages would be incorrect.

Parallel Tempering Monte Carlo (PTMC), also known as replica-exchange Monte Carlo, addresses this problem. In PTMC, N replicas of the system are simulated in parallel, each at a different temperature $T_1 < T_2 < \dots < T_N$. Replica j evolves independently from other replicas at its own temperature T_j by the Metropolis-Hastings algorithm. A replica at a high temperature T_h is likely to overcome energy barriers that are large multiples of $k_B T_1$, but it would produce a sample representative of temperature T_h , not T_1 . The key idea of PTMC is to pause the N simulations once every N_s steps, and attempt an exchange of replicas at temperatures T_k and T_{k+1} , where k is picked randomly between 1 and $N - 1$. A proposed exchange of replicas k and $k + 1$ is accepted with a probability.

$$P = \min \left\{ 1, \exp \left[\left(\frac{1}{kT_{k+1}} - \frac{1}{kT_k} \right) (U_{k+1} - U_k) \right] \right\}, \quad (2.68)$$

This rule obeys the principle of detailed balance: the rate for transitions $x_a \rightarrow x_b$ and $x_b \rightarrow x_a$ are

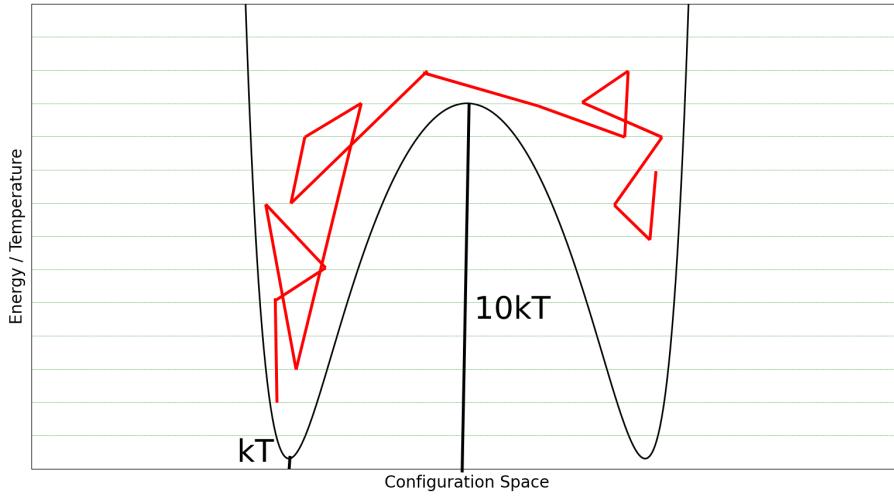


Figure 2.6: Schematic diagram showing how PTMC facilitates transitions across high energy barriers by exchanging replicas at different temperatures.

equal for every x_a, x_b . For replica pairs where $\Delta U = 0$, the acceptance probability is one.

In PTMC, the sampling at low temperatures is much more efficient. A replica initially near x_a at temperature T_1 eventually reaches the highest temperature T_N through a sequence of random exchanges. Once at T_N (or at a sufficiently high temperature) it can overcome energy barriers that are many times $k_B T_1$ and explore large regions of configuration space. A subsequent random sequence of exchanges brings the replica's temperature back to T_1 in a configuration that can be near x_b with significant probability. The efficiency of the PTMC algorithm can be assessed qualitatively by counting the number of *round trips* replicas undergo from T_1 to T_N and back to T_1 .

Figure 2.6 illustrates how a system trapped in a local minimum at low temperature can escape by swapping with a higher-temperature replica. At high temperature, the system has sufficient thermal energy to overcome energy barriers and may revert to a low-temperature replica in a new, potentially lower-energy configuration. This makes PTMC especially well-suited for studying the melting of clusters.

PTMC has been used before to study clusters. Neirotti *et al.* [118] used PTMC and showed that a 28-atom LJ cluster switches between octahedral and icosahedral forms depending on temperature. Frantsuzov *et al.* [119] mapped size-temperature phase diagrams and observed two-step melting

and surface premelting transitions. PTMC was used to simulate $\text{Ar}_n\text{-HCl}$ [120] and hydrogen-bonded water clusters [121]. PTMC was also successfully applied to study the thermodynamic properties of metallic systems, including gallium [122], aluminum [123], and bimetallic clusters [124]. Improvements to the original PTMC algorithm have been proposed. Calvo *et al.* [125] introduced a variant where all replica pairs are considered for swapping at every step, increasing the convergence rate. Nigra *et al.* [126] added “darting” moves between known low-energy configurations to accelerate sampling further.

In this thesis, PTMC is used not only to improve sampling but also to discover, or confirm, the global minimum (GM) configuration. In a typical simulation, there are ~ 30 replicas and a million steps and roughly half of the moves are accepted, creating a total of ~ 15 million distinct configurations. The lowest energy one is a good guess for the GM.

We save all replicas every $N = 50$ steps, yielding approximately 18,000 configurations per temperature over a typical million-step run. For each temperature, representative structures are identified among these configurations by evaluating geometric features (e.g., bond lengths, anisotropy; see Chapter 5) for every configuration pair (j, k) . Principal component analysis (PC1, PC2) is then performed on these geometric descriptors to locate the most probable geometric density. Clustering in this reduced PC2 space enables the selection of representative structures that best capture the dominant structures. These representative configurations provide an intuitive and visual summary of temperature-dependent structural evolution.

Chapter 3

Geometric Features and a Neural Network Classifier for Characterizing Melting-Like Transitions in Clusters.

Abstract

Melting-like transitions in clusters are normally identified by a peak in the heat capacity curve $C(T)$ at $T = T_c$. Computing $C(T)$ requires costly simulations with millions of steps. We discuss four easily calculated functions of temperature that help detect and characterize melting-like transitions. The first, f_1 (or W_U), is the width of the potential energy distribution which shows an abrupt increase near T_c . The other three are statistics of the ordered set of $N(N - 1)/2$ interatomic distances r_{ij} : (i) f_2 is a measure of dissimilarity to the lowest energy configuration, or global minimum; (ii) f_3 is the effective number of r_{ij} 's found in a small interval centered around $(r_1 + r_2)/2$ where r_1, r_2 are the positions of the first two peaks in the pair distribution function; and (iii) f_4 is a measure of non-uniformity in the distribution of the r_{ij} 's. Numerical tests with empirical potentials that model three types of bonding (van der Waals, covalent, and metallic) show that f_1, f_2, f_3 , and f_4 produce estimates for the middle of the melting region in general agreement with T_c . An Artificial Neural Network (ANN) classifier that takes, as inputs, f_2, f_3 , and many variants of f_4 , is used to calculate the solid fraction $F_S(T)$ and find the solid-liquid coexistence region between freezing and melting temperatures, $[T_f, T_m]$. Inflection point in $f_3(T)$ and $F_S(T)$ are very sensitive indicators of phase transitions. Estimates of T_c obtained from them converge one to three orders of magnitude faster, in simulation time, than those obtained with $C(T)$.

3.1 Introduction

Clusters X_n , made of n atoms of element X , exhibit melting-like transitions at a temperature T_c that depends on X and cluster size n [43, 44, 45]. When n is large, T_c goes down smoothly with cluster size [43]. But at small n ($n \lesssim 100$) the evolution of T_c with n is far from simple. It may show many local maxima and, sometimes, abrupt changes with addition of a single atom [51]. Clusters exhibit a range of temperature $[T_f, T_m]$ where solidlike and liquidlike phases coexist [42]. Some clusters show a premelting peak in heat capacity well below T_c [127]. Others melt at temperatures *higher* than the bulk [52]. A negative heat capacity has been found in some cases [128, 129, 130, 131]. These observations also apply to small clusters composed of more than one element.

The theory of cluster melting was well-developed by 1988 [42]. But details in melting behaviour, and T_c and related properties, vary greatly with chemical composition and size. No simple model can predict or explain them for a specific small cluster [132]. Determination of T_c requires difficult experiments or computations and is often made by observing a maximum in the heat capacity curve $C(T)$. Another common indicator of melting, the Lindemann index, is when the fluctuation in nearest-neighbour interatomic distances exceeds 15% [133, 134, 132]. Geometric indicators of melting, like a sudden change in shape or the loss of crystalline order, are sometimes used for clusters with thousands of atoms.

In computational work, costly simulations with millions of steps are often needed to reduce statistical uncertainties and get reliable $C(T)$ curves. Simulations can suffer from unreliable potentials or incomplete sampling. Machine Learning (ML) methods can accurately fit potentials [135, 136, 137, 138, 139] to DFT energies. But they are not yet fully developed, they are not easy to use, and they are significantly more costly than empirical two-body potentials. Efficient sampling [136] and ways to obtain converged results with shorter simulations are desirable. Ideally, they would produce converged results with simulations so short that energies and forces can be calculated from first principles. Meanwhile, the field of nanoscience has grown considerably and with it, the need to measure, understand, and predict melting in clusters and nanoparticles used in catalysis [140], electronics [141], and biondiagnostics [142]. The main result presented here are

computational techniques that cut the cost of simulations needed to predict melting points in small clusters. At the same time, these techniques give insight into melting-like transitions.

We briefly mention a few studies of cluster melting to illustrate methods for finding T_c and representative results. The T_c of sodium clusters were found to vary between 291 kelvin ($n = 2000$) and 307 kelvin ($n = 10000$) by tracking abundances of Na_n^+ ions by mass spectrometry as a function of temperature [128]. Caloric measurements on size selected Na_n^+ ($55 \leq n \leq 357$) showed that T_c goes through five or six oscillations as a function of n in a range of 260 ± 50 kelvin [128]. Measurements of the heat capacities of Al_n^+ ($n = 16-48$) showed melting for $n \geq 28$ at temperatures below $T_{m,bulk} = 934$ K at every n but one ($n = 48$) [127] and, in some cases, small secondary peaks in $C(T)$ indicating premelting or postmelting. It was also found that melting enhances the reactivity of Al_n clusters [143]. Breaux et al. measured heat capacities of Ga_n^+ ($n = 30-50, 55$) [144, 145]. They found a strong size dependence and T_c in a range from 500 to 800 K with peaks in $C(T)$ that are 200 to 300 K wide. There is a very high T_c (~ 800 K) for ($n = 45 - 47$) considering the bulk melting point of Ga (303 K). Values of T_c well in excess of $T_{m,bulk}$ were also observed for Sn_n^+ [52]. Changes in shape of Au_n ($n = 561$ to 2530) seen by scanning transmission electron microscopy [146] show that surface melting and core melting occur at very different temperatures, for instance $T_s \sim 885 \pm 25$ K and $T_c \sim 1150 \pm 100$ at $n \sim 561$ ($T_{m,bulk}(\text{Au}) = 1337$ K).

Early computational studies that used simple empirical potentials helped establish general concepts [42] and showed melting phenomena later confirmed with more accurate potentials [147, 52, 134]. Ab Initio Molecular Dynamics (AIMD) or Monte Carlo (AIMC) simulations have been done for a few small clusters, with energies and forces calculated by DFT. An AIMD study of Ga_n ($n = 7-12$) showed no melting at $n = 7$ and 8, T_c above $T_{m,bulk}$ at $n = 9-11$, and T_c below $T_{m,bulk}$ at $n = 12$. An AIMD study of Na_n [148] showed T_c in the range 206–280 K and a size dependence in good agreement with experiment [128]. Another AIMD study showed $T_c = 227$ K for Na_{20} [149], in qualitative agreement with experiment. ML potentials fitted to DFT [137, 138, 136, 135] allow simulations with a computing effort intermediate between those of empirical potentials and first-principles MD. A study of Na_n [139] by Monte Carlo (MC), with a MLIP, gave results

($T_c = 235$, premelting at 107 K) in close agreement with those of an AIMD study [149]. A study of Au_n ($n = 17\text{--}58$) with ML potential showed solid-liquid coexistence near T_c and found that melting begins with core atoms [150]. Besides heat capacity, many indicators of melting have been used in computational work: bond length fluctuations [133, 134], the radial density function [151], x-ray interference functions [151], the frequency spectrum (Fourier transform of the velocity autocorrelation function) [152], the diffusion coefficient [42], instantaneous normal mode frequencies [153], and various descriptors of shape or geometry.

Details of the simulations, interatomic potentials, functions, and classifier used to determine T_c are given in section 3.2. Results are discussed in section 3.3 with a focus on comparing T_c and simulation times obtained with different methods. We summarize our main findings and conclusions in section 3.4.

3.2 Methodology

We use T_c to represent the temperature at which heat capacity is maximum. A smaller peak is sometimes observed below T_c , indicating premelting. We use T_f and T_m to represent the freezing and melting temperatures. They are obtained by classifying atomic configurations as solidlike (S) or liquidlike (L), and taking T_f as the highest temperature where sampled configurations have fewer than 5%L, and T_m as the lowest temperature with fewer than 5%S.

We ran sufficiently long Parallel Tempering (PT) configuration space Monte Carlo (MC) [154] simulations to get converged heat capacities as references. The number of steps in those simulations were 10^6 (Ar_{20}), 4×10^7 (Si_{20}), and 4×10^7 (Ag_{20}), and the number of replicas (number of temperatures) were 27 (Ar_{20}), 60 (Si_{20}), and 67 (Ag_{20}). The first 10% of steps in every simulation were *equilibration steps*, the remaining 90% were used in computing averages. The heat capacity was calculated with the variance in potential energy

$$C_v = \frac{\sigma_U^2}{k_B T^2} = \frac{\overline{U^2} - \bar{U}^2}{k_B T^2} \quad (3.1)$$

We denote the full width at half-maximum of the probability density function of the potential energy with W_U or f_1 . In long simulations, we saved one out of every 1000 configurations for calculating the functions f_2 , f_3 , and f_4 , and for training the ANN classifier. At high temperatures, atoms sometimes evaporate from a cluster. We detect an evaporation event with a simple distance criterion and reject any such move. This is unphysical and introduces sampling errors. To control this error, we define $T_{evap.}$ as the lowest temperature where the fraction of moves rejected due to evaporation exceeds 10^{-4} , and discard results at temperatures above $T_{evap.}$.

3.2.1 Empirical Potentials

Three qualitatively different potentials were used to see how melting criteria perform in different situations. The potentials we chose are very simple to allow running multiple tests at a manageable cost. The first one is a Lennard-Jones (LJ) potential mimicking van der Waals bonding.

$$U_{LJ} = 4\epsilon \sum_{i=2}^n \sum_{j=1}^{i-1} \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad (3.2)$$

The second, denoted U_{LJV4} , is a valence-saturated LJ potential where each atom contributes at most four attractive terms. To calculate it, we find, for every atom i , the smallest distance to other atoms, $d_i = \text{Min}_j \{r_{ij}\}$, and define a cut-off function

$$\begin{aligned} f_{c,i}(r) &= 1 \quad \text{if } r < 1.3 d_i \\ &= 0 \quad \text{if } r > 1.6 d_i \\ &= \cos \left(\frac{\pi(r - 1.3d_i)}{0.3d_i} \right) \quad \text{otherwise} \end{aligned}$$

The choice to cut from 1.3 to 1.6 times d_i is arbitrary but suitable for modelling elements like Si that crystallize in the diamond structure. The coordination number of atom i is set equal to

$$c_i = \sum_{j \neq i} f_{c,i}(r_{ij}) \quad (3.3)$$

Attractive terms associated with atom i are multiplied by a distance-dependent weight w_{ij} :

$$w_{ij} = \text{Min}(2, 4 f_c(r_{ij})/c_i) \quad (3.4)$$

Atom i contributes a sum of repulsive LJ terms, a sum of weighted attractive LJ terms, and a sum of angular terms A_i

$$U_{LJV4,i} = 2\epsilon \sum_{j \neq i} \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - w_{ij} \left(\frac{\sigma}{r_{ij}} \right)^6 \right] + A_i, \quad (3.5)$$

$$A_i = \alpha \sum_{\substack{j > k \\ j, k \neq i}} w_{ij} w_{ik} \left(\frac{\sigma^2}{r_{ij} r_{ik}} \right)^6 \left(\cos \theta_{ijk} + \frac{1}{3} \right)^4, \quad (3.6)$$

$$U_{LJV4} = \sum_{i=1}^n U_{LJV4,i}. \quad (3.7)$$

Note the factor of 2 in the expression for U_{LJV4} , $w_{ij} \neq w_{ji}$, $\sum_j w_{ij} \leq 4$, and that the angular term favors angles of 109.5° . The parameters ϵ, σ, α were varied to fit, *very approximately*, the atomization energies of the silicon cluster. The resulting function is not a good model for silicon clusters, but it is a reasonable model of clusters held by covalent bonding.

The third potential is a tight-binding (TB) model of s -valent metallic bonding with seven adjustable parameters, $A_0, \alpha, H_0, \gamma, B_0, \beta, S$, plus two terms that go as $1/r^6$ and $1/r^8$ with parameters C_6, C_8 . A n -by- n model Hamiltonian is constructed with matrix elements H_{ij} that depend on interatomic distances r_{ij} and coordination numbers c_i .

Parameter	Ag ₈	Ag ₁₂	Ag ₁₆	Ag ₂₀
A_0	38879.99	22173.72	175983.40	45632.74
α	0.2124	0.2410	0.1910	0.2282
B_0	1.7999	2.1718	2.7199	2.7917
β	0.0953	0.0386	0.0782	0.0896
H_0	4.6643	5.1658	4.3425	4.7019
γ	0.0223	0.0115	0.0114	0.0223
S	1.0176	0.6344	0.6900	0.5550
C_6	80.23	203.18	95.31	177.40
C_8	0.00	185.76	139.86	0.00

Table 3.1: Tight-binding parameters optimized for various Ag clusters.

$$\begin{aligned}
f_{ij} &= A_0 e^{-r_{ij}/\alpha} \\
c_i &= \left(\sum_{j \neq i} f_{ij} \right)^2 / \sum_{j \neq i} (f_{ij})^2 \\
b_i &= B_0 (c_i^\beta) \\
H_{ii} &= -H_0 (c_i^{-\gamma}) \\
H_{ij} &= \frac{1}{2} (H_{ii} e^{-r_{ij}/b_i} + H_{jj} e^{-r_{ij}/b_j}) \\
U_M &= S \left[\sum_{i=1}^{n-1} \sum_{j=i+1}^n A_{ij} + \left(2 \sum_{i=1}^{n/2} (e_i - H_0) \right) \right] \\
&\quad + \sum_{i=1}^{n-1} \sum_{j=i+1}^n (-C_6/r_{ij}^6 + C_8/r_{ij}^8)
\end{aligned}$$

The A_{ij} 's are pairwise repulsions, the e_i 's are the $n/2$ lowest eigenvalues of matrix $\mathbf{H}$, the term with C_6 models long-range dispersion interactions, and the term with C_8 is added for improving the fit. We obtained four sets of 9 parameters by fitting separately to DFT energies of a varied set of configurations of Ag₈, Ag₁₂, Ag₁₆, and Ag₂₀. These DFT energies were obtained with the Gaussian software package [2] using TPSS exchange-correlation [83] and a LANL2DZ basis set [155]. The optimized parameters are given in Å, eV, and units derived from them in Table 3.1.

Table 3.2 shows fit statistics: m_U , σ_U , R_U are the mean, standard deviation, and range of the

DFT energies; RMSE is the root-mean-square error per cluster in meV ; MAE is the mean absolute error per atom in $meV/atom$; and cc is the correlation coefficient. The mean of the four MAEs is 8.2 meV/atom. This level of accuracy does not allow detailed predictions for silver clusters, but is good enough for our purpose which is to model metallic bonding in general. Similar comments apply to the other two potentials. Notwithstanding, for simplicity, we will refer to clusters described with these potentials as “Ar” (LJ), “Si” (LJV4), and “Ag” (M).

	Ag ₈	Ag ₁₂	Ag ₁₆	Ag ₂₀
N	240	136	145	154
m_U (eV)	−11.76	−18.00	−25.87	−34.37
σ_U (eV)	0.589	0.740	0.950	1.213
R_U (eV)	3.54	4.11	4.58	4.84
RMSE (meV)	48.4	138.4	153.5	191.9
MAE (meV/atom)	4.27	9.36	7.53	7.84
cc	0.9966	0.9824	0.9869	0.9874

Table 3.2: Fit statistics for the tight-binding potential modelling metallic bonding in Ag_{*n*}.

3.2.2 Indicators of Melting-Like Transitions.

A peak in the heat capacity curve $C(T)$ (Eq. 3.1) is a standard criterion for detecting melting-like transitions in clusters. However, in a macroscopic crystal, melting is a first-order transition that occurs sharply at the melting temperature T_m . At T_m , many things happen simultaneously: the internal energy exhibits a discontinuity due to the latent heat of fusion, fluctuations in interatomic distances increase sharply, atomic diffusion sets in, and the crystal loses its long-range order. Formally, in the thermodynamic limit, $C(T)$ shows a corresponding divergence (appearing experimentally as a discontinuity).

By contrast, when a cluster melts, these processes occur gradually over a *range of temperatures*, from the onset temperature T_f to the completion temperature T_m , and there is no reason to expect that a single temperature T_c ($T_f < T_c < T_m$) will stand out according to every melting criterion. Nevertheless, we take the temperature corresponding to the peak in the heat capacity, T_c , as a

convenient reference for assessing other structural and dynamical indicators of melting.

The second property that we use as indicative of melting is the width (full width at half-maximum) of the probability density function $f(U)$ of potential energy: this is denoted W_U or f_1 . Our PTMC simulations for Ar13 and Ar20 show that $f(U)$ has a single, unimodal peak when T is below T_f or above T_m , but $f(U)$ becomes bimodal and widens abruptly between T_f and T_m (Fig. 3.1). We take this as an indication of solid-liquid coexistence. Fig. 3.5(b) shows W_U for Ar20 as a function of temperature. Straight lines fit the data accurately below 20 K and above 42 K. When $20 < T < 42$, we see W_U is clearly above both lines. We identify 20 K with T_f , 42 K with T_m , and the intermediate region as SL coexistence. We analyzed W_U of other clusters in the same way.

For the next three other indicators of melting, we start by putting the $N = n(n-1)/2$ interatomic distances r_{ij} in increasing order. This gives the ordered set represented by $d_1 \leq d_2 \leq d_3 \leq \dots \leq d_N$. The first of those indicators is a measure of mean dissimilarity between configurations at temperature T and the global minimum (GM) geometry.

$$\delta(0, X) = \sqrt{\frac{\sum_{i=1}^N w_i (d_{0,i} - d_{X,i})^2}{\sum_{i=1}^N w_i}} \quad (3.8)$$

$$w_i = ((d_{0,i} + d_{X,i})/2)^{-8} \quad (3.9)$$

where $d_{X,i}$ and $d_{0,i}$ are the i 'th distance for geometry X and the GM, respectively. The weights w_i are proportional to the inverse distance to the power of 8. They emphasize short distances, which are most important for energy and many properties. We calculate the mean of $\delta(0, X)$ for configurations X at temperature T and write it as $\delta(T)$ or f_2 .

A plot of $\delta(T)$ is shown for one simulation of Ar13. As expected $\delta(T)$ increases with T . But the slope of $\delta(T)$ is not constant and Fig. 3.2(a) hints at a phase transition starting near 28 K. To extract information from this curve we make a nonparametric fit by LOWESS [156] (red curve) to the data points. We then take the derivative of that curve. The peak in Fig. 3.2(b) is at temperature $T_{c,\delta}$

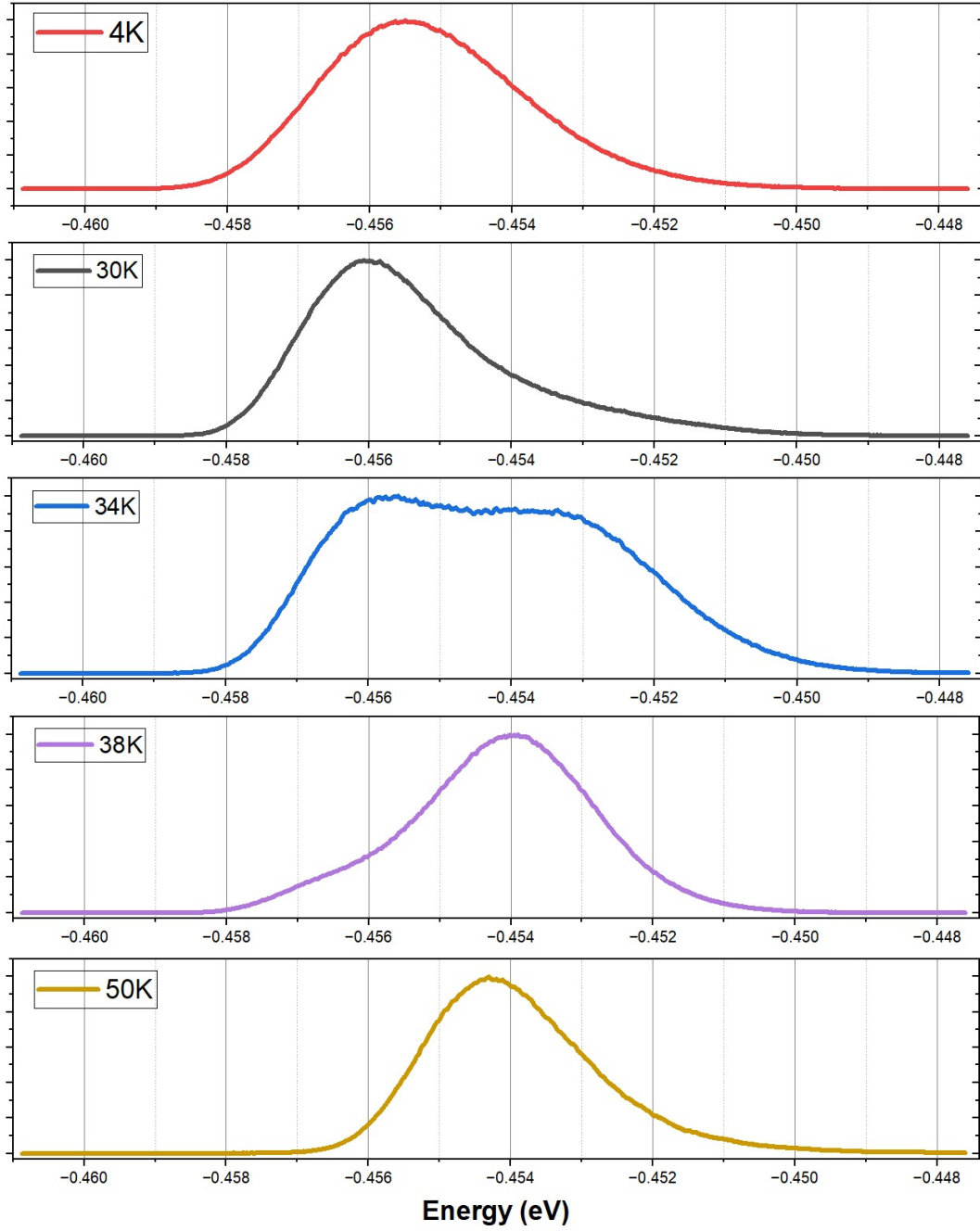
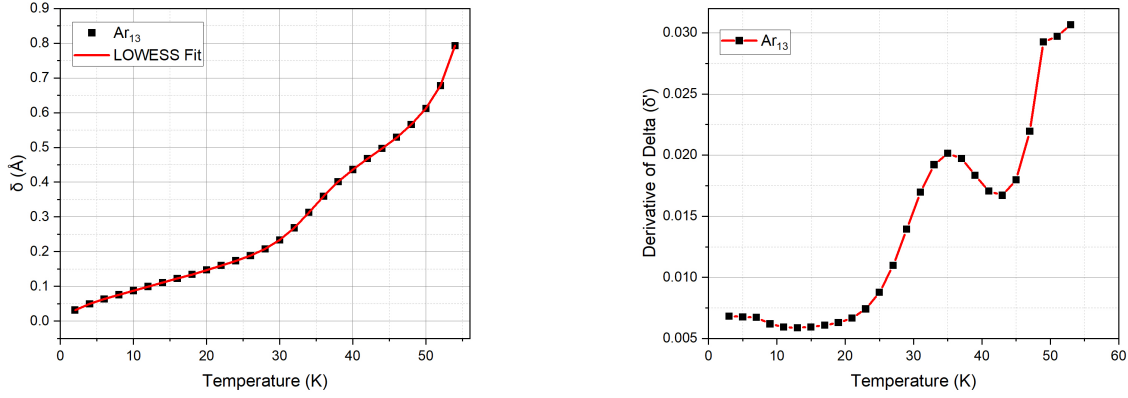


Figure 3.1: Bimodal energy distribution function $f(U)$ for Ar_{13} at different temperatures: $4K$, $30K$, $34K$, $38K$, and $50K$. At lower temperatures ($4K$ and $30K$), the distribution exhibits a single unimodal peak. Around $34K$, a clear bimodal structure develops, indicating the coexistence of two states. At higher temperatures ($38K$ and $50K$), the distribution returns to a single, broadened unimodal peak, consistent with a more homogeneous phase.



(a) Mean dissimilarity to the global minimum, $\delta(X, 0)$, as a function of temperature for Ar_{13} (square) and a LOWESS fit (line).

(b) Numerical derivative of the mean dissimilarity to the global minimum $\delta(T)$ with respect to temperature for Ar_{13} .

Figure 3.2: (a) Mean dissimilarity and (b) its derivative for Ar_{13} as functions of temperature.

where the dissimilarity of configurations to the GM increases the fastest. We take it as an indicator of melting, and $T_{c,\delta}$ as an approximation to T_c . In Fig. 3.2(b), the relatively low $d\delta/dT$ near 19 K and the local minimum at 44 K suggests SL coexistence in this temperature interval.

The next indicator is represented by G or f_3 . It is a measure of the mean number of interatomic distances that are near $(R_1 + R_2)/2$, where R_1 and R_2 are the positions of the first two peaks in the pair distribution function (distances to the first and second nearest neighbours), respectively. In a cold solid, every atom undergoes small oscillations around an equilibrium position, so all interatomic distances are close to R_1 or R_2 , or bigger than R_2 . Interatomic distances near $(R_1 + R_2)/2$ occur when the relation between a pair of atoms changes from nearest-neighbour (NN) to next-nearest-neighbour (NNN). They suggest diffusion in a liquid. In order to get a practical numerical definition of G , we first find the biggest gap in the ordered set of distances of the GM geometry

$$\Delta_k = \frac{d_{k+1} - d_k}{d_k} \quad (3.10)$$

and say that Δ_k is maximum when $k = k_{max}$. We define the middle of the gap, $d_{gap} = (d_{k_{max}} + d_{k_{max}+1})/2$, and set

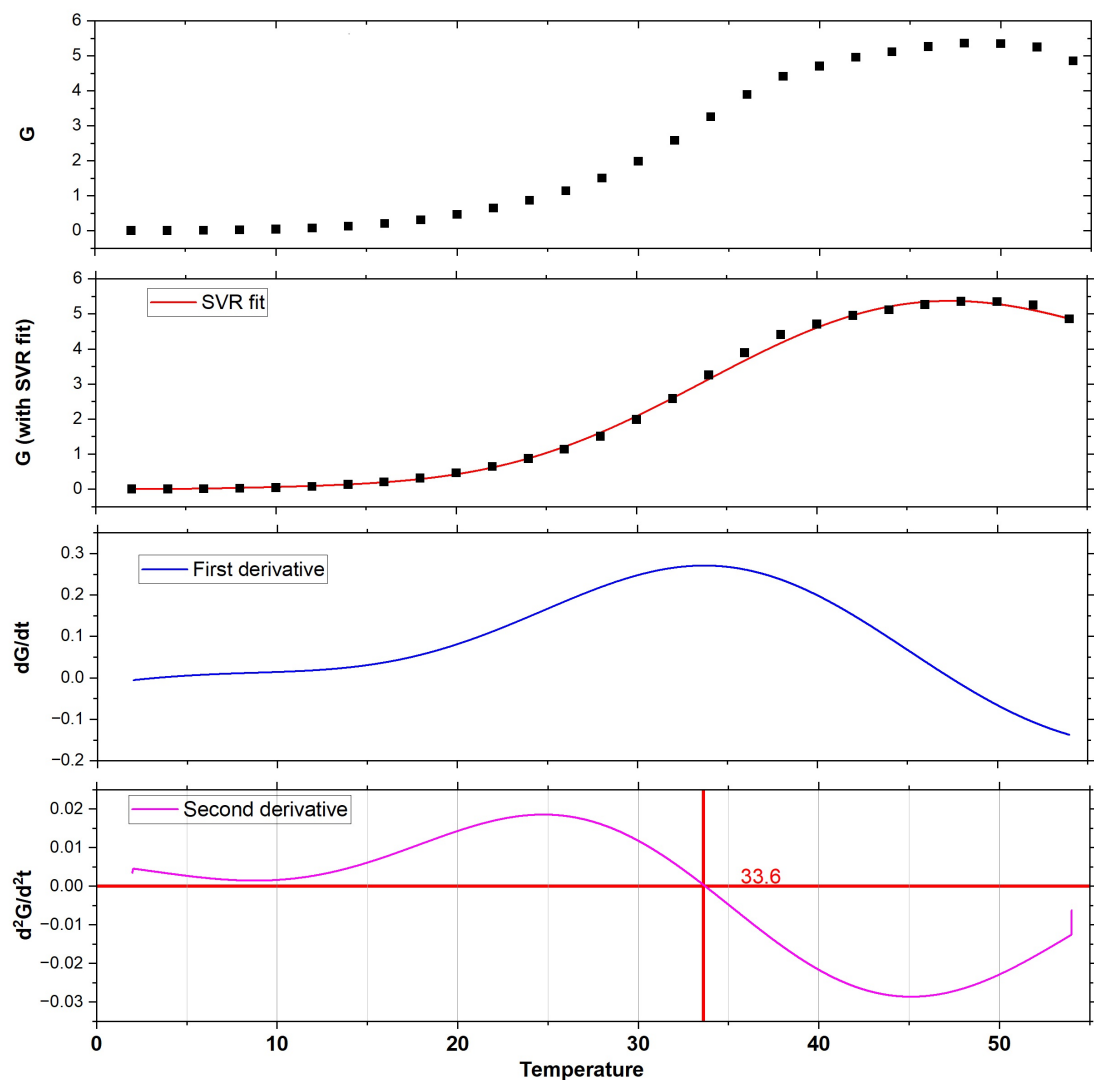


Figure 3.3: Temperature dependence of structural order in Ar_{13} analyzed via the G -value. From top to bottom: (a) Raw G -values plotted as a function of temperature; (b) Support Vector Regression (SVR) fit to the $G(T)$ curve; (c) First derivative dG/dT indicating rates of structural change; (d) Second derivative d^2G/dT^2 revealing inflection points and thermal transition signatures.

$$f_3 = G = \sum_{k=1}^N e^{-((d_k - d_{gap})/(\Delta_{kmax}/6))^2} \quad (3.11)$$

Dividing Δ_{kmax} by 6 in an arbitrary choice: we found it strikes a compromise between sensitivity in detecting liquid states and avoiding false positives. The curve of G vs T does not clearly show where melting occurs. A maximum in dG/dT (a zero in d^2G/dT^2) at a temperature $T_{c,3}$ implies that the rate of exchange among nearest and next-nearest neighbours increases fastest at $T_{c,3}$: we take that as an estimate of T_c . In simulations $G(T)$ and its derivatives, like all other quantities, are noisy. For a good determination of $T_{c,3}$, we first smooth out the $G(T)$ curve by Support Vector Regression (SVR) [157], then take the first and second derivatives. Fig. 3.3 shows $G(T)$, dG/dT and d^2G/dT^2 for data from a long Ar₁₃ simulation. The inflection point in $G(T)$, at 33.6 K, agrees with the maximum in $C(T)$ (at 34 K).

The next indicators are based on ordered distances are functions h that quantify non-uniformity in the distribution of interatomic distances. These functions depend on an integer parameter p that can be varied to create several measures of non-uniformity.

$$h_p = \frac{\left(\sum_{k=1}^N (d_{k+1} - d_k)^p\right)^{1/p}}{\bar{r}} \quad (3.12)$$

The denominator $\bar{r}$ is the mean over n atoms “ i ” of $r_{i,min}$, where $r_{i,min}$ is the distance between atom i and its nearest neighbour. Fig. 3.4 shows ordered interatomic distances in Ar₁₃ at 4 K, 22 K, 40 K, and 50 K, along with h_p values ($p = 4, 6, 8$): h_p decreases as T increases and the distribution becomes more uniform. An ANN classifier may be able to learn subtle differences among the set of functions $h_1, h_2, \dots$ between liquid and solid states. Accordingly, we used ten h_p functions ($p = 1, 10$) as inputs to an ANN classifier described in the next section.

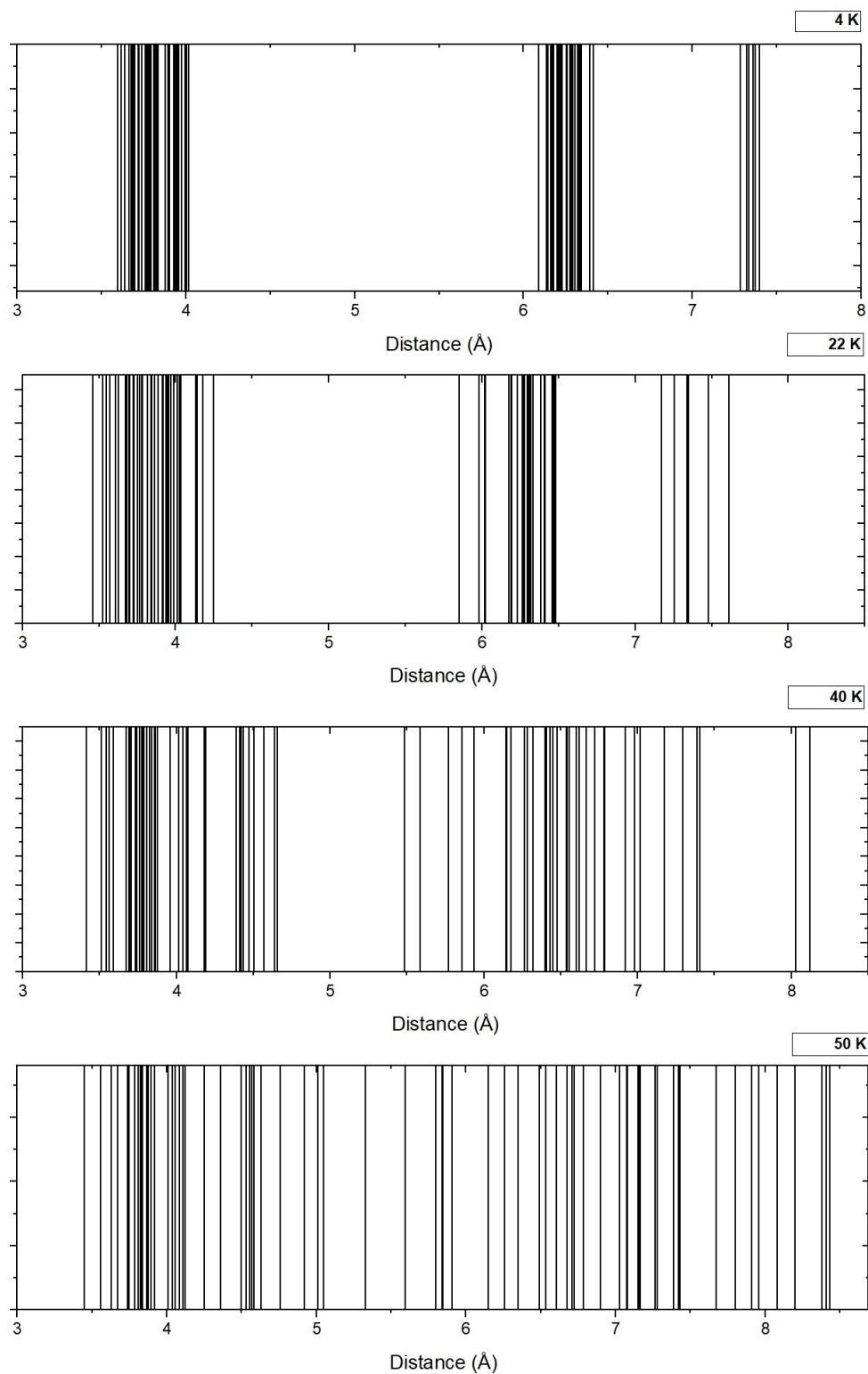


Figure 3.4: Interatomic distances in Ar_{13} at 4, 22, 34 and 50 K. The calculated h_4 , h_6 , and h_8 are: 0.542, 0.538 and 0.538 at 4 K; 0.464, 0.464 and 0.460 at 22 K; 0.296, 0.281 and 0.279 at 34 K; and 0.198, 0.176 and 0.168 at 50 K.

3.2.3 Artificial Neural Network Classifier

ANNs can learn patterns in data and do classification tasks [158, 159, 160]. Here, we aim to classify configurations as coming from a solid sample or a liquid sample. We devised a 3-layer feed-forward ANN classifier to discriminate between cluster configurations sampled in the solid (S) and liquid (L) states. The choice of input features (δ , G , and h_p) was motivated by their sensitivity to structural fluctuations associated with melting. Their detailed definitions and temperature-dependence are discussed in Sec. 3.2.2, where we show that δ highlights deviations from the global minimum structure, G is sensitive to diffusion events through nearest-neighbour to next nearest-neighbour transitions, and the h_p indicators quantify non-uniformity in interatomic distance distributions. Together, these descriptors capture complementary aspects of structure, making them well-suited to distinguish solid-like from liquid-like configurations. These features were selected after testing a broader set of candidate structural measures and were found to give the most consistent classification performance. While there is no prior work using exactly these descriptors for small cluster melting, our design was informed by general approaches in machine learning classification of phases of matter [161, 162]. A more traditional choice would be the Lindemann criterion, which has been widely used as a heuristic measure of melting in clusters and solids. However, in the present context of parallel tempering simulations with replica exchange, the Lindemann index is not practical: after configuration swaps between replicas, it is no longer possible to consistently track the same atom pair (i, j) across trajectories. This limitation motivates the use of alternative, permutation-invariant descriptors such as δ , G , and h_p , which remain well-defined under replica exchange.

Parameter	Value
Dropout Rate	0.05
Optimizer	Adam
Activation Function (Hidden)	Hard Sigmoid
Activation Function (Output)	Sigmoid
Number of Neurons (Hidden Layer)	12
Batch Size	512

Table 3.3: Optimal ANN hyperparameters selected using GridSearchCV

In training the ANN, we used batch normalization of features, sigmoid activation, dropout, and regularization options, and parameters which were found through *GridSearchCV* from *scikit-learn*, as summarized in Table 3.3. A shallow feed-forward architecture was adopted because the classification problem is relatively low-dimensional and the training dataset is moderate in size; deeper architectures were not required and risked overfitting. Preliminary tests with alternative classifiers *including logistic regression and random forests* yielded transition temperatures within approximately 5 – 10 K of those predicted by the ANN model. Across all models, performance metrics were consistently high (Receiver Operating Characteristic – Area Under the Curve (ROC AUC) ≥ 0.999 , accuracy ≈ 0.996 – 0.998 , F1 ≈ 0.996 – 0.998), indicating that the classification of solid-liquid states is largely insensitive to the specific model choice. While logistic regression achieved the lowest log-loss (0.006), the ANN classifier was retained owing to its better capacity for generalization and consistent behaviour under hyperparameter variation. These results demonstrate that the inferred transition temperatures are robust with respect to the choice of classifier and model fine-tuning.

We start by sampling configurations at the lowest temperature, T_1 , and the highest temperature T_K with fewer than 0.01% of steps giving an evaporation event, and label these configurations “S” and “L”, respectively. The classifier is trained on a subset of S and L configurations, then tested on a different subset of S and L configurations, and the classification accuracy is obtained. We then go through iterations, increasing the lower temperature from T_1 to $T_2, T_3 \dots$, each time retraining and testing the classifier, until its accuracy falls below 95% at some T_{k_s+1} : We arbitrarily designate T_{k_s} as the lower limit of the SL coexistence region. This approach is conceptually similar to the confusion scheme proposed in Ref. [161], where the critical point is inferred by sweeping over guessed labels and monitoring network performance to detect regions of classification confusion. Next we fix the lowest temperature to T_{k_s} and do a series of training and testing with upper temperature $T_K, T_{K-1}, \dots$, until we find a temperature $T_{k_\ell-1}$ where the classification accuracy is less than 95%: we designate T_{k_ℓ} as the upper limit of the solid-liquid coexistence region. We then sample configurations labelled “S” from four low temperatures $T_{k_s}, T_{k_s-1}, T_{k_s-2}, T_{k_s-3}$, and

configurations labeled “L” from four high temperatures T_{k_ℓ} , $T_{k_\ell+1}$, $T_{k_\ell+2}$, $T_{k_\ell+3}$, and do a final training and testing of the ANN classifier.

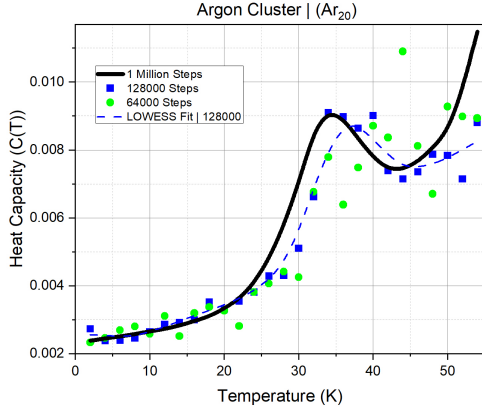
3.3 Results

Simulations were carried out for Ar_n , Si_n , Ag_n clusters, with $n = 7, 8, 10, 13, 18, 19, 20$. We focus on 20-atom clusters in discussing different ways to obtain melting points, but similar results were found at other cluster sizes. The main results reported in this section are that: (a) the values of T_c estimated from heat capacity and those estimated with W_U , δ , d^2G/dT^2 and the ANN classifier generally agree; and (b) the d^2G/dT^2 method and ANN classifier are computationally much more efficient than the other methods.

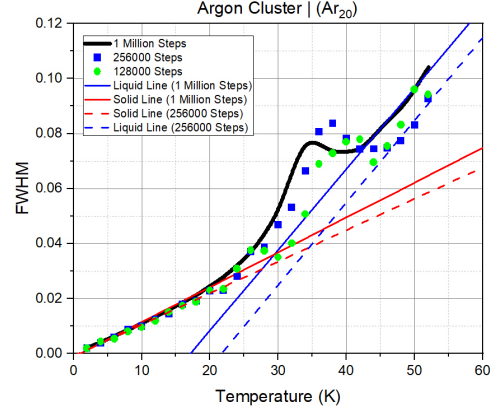
3.3.1 Argon

PTMC runs were carried out for Ar_n for 26 temperatures ranging from 2 to 54 K with a 6 – 12 Lennard-Jones potential with $\sigma = 3.3513$ and $\epsilon = 0.0123$. A peak in $C(T)$ is a well-established way to determine T_c . We did simulations with increasing number of steps until the position T_c of the heat capacity peak converged. This was achieved with a million steps, yielding $T_c = 34$ K (see the black curve in Fig. 3.5(a)). We take this T_c as a reference for assessing other methods. With 128,000 steps and a LOWESS fit to the data points we get a reasonably well-defined peak near 34 K, but with half as many steps we do not. In that sense, $N_s = 128000$ is the smallest number of simulation steps needed for a reliable T_c and is a rough measure of the “cost” of using $C(T)$ to obtain T_c . Throughout this section we will use values of N_s to characterize the cost of different methods.

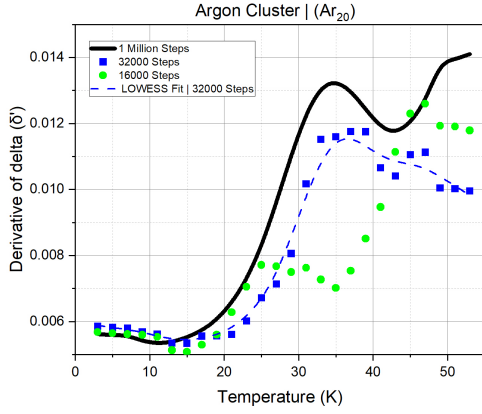
With one million steps (black curves) we see that W_U (Fig. 3.5(b)), δ (Fig. 3.5(c)), and d^2G/dT^2 in Fig. 3.5(e) all give essentially the same T_c : 34 K. The solid fraction $F_S(T)$ (Fig. 3.5(d)) has a sigmoid shape and reaches 50% at 31 K. The dotted horizontal lines show where $F_S = 95\%$ and 5%: the corresponding temperatures, T_f and T_m , are 23 K and 40 K. These are consistent with



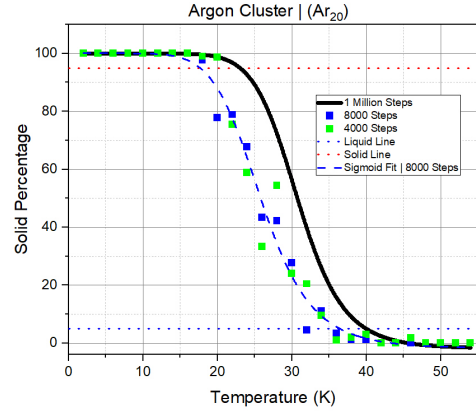
(a) Heat capacity $C(T)$ curve



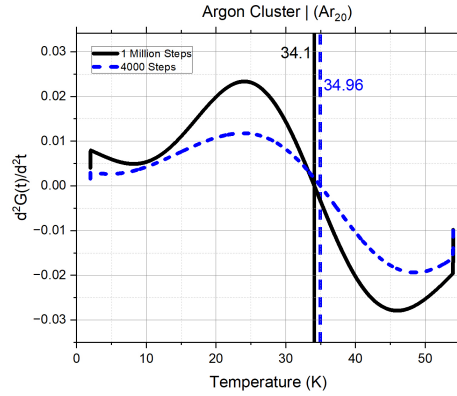
(b) Width of the potential energy distribution



(c) Derivative of δ with respect to temperature



(d) Percentage of configurations classified as solid



(e) Second derivative of G with respect to temperature

Figure 3.5: Temperature dependence of properties used to detect melting for Ar_{20} : (a) $C(T)$, (b) W_U , (c) $d\delta/dT$, (d) solid fraction F_S , and (e) inflection point d^2G/dT^2 . The solid black line corresponds to simulations with one million steps; blue squares show results from the shortest simulations ($N_{\min}$ steps) used to estimate T_c ; green circles indicate simulations with $N_{\min}/2$ steps. Dashed lines represent LOWESS linear or sigmoid regression fits.

	$C(T)$	W_U	$d\delta/dT$ (Å)	F_S	d^2G/d^2T
Ar ₇	22	18 - 34	21	18 - 36	24
Ar ₈	-	20 - 34	25	18 - 36	25
Ar ₁₀	24	20 - 32	23	20 - 36	24
Ar ₁₃	34	28 - 38	34	20 - 40	34
Ar ₁₈	32	24 - 36	31	24 - 38	33
Ar ₁₉	32	26 - 38	33	24 - 38	33
Ar ₂₀	34	22 - 42	34	23 - 40	34

Table 3.4: Melting points (T_c) and SL coexistence range (T_f – T_m) for Ar_{*n*} modeled with a Lennard-Jones potential.

the width and shape of the peak in heat capacity (it extends from roughly $T_f = 22$ to $T_m = 44$ K) and the peak in $\delta(T)$. The $W_U(T)$ curve also gives information about the range of temperatures where solid and liquid phases coexist. It can be fitted with two straight lines, one for temperatures below 22 K, the other, above 42 K (3.5 (b)). Many properties that change during melting may give equally valid, but different, information and estimates of T_c , T_f , and T_m . For Ar₂₀ we see very good agreement between determinations of T_c , T_f , and T_m based on $C(T)$, W_U , δ , F_S and G . This is not always the case, as we will show in the discussion of Si and Ag clusters.

The smallest number of steps “ N_s ” for a reliable determination of T_c using $C(T)$, δ and G are 128000, 32000 and 4000, respectively (see blue squares in Fig. 3.5). The N_s values for a rough estimate of T_f and T_m are 256000 for W_U and 8000 for F_S . It is clear that G and F_S give a big computational advantage over the other ways of determining T_c , T_f , T_m .

Table. 3.4 shows T_c estimates derived from the heat capacity, $d\delta/dT$ and d^2G/dT^2 , and the SL coexistence range T_f – T_m obtained with W_U and F_S . The center of $[T_f, T_m]$ intervals can be taken as rough estimates for T_c . We see very good agreement between all five determinations of T_c except at $n = 7, 8$.

3.3.2 Silicon

The curves of $C(T)$, W_U , $d\delta/dT$, F_S , and d^2G/dT^2 vs T for Si₂₀ are in Fig. 3.6. The longest simulation (40 million steps), used as reference, gives similar determinations of T_c by analyzing

	$C(T)$	W_U	$d\delta/dT$ (Å)	F_S	d^2G/dT^2
Si ₇	2067	1867 - 2288	1917	1448 - 2532	2100
Si ₈	2362	2257 - 2472	2344	1744 - 2966	2350
Si ₁₀	2803	2949 - 3434	2733	748 - 2174	3169
Si ₁₃	872	552 - 917	767	676 - 1124	717
Si ₁₈	1182	1244 - 1775	1153	872 - 1603	1158
Si ₁₉	2292	2061 - 2510	2309	1015 - 1964	2295
Si ₂₀	1375	1068 - 1666	1250	755 - 1584	1269

Table 3.5: Melting points (T_c) and SL coexistence range (T_f – T_m) for Si_{*n*} modelled with the LJV4 potential.

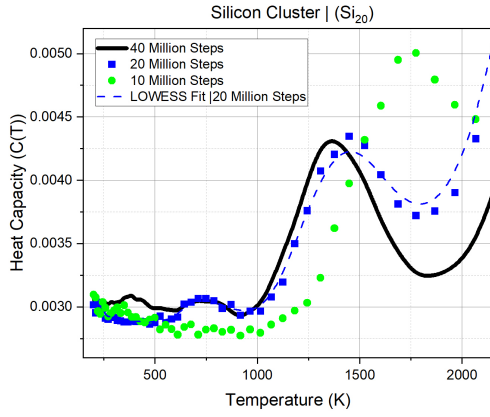
heat capacity (1375 K), $d\delta/dT$ (1250 K), and d^2G/dT^2 (1269 K), but somewhat different values of T_f and T_m from W_U (1068 – 1666 K) and F_S (755 – 1584 K). The figure also shows, for each method, the curves obtained with the smallest number of steps N_s giving results close to convergence and to the reference. Here, too, F_S and d^2G/dT^2 give nearly converged results with much fewer simulation steps than the other three methods.

Table 3.5 shows results for Si clusters of different sizes. The T_c values obtained with $C(T)$ and δ , and the mean of T_f and T_m from W_U , are in close agreement. These three methods give the same order of increasing T_c : Si₁₃, Si₁₈, Si₇, Si₁₉, Si₈, Si₁₀. The center of intervals from F_S agree with the rest except for Si₁₀ and Si₁₉, where they are lower. The T_c values obtained from d^2G/dT^2 agree with those from $C(T)$, δ , and W_U except for Si₁₀ where it overestimates by roughly 350 K relative to the others.

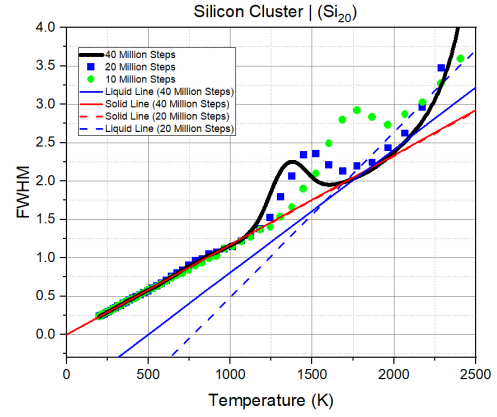
3.3.3 Silver

For Ag₂₀, the converged values of T_c obtained with 40 million simulation steps, are 468 K ($C(T)$), 506 K (W_U , middle of S–L coexistence interval), 473 K ($d\delta/dT$), 516 K (d^2G/dT^2), and 473 K ($F_S = 50\%$). The T_f – T_m interval is approximately 262–750 K using W_U , and 370 – 628 K using F_S . The middle of the S-L coexistence region is determined by F_S , $(262 + 750)/2 = 473$, gives an estimate of T_c in good agreement with the other four.

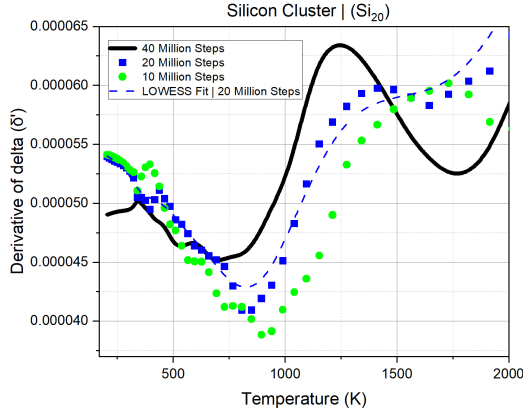
The smallest number of simulation steps needed to get nearly converged curves and T_c (or T_f ,



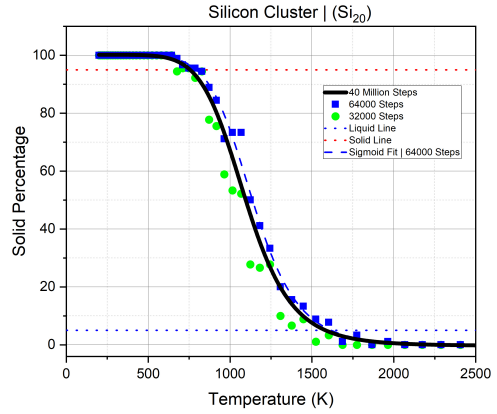
(a) Heat capacity ($C(T)$) curve



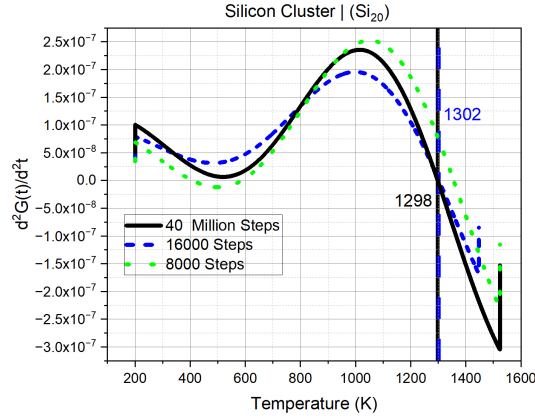
(b) Width of the potential energy distribution



(c) Derivative of δ with respect to temperature

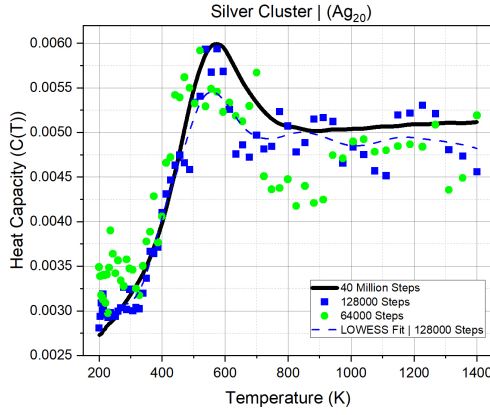


(d) Percentage of configurations classified as solid

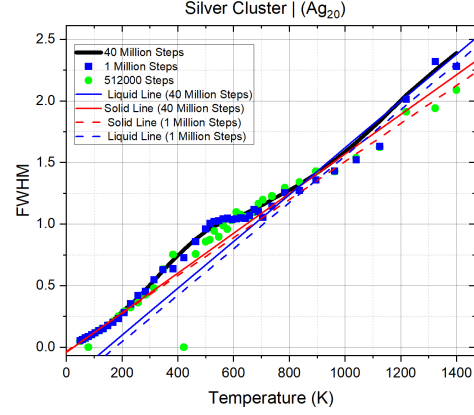


(e) Second derivative of G with respect to temperature

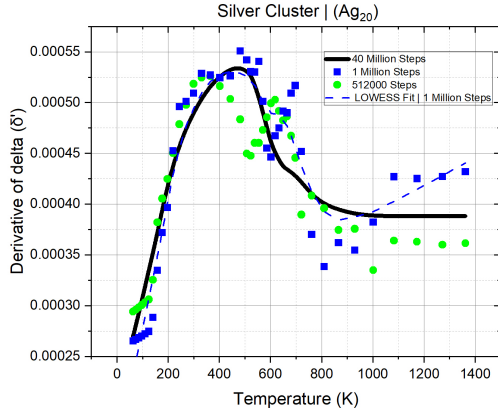
Figure 3.6: Temperature dependence of properties used to detect melting for Si_{20} : $C(T)$, W_U , $d\delta/dT$, solid fraction F_S , and inflection point d^2G/dT^2 . The solid black line is for simulations with 40 million steps; blue squares are for the shortest simulations ($N_{\min}$ steps) used to estimate T_c ; green circles are for simulations with $N_{\min}/2$ steps; dashed lines show a LOWESS linear or sigmoid regression.



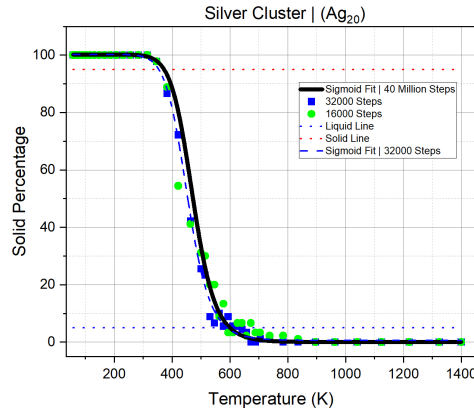
(a) Heat capacity ($C(T)$) curve



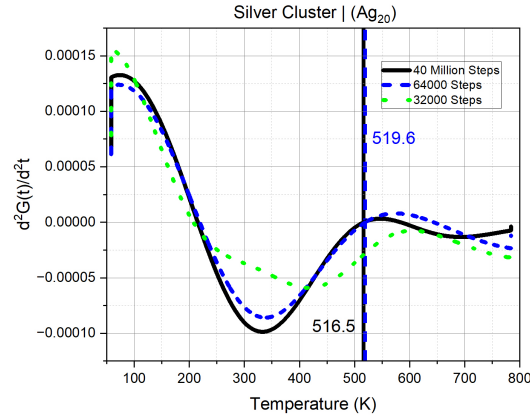
(b) Width of the potential energy distribution



(c) Derivative of δ with respect to temperature



(d) Percentage of configurations classified as solid



(e) Second derivative of G with respect to temperature

Figure 3.7: Temperature dependence of properties used to detect melting for Ag_{20} : $C(T)$, W_U , $d\delta/dT$, solid fraction F_S , and inflection point d^2G/dT^2 . The solid black line is for simulations with 40 million steps; blue squares are for the shortest simulations ($N_{\min}$ steps) used to estimate T_c ; green circles are for simulations with $N_{\min}/2$ steps; dashed lines show a LOWESS linear or sigmoid regression.

	$C(T)$	W_U	$d\delta/dT$ (Å)	F_S	d^2G/d^2T
Ag ₈	328	267 - 470	282	285 - 705	312
Ag ₁₂	399	294 - 555	334	313 - 699	316
Ag ₁₆	427	300 - 613	322	374 - 672	364
Ag ₂₀	468	262 - 750	473	370 - 628	516

Table 3.6: Melting points (T_c) and SL coexistence range (T_f – T_m) for Ag_{*n*} modelled with a tight-binding potential modelling metallic bonding.

T_m) are 1 million for $C(T)$, 1 million for W_U , 1 million for $d\delta/dT$, and only 32000 for F_S and 64000 for d^2G/dT^2 . Again, there appears to be a significant computational advantage to using F_S and d^2G/dT^2 relative to other methods. This makes the F_S and d^2G/dT^2 methods attractive for use with first-principles simulations or the study of large clusters described with complex ML potentials.

The agreement between the five methods is not as good for the smaller silver clusters ($n = 8, 12, 16$), with discrepancies in T_c of 10% to 25%. The better agreement among methods seen for Ag₂₀ could be due to the closed electronic shell of Ag₂₀ (a feature reproduced by our tight-binding model), or the fact that Ag₂₀ is closer to the bulk limit where all indicators of melting are expected to converge to a common value of T_c .

The tight-binding potential we used is in error, relative to DFT, by 4 to 9 meV/atom, corresponding roughly to errors of 50 to 150 K. This is not very accurate: a better potential would be needed to model silver clusters realistically. But it is sufficiently accurate to draw a few conclusions about silver clusters. First, the position of the peak in heat capacity (and the melting-like transition) for these clusters are in a range from 250 to 650 K roughly, and it increases with size. This is far below the bulk melting of silver, 1235 K. Second, the width of the peak in $C(T)$, and other estimates of $T_m - T_f$, is roughly 200 to 300 K, which is very large. (The heat capacity of Ag₈ is flat at higher temperatures; there is no well-defined peak.) Third, we see no evidence of premelting in any of the four Ag_{*n*} clusters.

We observe two types of $G(T)$ curves among the different clusters. Examples of the first type are Ar₁₃ (Fig. 3.3), Ar₂₀ (Fig. 3.5(e)), and Si₂₀ (Fig. 3.6(e)). For those, G and dG/dT increase

smoothly with T , and the second derivative of G goes from a large positive value to a large negative value by crossing zero at a well-defined temperature $T_{c,3}$ below $T_{evap.}$. We take $T_{c,3}$ as an estimate for T_c . An example of the second type is Ag_{20} (Fig. 3.7(e)). In those cases, d^2G/dT^2 goes abruptly through zero at a temperature well below T_c , and approaches zero and becomes quite flat at a higher temperature that is near T_c .

3.4 Conclusion

We discussed four temperature-dependent properties, besides the heat capacity $C(T)$, that are easily calculated from the output of atomistic simulations for characterizing melting-like transitions. They are: W_U , the width of the potential energy distribution; δ , the mean dissimilarity of configurations to the global minimum (and its first derivative); G , the effective number of atom pairs separated by a distance close to the average of the first two peaks in the pair distribution function (and its second derivative); and $h(T; p)$, a measure of non-uniformity for $g(r)$. We also used a classifier that takes δ , G , and ten variants of h as inputs and calculates the fraction F_S of configurations of “solid” type. The heat capacity $C(T)$, δ , and G yield estimates of “melting points”, T_c , whereas analysis of $W_U(T)$ and $F_S(T)$ curves both give a range, T_f – T_m . The mean of T_f and T_m can be taken as determinations of T_c from W_U , and from F_S .

Numerical tests on 18 cluster models characterized by van der Waals, covalent, and metallic bonding show that peaks in $C(T)$ and $d\delta/dT$, and inflection points in G , give similar T_c values. The agreement between the three tends to be better for Ar_n and Si_n , and for bigger clusters. The T_c derived from W_U are close to those from $C(T)$, δ , and G except for Si_{18} and Ag_8 . The T_c derived from F_S is not always consistent with the others.

Agreement between the two estimates of T_f and T_m is very good for Ar_n clusters, good for Ag_n , and poor for Si_n . We speculate that the poor agreement for Si_n and the smallest Ag_n cluster is due, at least partly, to the inherent complexity of phase transitions in these small clusters, which often melt over a wide range of temperature. The ratio of the width of the peak in heat capacity to its

position is at least 0.4 in Ar_{20} , Si_{20} , and Ag_{20} , and it is bigger in some of the other clusters. It is to be expected that related, but different, phenomena accompanying melting are not all triggered at the same temperature. Tracking several properties, such as the ones described here, allows a fuller description of melting-like transitions in clusters. It must be pointed out that many other indicators of melting have been described before [133, 134, 42, 151, 152, 153].

We found a significant computational advantage in using d^2G/dT^2 for determining T_c , and a classifier and F_S for determining T_f and T_m . In numerical tests, they give nearly converged values with several simulations steps that are one to three orders of magnitude smaller than what is needed for the heat capacity C , the width of the potential energy distribution W_U , or the similarity to the GM configuration δ . This speed-up could help study bigger clusters or calculate more accurately energies by first-principles or with complex ML potentials.

Chapter 4

Melting Transitions in Small Aluminum Clusters Simulated with Energies Approaching DFT Accuracy.

Abstract

We present a computational framework to predict melting points of atomic clusters with near-DFT accuracy, combining global optimization, single-point TPSS/SDD energies, and an equivariant deep learning potential (Allegro). Trained on 3,000–5,000 configuration’s DFT energies spanning solid–liquid states, the model achieves validation errors below 10 meV/atom. Parallel tempering Monte Carlo with 35 temperature replicas and 10^6 steps enables efficient sampling over 35–40 million energy evaluations with verified convergence. For Na_{20} , a melting point of 250 ± 30 K is obtained, consistent with reported 200–300 K values, well below the bulk melting temperature of 371 K. For aluminum clusters, cationic Al_n^+ ($n = 9$ –16), neutral Al_n ($n = 12$ –14), and anionic Al_n^- ($n = 12$ –14) show nonmonotonic size- and charge-dependent melting. Al_{11-16}^+ clusters melt above the bulk 933 K, while Al_9^+ and Al_{10}^+ melt at 305 K and 710 K, respectively, suggesting enhanced geometric shell stabilization. This framework offers an efficient and transferable method for probing finite-size phase transitions in any small clusters with DFT-level accuracy.

4.1 Introduction

Melting temperatures in atomic clusters generally decrease with decreasing size, a trend attributed to their high surface-to-volume ratio [163]. Below $n \lesssim 50$, however, the melting behaviour becomes irregular due to the increasing influence of quantum and electrostatic effects. These transitions are relevant for nanoscale applications in catalysis [164], materials science [165], and biondiagnostics [166].

Sampling many cluster configurations remains challenging due to statistical noise and the limitations of empirical interatomic potentials. Accurate modelling requires quantum methods such as density functional theory (DFT), but these scale poorly with system size. Parallel tempering Monte Carlo (PTMC) and machine-learned interatomic potentials provide computationally efficient alternatives for sampling configuration space and estimating thermodynamic properties with high accuracy. These methods are particularly valuable given the limited experimental access to isolated clusters, where structural and thermal characterization remains difficult [167, 168]. While spectroscopy and calorimetry have been applied, experimental data on small clusters are sparse.

In this study, we investigate the melting behaviour of aluminum clusters (Al_n) using PTMC simulations and a machine-learned neural network potential. Aluminum clusters offer an ideal test system for several reasons. First, experimental melting temperatures and heat capacities are available for several small Al clusters, enabling direct validation of simulations [169, 170]. Second, theoretical studies show that structural and thermodynamic properties of aluminum clusters are strongly charge-dependent [171, 172], allowing meaningful benchmarking of simulation accuracy. Third, aluminum is widely used in aerospace, electronics, and catalysis, and understanding its nanoscale thermodynamics is crucial for designing nanoscale materials and ensuring thermal stability. Experimental studies have reported melting points and heat capacities for Al clusters with $n = 16\text{--}342$, but melting trends become irregular below $n < 100$ and measurements lose resolution at smaller sizes [169, 170]. Recent work using deep neural network-based potentials has modelled Al clusters up to 342 atoms, with melting temperatures in agreement with experiment for sizes $n \gtrsim 50$ [173]. We focus instead on smaller clusters ($n = 9\text{--}16$), where quantum effects and

charge dependence are more significant, and accurate simulation remains a challenge.

To address this, we developed a simulation framework that integrates global optimization, DFT energy evaluations, and an Allegro neural network potential based on an E(3)-equivariant graph architecture [174]. We tested the framework on Na_{20} and applied it to Al_n clusters: cations with $n = 9\text{--}16$, neutrals with $n = 12\text{--}14$, and anions with $n = 12\text{--}14$. Melting temperatures were determined using four indicators: the heat capacity $C(T)$, potential energy distribution $W_U(T)$, geometrical order parameter $d\delta/dT$, and the solid fraction F_s obtained from an artificial neural network (ANN) classifier. DFT-level simulations of melting in small, charged clusters were performed using well-converged Monte Carlo sampling, allowing for a detailed investigation of melting transitions.

4.2 Computational Methods

4.2.1 Generating data sets of geometries and energies

The neural network potential for a n -atom cluster is fitted to a set of configurations X_j and energies U_j : X_j is a vector of $3n$ cartesian coordinates, and U_j is an energy calculated with the Gaussian software by Density Functional Theory (DFT) with TPSS exchange-correlation and a SDD pseudopotential and basis set. For Na_{20} , we used the same method as Chiriki *et al.* [175], PBE/def2-TZVP DFT, to allow a more direct comparison and validation of our procedure. In order to get a potential suitable for simulating melting, the data set should include configurations close to the global minimum (GM) X_0 , with energy near U_0 , and others that sample a wide range of geometries with energy up to $U_0 + U_h$. We do this by global optimization as described below.

Random configurations are generated, each time with the first atom at the origin. The $n - 1$ other atoms are added, one at a time, by taking a random point x inside a sphere of radius r_a centered at the origin, where r_a is the atomic radius of Al. The k 'th atom is placed at a random position, far away, then moved by small increments toward x until the shortest distance to one of the previous $k - 1$ atoms is smaller than $2r_a$. After adding the last atom, coordination numbers

(CN) of the atoms are calculated using a simple distance criterion. If the smallest CN is smaller than 3, the configuration is rejected and a new attempt is made. This is repeated until we have N initial configurations. For every atom i in a configuration, the mean distance to its neighbors, $\bar{r}_i$, is calculated. The DFT energies for the N configurations are calculated and saved. For every configuration, four parameters are calculated and saved: the smallest and biggest atomic CN, and the smallest and biggest $\bar{r}_i$. This gives a dual representation of configurations: cartesian coordinates X , and a set of four descriptors p ($\text{CN}_{\min}, \text{CN}_{\max}, \bar{r}_{\min}, \bar{r}_{\max}$).

Next come $(M - 1)$ cycles where N new configurations are created each time. At cycle m , a configuration X_r is picked at random among the mN previously saved with energy bias (higher probability of selecting a lower energy configuration) and a random set of parameters p_q is picked, also with energy bias ($r \neq q$). The configuration is modified by moving every atom randomly over a distance smaller than r_a . Then, an objective function F is calculated by summing n terms, one for each atom. Each term is zero if the CN and $\bar{r}$ of that atom is inside the interval specified in p_q . Otherwise, a penalty proportional to the square of the distance to the nearest limit of the interval gets added to F . In essence, F depends on how many atoms “break the rules” specified by p_q and on how much they deviate from them. A rough minimization of F is done by simulated annealing. The result is a new configuration that inherits characteristics from two earlier solutions, r and q , that were selected with an energy bias. The coordinates, descriptors, and DFT energy of the new configuration are obtained and saved.

For our purpose, it is not necessary to find the GM. But it is essential to create a diverse set of configurations, most of which have energy below $U_0 + U_h$. This is accomplished by gradually increasing the energy bias from very weak in the first cycle (to promote diversity) to very strong near the end (to increase the probability of finding the GM). The MN configurations and energies (X_j, U_j) are then screened to remove those with energy above $U_0 + U_h$. A suitable *approximate* upper energy is $U_h = (3/2)nk_B T_h$, where T_h is the highest temperature in the simulation. The configurations remaining after screening are used to fit the potential.

Finally, we perform a small number of iterations (no more than two), in which we first carry out

a PTMC simulation with the ANN potential, then select a few hundred configurations (including the one with the lowest ANN energy), and calculate their DFT energies. These new data points are added to the training set before refitting the ANN model. This iterative procedure ensures that the global minimum identified by the ANN is consistent with the one predicted by DFT. We refer to this dataset generation and sampling as **GLOBO** hereafter.

4.2.2 Neural Network Potential

To enable accelerated energy predictions during Monte Carlo replica exchange simulations, we trained an empirical neural network potential that benefits from direct GPU acceleration, favourable batch-wise prediction efficiency, and significantly improved scaling with system size, with minimal loss of accuracy compared to direct *ab initio* calculations.

For this work, we utilize the *Allegro* architecture, a graph neural network potential that is both strictly local and equivariant [174, 176]. Briefly, Allegro predicts potential energies (as well as optional vector and tensor quantities such as atomic forces and stresses) from N input configurations of M atoms specified by their cartesian coordinates, $\vec{R} \in \mathbb{R}^{3NM}$, and their atomic numbers, $\vec{Z} \in \mathbb{R}^{NM}$. Each configuration is represented by a 3D cartesian graph, whose nodes are atoms and whose edges are pairwise distances. The features of the nodes and edges are transformed by passing through collections of *update layers*, or *interaction blocks*, in the network, as described below. We refer the reader to the work of Allegro’s original authors for finer details [174].

In the following discussion, we use superscripts to denote quantities after passing through the l -th interaction block of the network. Additive biases are omitted for clarity in all linear transformations (represented by W). Allegro transforms initial inputs into sets of scalar and equivariant features. The initial scalar (two-body) node features, $\vec{X}$, are generated from a nonlinear transformation of combined atomic numbers $\vec{Z}$ and pairwise distances $\vec{R}_{ij}$:

$$X_{ij}^{l=0} = \sigma(W_{two-body}(Z_{i,ONE-HOT} || Z_{j,ONE-HOT} || B(R_{ij}))) \quad (4.1)$$

where W_{embed} is a linear transformation that is parameterized during model training, $Z_{i,ONE-HOT}$ represents a one-hot encoding of a central atom i and its neighbouring atoms, $||$ represents direct vector concatenation, $B(R_{ij})$ represents the projection of pairwise distances on a basis of K (enveloped) Bessel functions, and σ represents an element-wise non-linear function. The initial equivariant features are, in turn, produced using these initial scalar features, but instead involve a projection of distances onto the spherical harmonics, weighted by the previously computed two-body scalar features:

$$V_{ij,nlp}^{L=0} = w_{ij,nlp}^{L=0} \vec{Y}_{ij,lp} \quad ; \quad w_{ij,nlp}^{L=0} = W_{embed} X_{ij}^{L=0} \quad (4.2)$$

where the scalar two-body weights, $w_{ij,nlp}^{L=0}$, are produced through a linear embedding transformation, W_{embed} , over spherical harmonic numbers $\{n, l, p\}$.

Allegro defines its update function U by (a) embedding the central atom’s environment via a machine-learned equivariant tensor product, (b) aggregating information from neighbouring atoms, and (c) using the output to update both scalar and equivariant features, which are then passed as inputs to the next tensor product layer. By exploiting the bilinearity of the tensor product, step (b) can be compactly expressed as a single tensor product over a sum of weighted spherical harmonics evaluated over all neighbours of the central atom, effectively representing the embedding of the atom’s local environment as:

$$V_{ij,n,(l_1,p_1,l_2,p_2) \rightarrow (l_{out},p_{out})}^L = V_{ij,n,l_1,p_1}^{L-1} \otimes \left(\sum_{k \in \mathcal{N}_i} w_{n,l_2,p_2}^{ij,L} Y_{l_2,p_2}^{ik} \right) \quad (4.3)$$

where, $\mathcal{N}_i$ represents the *neighborhood* of the i^{th} central atom, and

$$w_{n,l_2,p_2}^{ij,L} = MLP_{embed}^L(x^{ik,L-1})_{n,l_2,p_2} \quad (4.4)$$

where MLP represents a learnable, multilayer perceptron. The update to the scalar features, which incorporates a residual addition with the scalar features of the previous layer, is defined as:

$$x^{ij,L} = x^{ij,L-1} + MLP_{scalar}^L \left(x^{ij,L-1} \parallel \bigoplus_{(l_1,p_1,l_2,p_2)} V_{ij,n,(l_1,p_1,l_2,p_2) \rightarrow (l_{out}=0,p_{out}=1)}^L \right) \cdot u(r_{ij}) \quad (4.5)$$

Where $\bigoplus$ represents concatenation over all tensor product paths (by default, all allowable paths that are consistent with $l_{out} \leq l_{max}$). The equivariant features for the next layer are also updated according to a linear combination:

$$V_{n,l,p}^{ij,L} = \sum_{n' \in (l_1,p_1,l_2,p_2)} w_{n,n',(l_1,p_1,l_2,p_2) \rightarrow (l,p)}^L V_{n',(l_1,p_1,l_2,p_2) \rightarrow (l,p)}^{ij,L} \quad (4.6)$$

After the final tensor product layer, a prediction of the pairwise system energies is predicted with an output MLP:

$$E_{ij} = MLP_{output}(x^{ij,L_{tot}}) \quad (4.7)$$

In this work, we trained system-specific empirical Allegro models for predicting energies only. It is worth noting that single, transferable Allegro models may be trained to predict energies on arbitrary systems. However, strategies for creating accurate transferable models represent active research and are likely heavily influenced by training dataset composition, training routines/strategy, and computationally expensive hyperparameter searches [177]. It is also well known that neural network potentials typically extrapolate poorly on unseen/distorted geometries (such as those that may be encountered if the model is used for molecular dynamics or Monte Carlo simulations) [178, 179]. To this end, and following similar other works, we add an empirical ZBL repulsion term (depending only on atomic numbers) that prevents poor, extrapolative energy predictions in regions where atomic distances are smaller than those seen in the training dataset by enforcing asymptotically infinite interaction energies [176, 180]. The Allegro model will be referred to as the “NN potential” for ease.

4.2.3 Criteria used to identify melting

Unlike bulk solids, clusters melt over a *range* of temperatures from T_f (freezing) to T_m (melting) centered around a temperature we denote T_c . Melting-like transitions and T_c are often identified by a peak in the heat capacity curve, $C(T)$, at T_c [181]. Another useful criterion is obtained from the width (full width at half maximum, FWHM) of the probability function of the potential energy distribution, denoted here by $W_U(T)$. It was observed that $W_U(T)$ increases suddenly over a range of temperatures corresponding to T_f and T_m [181]. The curve $W_U(T)$ can be fitted to a straight line for $T < T_f$ and $T > T_m$, but not when $T_f < T < T_m$. This gives a sensitive way for determining T_f and T_m . Both $C(T)$ and $W_U(T)$ are energy-based indicators. Various geometric criteria have been proposed to detect melting and estimate T_c , including the Lindemann criterion (interatomic distance fluctuations that exceed 15%) [182] and shape descriptors (clusters often become quasispherical upon melting).

The geometric criteria used here are calculated by sorting the $N = n(n - 1)/2$ interatomic distances (n atom cluster) in each configuration into ascending order. The first of these, denoted as δ , is a weighted root-mean-square deviation between the ordered distances in the configuration at temperature T and those in GM. The peak of the derivative of $\delta(T)$ provides an estimate of T_c . This feature is also used as an input to the ANN classifier. The second one is G , closely related to the integral of the pair distribution function, $g(r)$, over a small range $[r_m - \epsilon, r_m + \epsilon]$. Here, r_m is the average of the positions of the first two peaks in $g(r)$, i.e., the distances r_1 and r_2 between nearest and next-nearest neighbours, and ϵ is on the order of $(r_2 - r_1)/20$. This value is included as an input to the ANN. An inflection point in $d^2G(T)/dT^2$ gives a temperature T_G , which in some cases coincides with T_c , and may serve as a complementary structural feature to other melting criteria. The third indicator is the solid fraction F_s , defined as the output of a three-layer feed-forward ANN classifier trained to discriminate between solid-like and liquid-like configurations. The ANN takes as input the values of δ , G , and ten permutation-invariant non-uniformity descriptors h_p ($p = 1-10$), which quantify differences between successive sorted distances normalized by the mean nearest-neighbour length. The classifier is trained using the confusion scheme of van Nieuwenburg et

al. [161]. The ANN architecture is adapted from Ref. [181], with a revised labelling protocol. Temperatures below a chosen T_{solid} are labelled as solid, and those above T_{liquid} as liquid, rather than selecting a fixed number of points in each regime. This approach may result in class imbalance if one phase dominates the sampled temperature range. To compensate, class weights are applied during training using the Keras framework, assigning a higher weight to the minority class to mitigate the bias introduced by the imbalance. The temperature dependence of F_s is then used to estimate T_f and T_m using the [95%, 5%] threshold criterion. These geometric descriptors were found to be sensitive indicators of melting-like transitions [181].

4.2.4 DFT-Accuracy Neural Network-Monte Carlo Framework

Figure 4.1 outlines the framework. Melting transitions cause atomic rearrangements that reshape the potential energy surface (PES); thus, a dynamic retraining protocol is employed. Structural diversity in training data is preserved by integrating a sampling–retraining loop triggered by model errors during PTMC simulations.

Initial geometries are generated using GLOBO and filtered based on a $4eV$ energy cutoff from the lowest-energy structure. This restricts sampling to energetically relevant regions of the potential energy surface (PES). DFT single-point calculations are performed using TPSS-TPSS/SDD in Gaussian 16 [2], with distributed GPU jobs. The initial dataset (~ 2000 structures) is converted into '.npz' format for Allegro.

The NN potential employs an E(3)-equivariant local convolutional architecture [174] with continuous filter parameterization acting on local neighbor environments, using a radial cutoff of $r_{\text{cut}} = 8 \text{ \AA}$, spherical harmonics up to $l = 2$, a batch size of 32, and a per-atom MSE loss on total energy. The learning rate is adapted via a ReduceLROnPlateau scheduler. Training is performed on NVIDIA A100 GPUs. If Training energy MAE $< 10 \text{ meV}$, the model is deployed via a PyTorch–Flask inference server; else, the loop repeats with new data. The trained model drives PTMC simulations (100,000 steps, 20 temperatures) on an AMD EPYC CPU cluster. To handle atom evaporation at high temperatures, configurations in which any atom moves beyond a cutoff

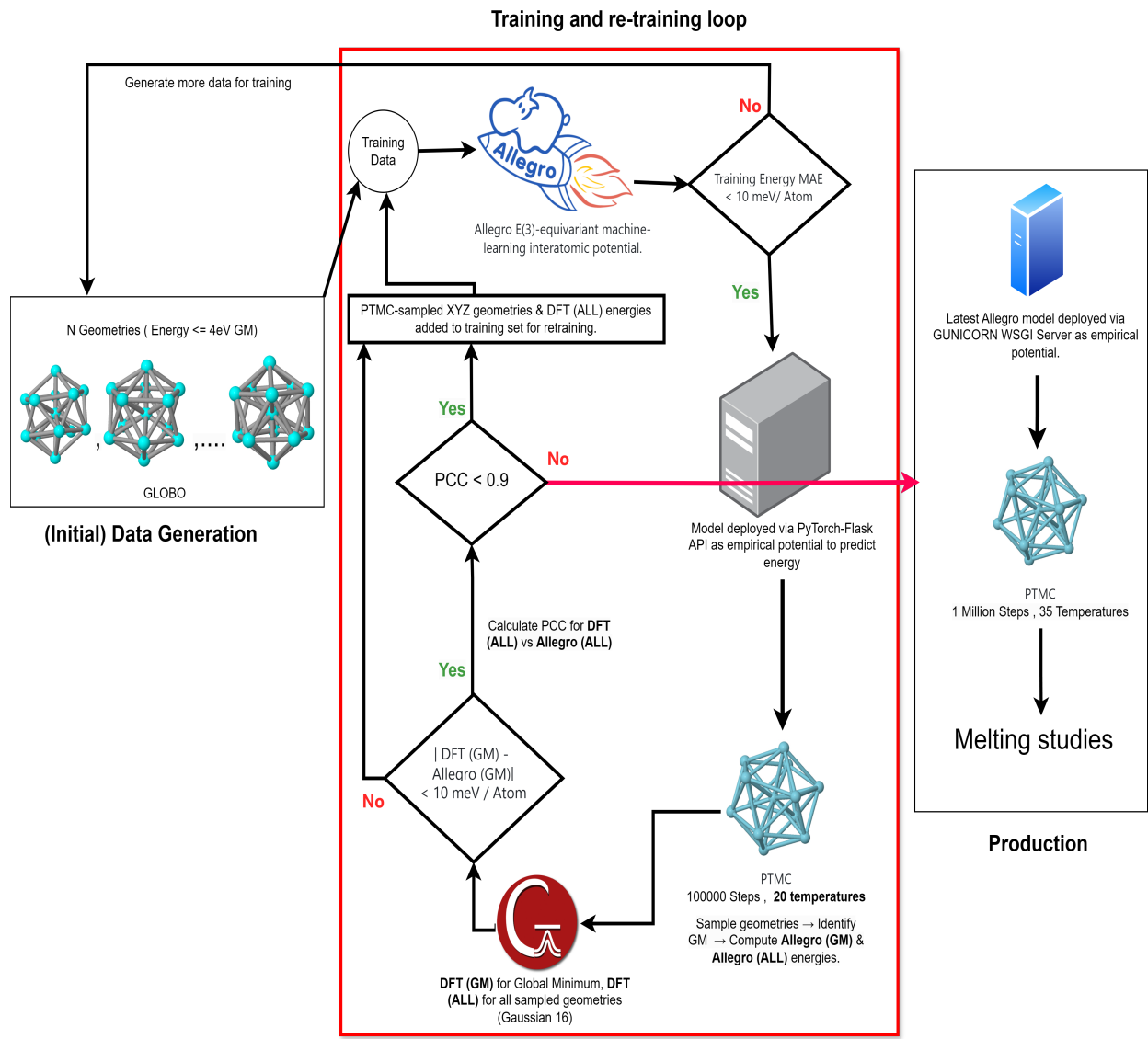


Figure 4.1: Flowchart of DFT-Accuracy Neural Network-Monte Carlo Framework

radius from the cluster center are replaced with the most recent valid configuration. Simulations are discarded entirely if such evaporation events occur in more than 0.01% of total Monte Carlo steps. Each MC configuration is evaluated using the trained neural network potential; approximately 1000 structures, including the global minimum (“Allegro (GM)”), are passed to DFT for benchmarking. If the Allegro (GM) energy deviates from DFT by more than 10 meV, retraining is triggered. If GM energies agree (within 10 meV), the Pearson correlation coefficient (PCC) is computed over all sampled geometries. A $PCC < 0.9$ triggers retraining; otherwise, the model is promoted to

production and served via Gunicorn with multiple workers.

A final PTMC run (1,000,000 steps, 35 temperatures) is used for thermodynamic analysis. $C(T)$ and FWHM distributions are computed from ensemble data along with the geometric features; Allegro (GM) is revalidated via DFT. The model incorporates ZBL short-range repulsion to maintain stability in unexplored regions of the potential energy surface (PES). Continuous DFT feedback and retraining ensure generalizability across Al_n^q clusters (q = neutral, cationic, anionic) with no additional hyperparameter tuning. The total uncertainty in melting temperature (T_{melt}) arises from four sources: PTMC sampling, LOWESS fitting, error in the DFT method (TPSS/SDD), and Allegro MAE. The combined uncertainty, calculated via quadrature, is estimated as $\pm(20\text{-}100)$ K.

4.3 Result and Discussion

We used the methods of section 4.2 to estimate T_c , T_f and T_m for Na_{20} , Al_n^+ ($n = 9\text{-}16$), Al_n ($n = 12\text{-}14$) and Al_n^- ($n = 12\text{-}14$). The inflection point T_G from d^2G/dT^2 is also reported in Table 4.1 but only coincides with T_c in only 7 of 14 cases. Possible reasons include limited temperature resolution near melting, numerical instability from SVR-based derivatives, or atomic swapping within motifs such as icosahedra, which changes neighbour identities while preserving overall geometry. This result will not be discussed further below. We first discuss Na_{20} results that were used to validate the computational approach, and then Al_{16}^+ because it is the smallest aluminum cluster, where simulations can be compared to experimental data data [169, 170]. The remaining sections show the results of small Al clusters of varying sizes and charge states.

4.3.1 Na_{20} and validation of the method

Table 4.1 shows T_c obtained from the heat capacity and derivative of δ , and $[T_f, T_m]$ obtained from $W_U(T)$ and F_s . The T_c found from $C(T)$ for Na_{20} , 250 K, agrees with the one reported by Chiriki *et al.* [175] who did MC simulations with a feed-forward NN potential fitted to a different variant of DFT. It is also consistent with experimental results on larger Na_n clusters [183, 184]

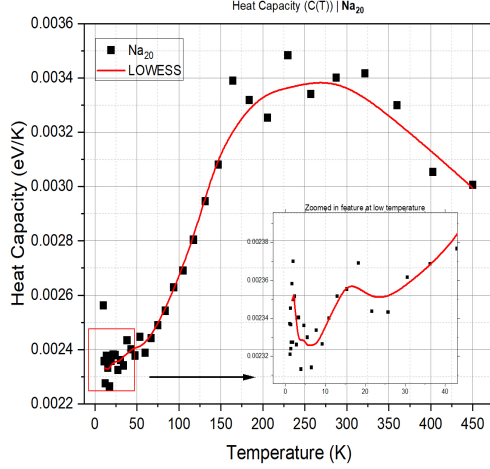
Cluster	T_c (K) from C(T)	T_f, T_m (K) from W_U	T_c (K) from δ	T_f, T_m (K) from F_S	T_G (K) from d^2G/dT^2	U_0 (eV) (Allegro)	U_0 (eV) (DFT)	MAE (meV/atom) Model Accuracy	R^2
Na ₂₀	250	117, 257	157	145, 283	229	-15.137	-15.094	1.60	0.978
Al ₉ ⁺	322	212, 358	231	179, 586	305	-17.381	-17.411	9.07	0.965
Al ₁₀ ⁺	670	397, 1252	540	479, 1135	618	-20.403	-20.364	5.52	0.989
Al ₁₁ ⁺	1100	916, 1543	1149	804, 1660	1010	-23.187	-23.154	6.30	0.991
Al ₁₂	343 1764	271, 615 1396, 1982	296 1664	965, 1964	1700	-26.415	-26.507	9.55	0.994
Al ₁₂ ⁺	390 1250	236, 670 1017, 1713	346 1251	980, 1659	1160	-26.187	-26.211	3.03	0.991
Al ₁₂ ⁻	589 1569	492, 785 1396, 1764	572 1450	964, 1877	1100	-29.430	-29.416	2.09	0.996
Al ₁₃	1982	1569, 2228	1830	1387, 2105	1300	-30.465	-30.422	2.83	0.997
Al ₁₃ ⁺	490 1750	397, 603 1390, 2110	823 1784	1074, 1891	1200	-29.994	-30.012	8.11	0.996
Al ₁₃ ⁻	2200	1241, 3165	2019	1346, 2802	2090	-34.037	-34.029	0.76	0.981
Al ₁₄	1982	1396, 2505	1911	1276, 2319	914	-33.455	-33.367	3.97	0.996
Al ₁₄ ⁺	2000	1390, 2342	1996	1127, 2164	910	-33.538	-33.487	5.00	0.997
Al ₁₄ ⁻	1764	1396, 2228	1603	1208, 2179	1235	-35.822	-35.806	5.16	0.995
Al ₁₅ ⁺	1600	1128, 2342	1487	1047, 1955	-	-35.627	-35.522	5.08	0.995
Al ₁₆ ⁺	1543	670, 1555	1351	996, 1744	1532	-38.297	-38.303	6.72	0.997

Table 4.1: Melting temperatures of sodium and aluminum clusters in K, T_c (from $C(T)$), T_f and T_m (from W_U), T_c (from $d\delta/dT$), T_f and T_m (from F_s), T_G from d^2G/dT^2 , global minimum energy U_0 (Allegro and DFT), mean absolute errors (MAE) of the trained model (in meV/atom) and Pearson correlation coefficient R^2 between Allegro and DFT energies.

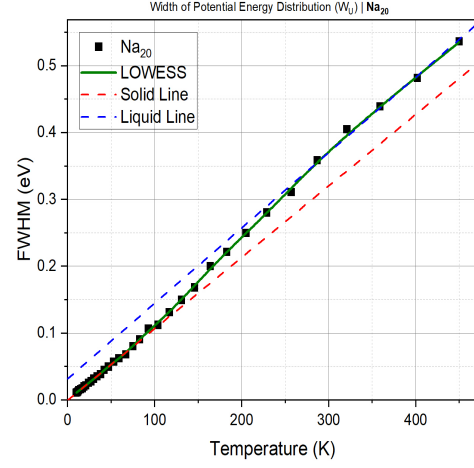
that showed melting points in the range [200, 300] K, well below the bulk melting point (371 K). Chiriki *et al.* reported a small peak near 110 K indicative of premelting. We do not find this (see Fig. 4.2(a)), but the geometric feature $d\delta/dT$ exhibits a peak near 150 K, followed by a smaller cusp around 250 K (see Fig. 4.2(c)). This feature is sensitive to structural changes and may reflect premelting behaviour. The $W_U(T)$ and F_s indicate the onset of melting near 131 K. We conducted an additional run of PTMC with a fine sampling of temperatures ranging from 0 to 40 K. It shows a very small feature near 18 K (onset in Fig. 4.2(a)). (With relatively short PTMC simulations, $C(T)$ becomes unreliable at very low T .) Premelting features have been found many times before, see, for instance Ref. [33, 175, 185, 186]. The lowest energy structure we observe in a million steps of PTMC simulation is a double icosahedron with a capping atom (Fig. 4.3(b)). It differs from the GM found by Chiriki *et al.* by the position of a single atom: this could account for the different $C(T)$ near 110 K. Earlier computational studies reported size-dependent T_c for Na_n in the range 200-300 K [32, 33, 187, 184].

A scatter plot of DFT and Allegro potential energies is shown in Fig. 4.3(a). The NN potential fits DFT with a mean absolute error (MAE) of 1.6 meV/atom and a correlation coefficient (R^2) of 0.978 for Na_{20} . This introduces an uncertainty of approximately 20 K in melting points. Additional uncertainties on T_c, T_f, T_m come from errors rooted in the DFT calculations, statistical errors of simulations with a finite number of steps, and numerical errors associated with the smoothing of data with LOWESS or sigmoid fit.

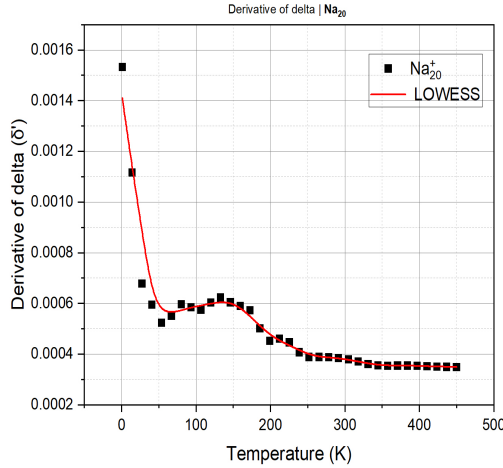
Fitting errors for Al clusters are larger than for Na_{20} , but are similar in a relative sense, ie, when divided by the cohesive energy of Na and Al, 1.11 and 3.39 eV/atom, respectively. The MAE for Al clusters vary a lot with cluster size and charge, from 0.8 to 9.6 meV/atom. The very low MAE found for Al_{13}^- can be understood by considering its closed electronic shell (40 valence electrons) and very high melting point (2200 K). In our simulations Al_{13}^- never melts. It goes from solid to gas in a way we can not characterize fully because our method breaks down when there is more than one evaporation event per 10000 steps. Leaving Al_{13}^- aside, trained NN potentials (MAE) vary between 2.1 (for Al_{12}^-) and 9.6 meV/atom (for Al_{12}). This corresponds to errors of roughly



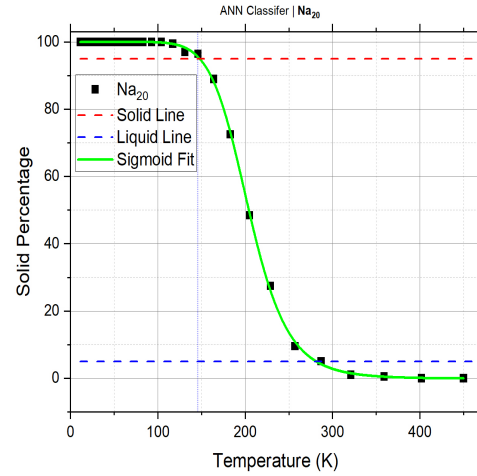
(a) Heat capacity ($C(T)$) vs. temperature (K) for Na_{20} . The solid red line is a LOWESS fit to data. The inset shows results of a PTMC run over a range of 1 to 40 K, with a small peak near 18 K.



(b) Width W_U of the probability distribution of potential energy vs temperature (K). The red and blue dashed lines are linear fits at low T (solid phase) and high T (liquid phase), respectively. The green line is a LOWESS fit.

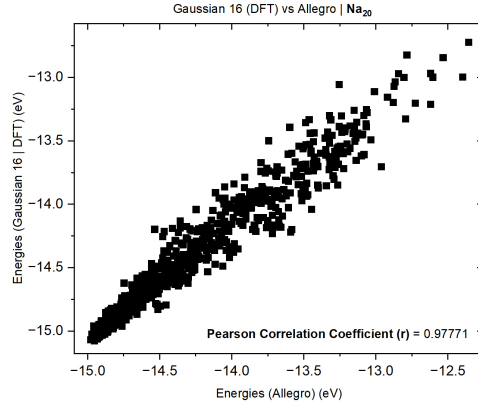


(c) Derivative of δ ($d\delta/dT$) vs. temperature (K) for Na_{20} . The solid red line is a LOWESS fit to data.

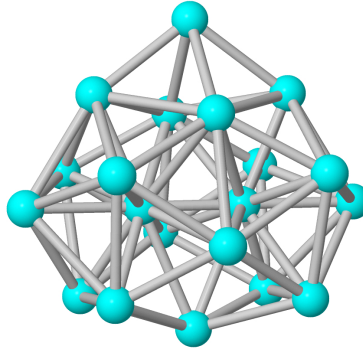


(d) Percentage of configurations classified as solid F_s vs temperature (K). The red and blue dashed lines are the [95%, 5%] cutoffs, respectively. The green line is a sigmoid fit.

Figure 4.2: $C(T)$, $W_U(T)$, $d\delta/dT$ and F_s for Na_{20} .



(a)



(b)

Figure 4.3: (a) Energies calculated by DFT vs NN potential. (b) Lowest-energy structure of Na_{20} obtained after one million steps of parallel tempering Monte Carlo.

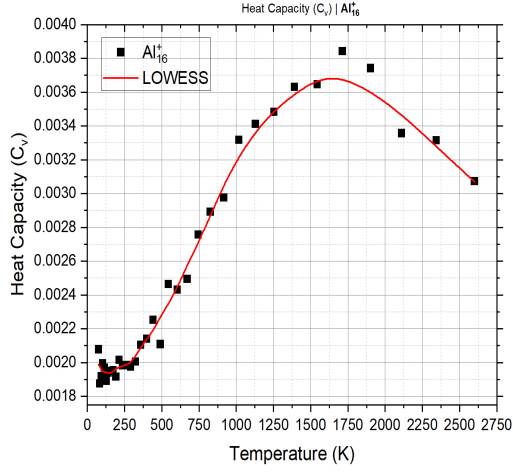
20 to 100 K on melting points. The R^2 correlation coefficients are between 0.965 and 0.997. The difference in the GM energy calculated with DFT and with the ML potential is 0.04 eV on average and is never more than 0.11 eV. This suggests the NN potential can reproduce trends that would be seen if the simulations were done entirely with DFT. The scatter plot of DFT energy against Allegro energy for Al_{16}^+ is shown in Fig. 4.5(a).

4.3.2 Al_n^+

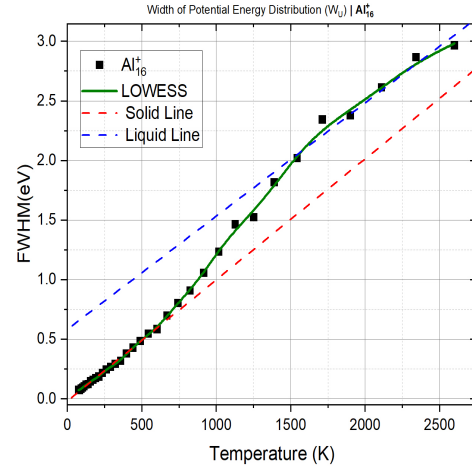
The melting point of aluminum is 933.5 K. Heat capacities for Al_n^+ ($n = 16$ to 48) were measured by Jarrold et al. [169] over a range of temperatures from 77 to 1100 K. Prominent peaks are seen for clusters with $n \geq 35$, except $n = 48$, with T_c values ranging from 600 to 850 K. Smaller peaks are seen at size $n = 27$ to $n = 34$ with T_c varying between 575 and 700 K. There are no clear features in heat capacity in the size range $n = 16$ to 26 except, maybe, an increase at high temperature suggesting peaks above 1100 K at sizes $n = 17, 20$ and 21.

Most clusters melt at temperatures lower than the bulk. But there are exceptions. Sn_n^+ ($n = 10$ –30) [188] and Ga_{17}^+ [189] either do not melt (they sublime), or they melt at temperatures above the bulk melting point. And Ga_n^+ ($n = 39, 40$) melt at 550 K, well above 302.9 K (the melting point of gallium). Like tin and gallium, aluminum is a *sp*-valence metal and has cluster equilibrium geometries very different from the bulk crystal determined to some degree by directional *p*-bonding. It is conceivable that small Al_n clusters could melt at temperatures higher than the bulk.

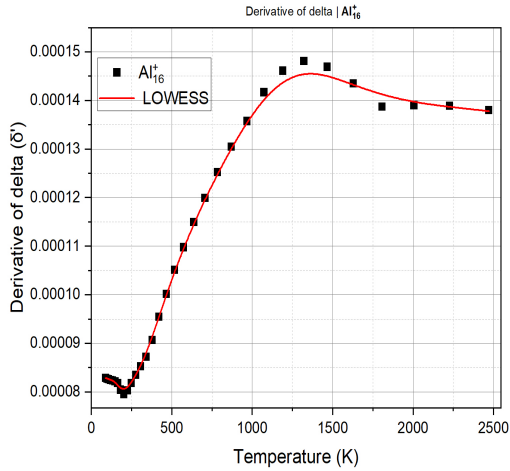
The melting points derived from our simulations, T_c from $C(T)$, are (in kelvin): 322 ($n = 9$), 670 ($n = 10$), and 1100 or higher ($n = 11$ –16), see Table 4.1. They generally agree with trends in the heat capacity experimental data [169]. The simulated T_c ($C(T)$) for Al_{16}^+ , 1543 K, is well above 1100 K and explains why no peak was observed in heat capacity. The high T_c values found here for Al_n^+ ($n = 11$ –16) are consistent with the absence of peaks in heat capacity below 1100 K in experiments for $n < 27$ and with what appears to be onset of melting near 900 K at $n = 17, 20, 21$. We see big fluctuations in T_c between 300 and 2000 K ($n = 9$ to 16), in qualitative agreement with significant, but smaller, fluctuations in experiment (600 to 900 K) at sizes $n = 27$ to 48. The T_c ($C(T)$) for Al_{16}^+ is not too far from what was found in a molecular dynamics study with an empirical Gupta potential [190], 1300 K. Fig. 5(b) shows the GM of Al_{16}^+ found in PTMC simulations. It is a distorted icosahedron with three capping atoms (Fig. 4.5(b)).



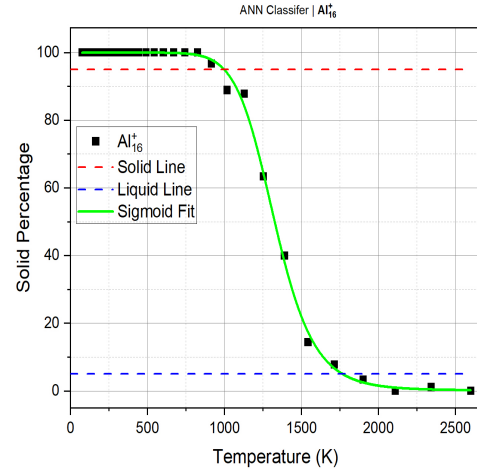
(a) Heat capacity ($C(T)$) vs. temperature (K) for Al_{16}^+ . The solid red line is a LOWESS fit.



(b) Width W_U of the probability function of the potential energy vs temperature (K) The red and blue dashed lines are straight line fits at low (red) and high (blue) temperatures. The green solid line is a LOWESS fit.

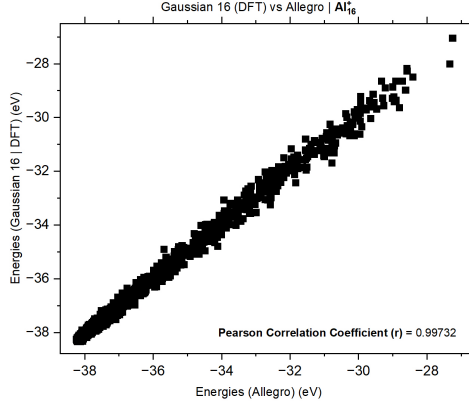


(c) Derivative of δ ($d\delta/dT$) vs. temperature (K) for Al_{16}^+ . The solid red line is a LOWESS fit to data.

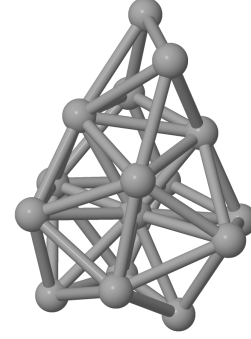


(d) Percentage of configurations classified as solid F_s vs. temperature (K). The red and blue dashed lines are the [95%, 5%] cutoffs, respectively. The green line is a sigmoid fit.

Figure 4.4: $C(T)$, $W_U(T)$, $d\delta/dT$ and F_s for Al_{16}^+



(a)

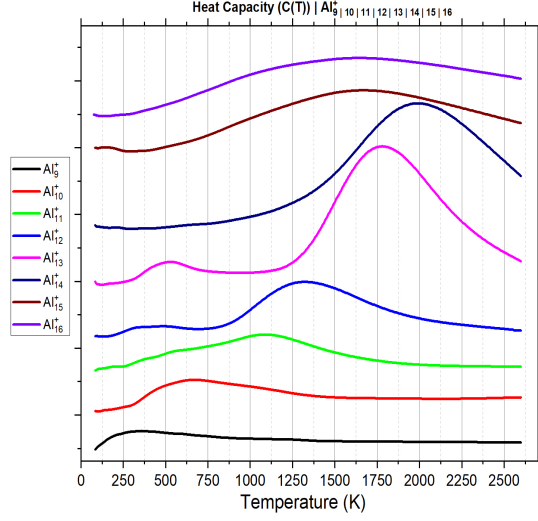


(b)

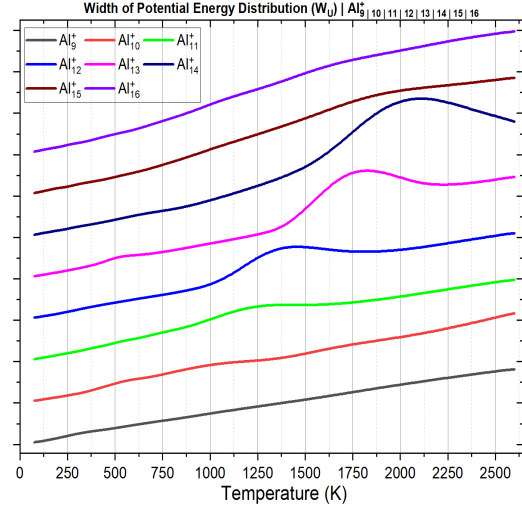
Figure 4.5: (a) Energies calculated by DFT vs NN potential. (b) Lowest-energy structure of Al_{16}^+ obtained after one million steps of parallel tempering Monte Carlo.

The T_c values calculated from the derivative $d\delta/dT$ generally agree with those obtained from the peak in heat capacity $C(T)$ (see Table 4.1). The freezing and melting points T_f and T_m , determined from the potential energy distribution W_U and the ANN classifier output F_s (columns labelled W_U and F_s in Table 4.1), consistently bracket the T_c values derived from $C(T)$. The standard error percentage was calculated as the standard error divided by the mean of four melting-point indicators: T_c from $C(T)$, T_c from $d\delta/dT$, the midpoint of T_f and T_m from W_U , and the temperature where the solid fraction F_s reaches 50%. This percentage is generally within $\sim 1\%$ for the main melting transition across all clusters. However, for clusters exhibiting premelting behaviour, the uncertainty near the lower-temperature transition is higher. Specifically, in Al_{12} , Al_{12}^- , Al_{12}^+ , and Al_{13}^+ , the standard error percentage of the premelting feature exceeds 3% in some cases, whereas for the main melting transition it remains near 1%.

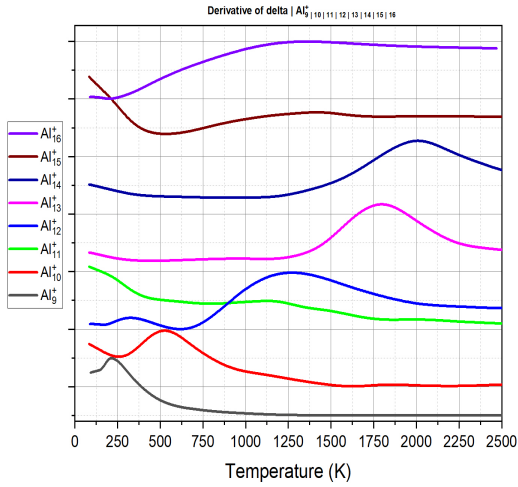
Premelting signatures are observed in $C(T)$, W_U , and $d\delta/dT$ for these clusters, but not in F_s . This limitation arises from the binary architecture of the ANN classifier, which is trained to distinguish only solid and liquid configurations using binary cross-entropy loss and a hard sigmoid activation. As a result, the model cannot capture configurations in intermediate regimes. A categorical classification—with three output classes and a softmax activation—could enable the detection of premelting by introducing an explicit intermediate state.



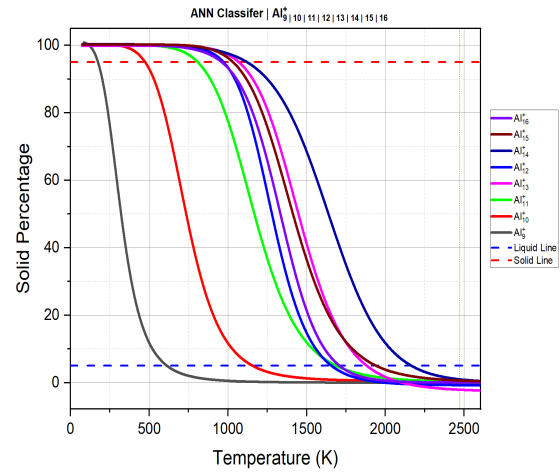
(a) $C(T)$ vs Temperature (K)



(b) W_U vs Temperature (K)



(c) $d\delta/dT$ vs Temperature (K)



(d) F_s vs Temperature (K)

Figure 4.6: Indicators of melting for cationic clusters of Al_9^+ (black), Al_{10}^+ (red), Al_{11}^+ (green), Al_{12}^+ (blue), Al_{13}^+ (pink), Al_{14}^+ (dark blue), Al_{15}^+ (brown), and Al_{16}^+ (violet). All curves are vertically shifted for clarity and presented in arbitrary units, except for F_s .

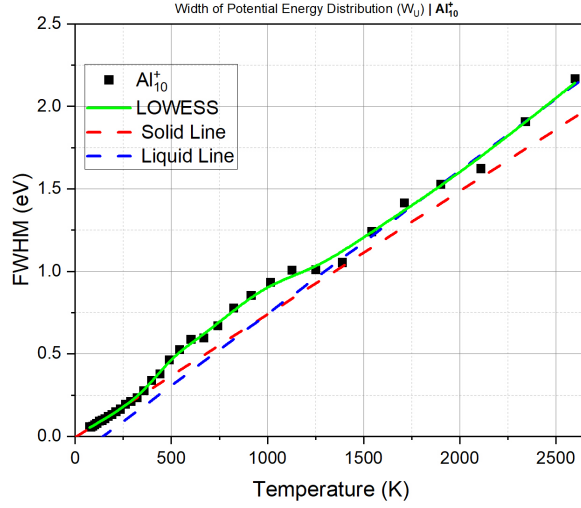


Figure 4.7: Width of potential energy probability function, W_U , for Al_{10}^+ showing nonlinear behavior in the solid-liquid coexistence region.

All criteria are plotted for positively charged aluminum clusters in Fig. 4.6. The curves are shifted along y for clarity. Some W_U curves appear featureless in Fig. 4.6 because of the compressed scale on the y axis, but a closer look clearly shows the nonlinear region where solid and liquid coexist as shown, for instance, for Al_{10}^+ (see Fig. 4.7).

To summarize trends in Al_n^+ results: $T_c > T_{m,bulk}$ in every case except $n = 9$ and 10; as n goes from 9 to 16, the average T_c (both $C(T)$ and $d\delta/dT$) goes from 376 to 605, 1124, 1250, 1767, 2000, 1543, and 1447 K; and solid-liquid coexistence region marked by W_u and F_s , are very wide, 600 to 1200 K (except for Al_9^+); small premelting peaks are observed below 500 for $n = 12$ and 13.

4.3.3 Al_n and Al_n^- ($n = 12, 13, 14$)

Experiments are often done on cluster cations or anions because it makes it possible to guide and detect them efficiently. We simulated clusters of different charge states at $n = 12, 13$ and 14 to see how sensitive properties are to charge. We chose to look at $n = 12, 13$ and 14 because, at $n = 13$ the ground state equilibrium configuration could be the compact, quasispherical, high-symmetry icosahedral geometry. Furthermore, Al_{13}^- is special because of its closed electronic shell ($n_e = 40$)

predicted by the jellium model and confirmed by first-principles electronic structure calculations.

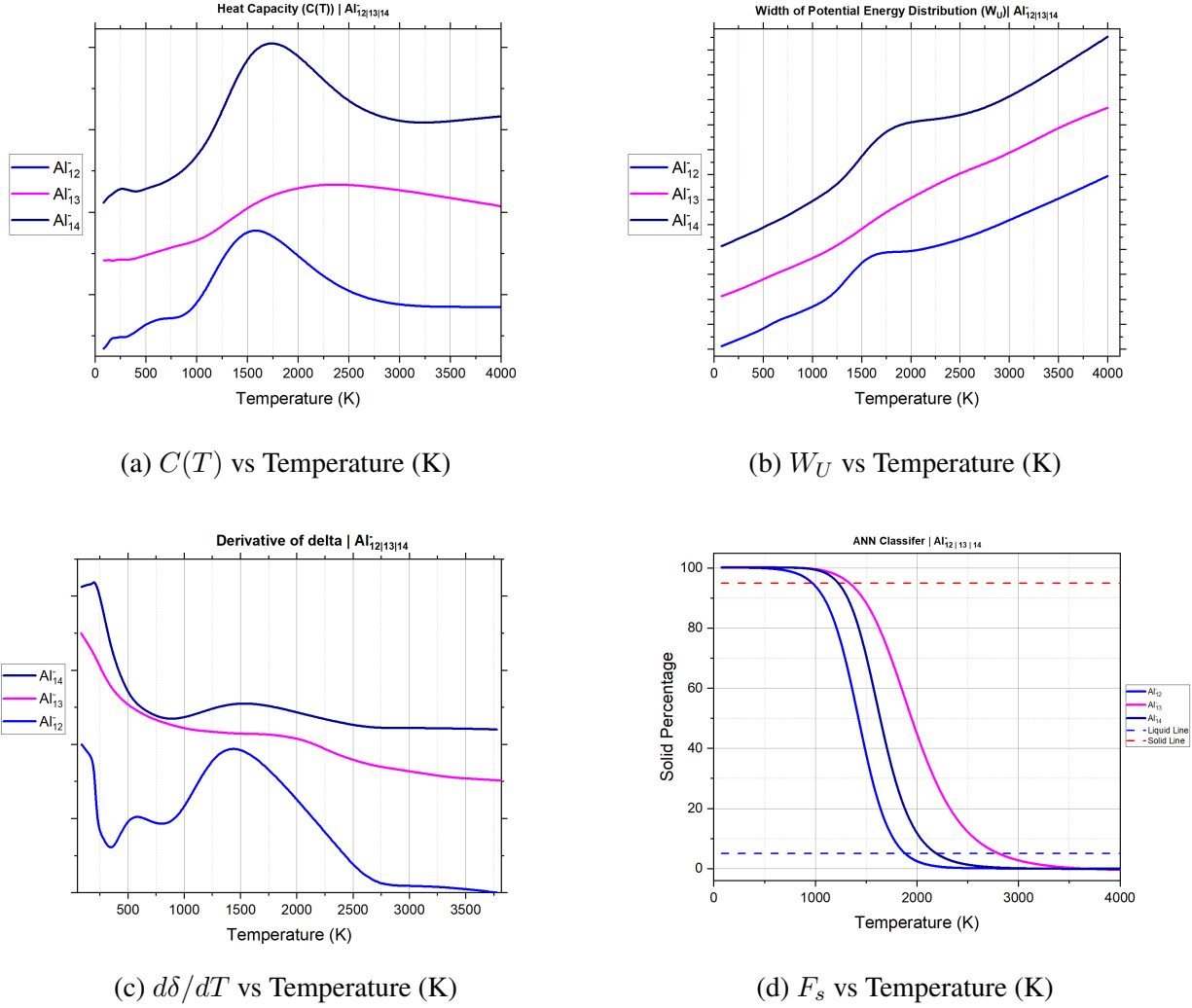
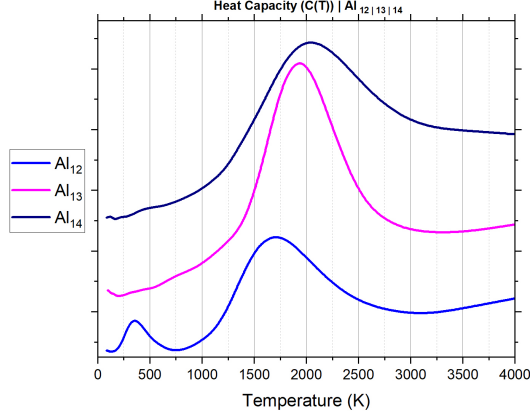


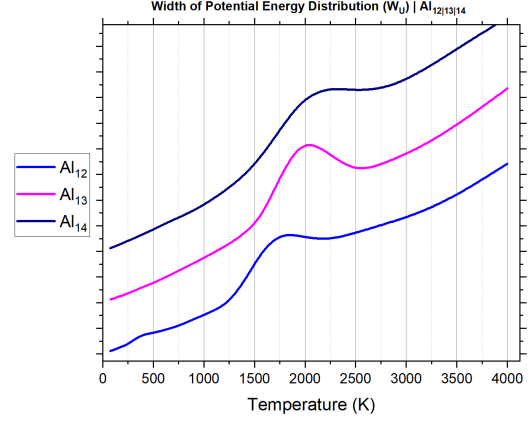
Figure 4.8: Indicators of melting for anion clusters of Al_{12}^- (blue), Al_{13}^- (pink), and Al_{14}^- (Royal blue). All curves are vertically shifted for clarity and presented in arbitrary units, except for F_s .

As expected, the melting point of Al_{13}^- is the highest: it is more than twice the bulk value. This is another unique property of Al_{13}^- consistent with its superatomic character [191, 192]. Interestingly, Al_{13}^- does not have the highest T_f . Both $C(T)$, $W_U(T)$ and $d\delta/dT$ curves are quite flat for Al_{13}^- , but not for Al_{13} , (see Fig. 4.9(a)) or Al_{13}^+ (see Fig. 4.6(a)). The T_f and T_m values found by F_s for the same are extremely broad, approximately 1500 K. This is a striking example where adding a single electron has a big effect on the properties of a small cluster. There is no simple trend in how T_c of Al_n^q changes as a function of charge q for fixed n , or how it changes with n (12, 13, 14) for fixed

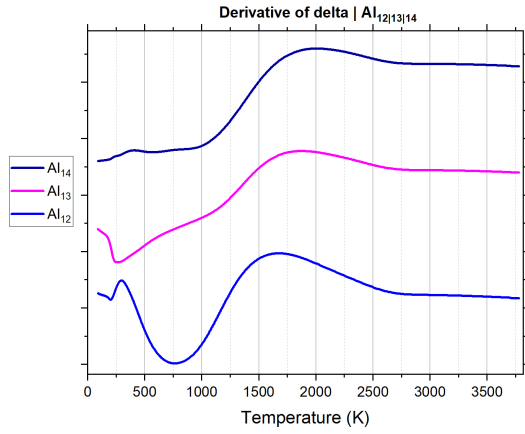
q . Leaving Al_{13}^- aside, there is no meaningful difference in T_c of cluster species with even or odd number of electrons either. The T_c of Al_{12}^q species are all smaller than those of the corresponding Al_{13}^q species, but the T_c of Al_{14}^q species are rather big compared to the 11 other Al_n^q species, Al_{13}^- excepted. Charge has a large effect on the melting points of these small clusters, and it is not easily explained.



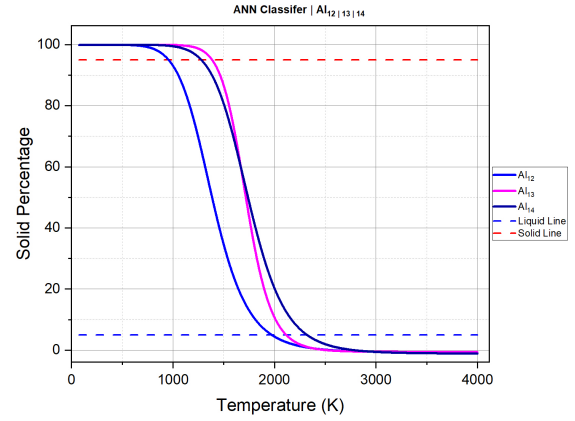
(a) $C(T)$ vs Temperature (K)



(b) W_U vs Temperature (K)



(c) $d\delta/dT$ vs Temperature (K)



(d) F_s vs Temperature (K)

Figure 4.9: Indicators of melting for neutral clusters of Al_{12} (blue), Al_{13} (pink), and Al_{14} (Royal blue). All curves are vertically shifted for clarity and presented in arbitrary units, except for F_s .

4.4 Conclusion

We described a procedure for simulating clusters as a function of temperature and for determining their freezing and melting point. Here, we used a well-established parallel tempering Monte Carlo method, but the procedure could easily be extended to molecular dynamics simulations. The key aspects of the procedure are: a) a short global optimization that generates a dataset of a few thousand diversified configurations, including the global minimum, and their DFT energy; b) a fit to the dataset using an equivariant deep learning interatomic potential that achieves an accuracy in the range of 1 to 10 meV/atom for Al_n clusters; c) energy ($C(T)$ and W_U) and geometry-based properties ($d\delta/dT$ and F_s) that are sensitive to melting-like transitions. The inflection criterion $d^2G(T)/dT^2$ provided structural indicators close to T_c , but requires further analysis and is best used in combination with other criteria. Results obtained for Na_{20} agree with those of prior computational studies, and results for Al_n^+ ($n = 9$ to 16) are consistent with trends found in experiments on slightly larger Al_n^+ clusters. This shows the procedure is correct and achieves a valuable degree of accuracy. Each of the three parts in the procedure is quite general and could be used to study clusters of any chemical composition. The computational cost, however, is significant. It currently limits applications to clusters with $n \lesssim 20$ for most elements, and with maybe twice as many atoms for elements in groups 1, 2, and 10, where s bonding dominates.

Simulations indicate that small Al_n^+ clusters $n < 17$ often melt at temperatures far above the bulk melting point of 934 K. The closed-shell superatom Al_{13}^- has an exceptionally high melting point at 2200 K. It is unclear whether it even melts. It may transition directly from the solid to the gas phase at $T \gtrsim 2200$. The heat capacity curve of Al_{13}^- is relatively flat (pink curve in Fig. 4.8(a)), and our potential and method can not reliably simulate evaporation. Leaving Al_{13}^- aside, there is no simple pattern in the melting points of other cluster species as a function of size or charge: the three with highest average T_c are Al_{14}^+ , Al_{14} , and Al_{13} ; the three with lowest average T_c are Al_9^+ , Al_{10}^+ and Al_{11}^+ . The apparent increase in T_c with size from $n = 9$ to $n = 16$ is non-monotonic, and must reverse itself as bigger sizes since many melting points were found in the range of 600 to 900 K (for $n = 27$ to 48), and the bulk melts at 934 K.

Chapter 5

A Machine-Learned DFT-Based Global Optimization Framework for Atomic Clusters: Application to Neutral and Charged Aluminum Clusters

Abstract

Aluminum clusters show size- and charge-dependent structural and melting behaviour that is difficult to characterize due to their complex energy landscapes. We combine density functional theory with an E(3)-equivariant machine-learned potential trained on DFT data to explore candidate structures using parallel tempering Monte Carlo sampling. Systems studied include Al_n^+ ($n = 9-16$) and neutral and anionic Al_n ($n = 12-14$). Global minima and low-energy isomers were refined with TPSS/SDD geometry optimization and harmonic vibrational analysis. Ionization energies, electron affinities, and vertical ionization potentials were computed and compared with published reference data, showing good agreement. The machine-learned potential yields a mean absolute energy error of less than $10\text{meV}/\text{atom}$ relative to the DFT reference. Structural changes during melting were examined using principal component analysis of atomic density distributions, which identified representative structures and distinguished between partial and complete melting. This global optimization protocol, demonstrated for aluminum clusters, may be extended to other atomic clusters with appropriate training data.

5.1 Introduction

Small aluminum clusters, consisting of n atoms (Al_n), have attracted significant interest as models for nanoscale metallic systems. Beyond their size-dependent physical properties, these clusters serve as components in materials with novel electronic, optical, and catalytic characteristics [193]. Unlike bulk aluminum, they exhibit discrete electronic states and intricate geometries, making them valuable for fundamental studies in nanoscience and physical chemistry [194]. However, their structural characterization is challenging due to the multitude of low-energy isomers populating the potential energy surface (PES) [193]. Identifying the global minimum becomes increasingly complex with cluster size, owing to the rapid growth of configurational space and the interplay between metallic bonding and quantum shell effects [195].

Density functional theory (DFT) and related *ab initio* methods have revealed systematic trends among small Al clusters. Among these, Al_{13} and its different charge states/electron counts — particularly its anionic form, Al_{13}^- are of particular interest because of their quasispherical shape and superatomic character. With 40 valence electrons, Al_{13}^- adopts a highly symmetric icosahedral geometry with a relatively large HOMO-LUMO gap, making it a "magic number" cluster [195]. The neutral Al_{13} (39 valence electrons) undergoes a Jahn–Teller distortion, while the cationic Al_{13}^+ assumes a less symmetric geometry. These differences highlight the structural sensitivity to charge state and electron count.

Additionally, the icosahedral structure of a 13-atom aluminum cluster is frequently observed as a structural motif in larger clusters. For example, Al_{14} is typically described as a capped icosahedron, with the nature of the cap depending on the charge state [195]. Al_{15} and Al_{16} also tend to retain the icosahedral shape, incorporating additional atoms on the surface. In contrast, for clusters with $n > 20$, competing geometries become more favourable, while smaller clusters ($n < 12$) exhibit distinct polyhedral forms, such as the pentagonal bipyramidal structure of Al_7 .

Cluster stability shows non-monotonic trends with size, partly due to electronic shell closures. Li *et al.* [196] demonstrated that Al_7 and Al_{10} are relatively inert toward O_2 due to closed electronic subshells, while Al_8 is highly reactive. Similarly, Ladir *et al.* [197] showed through DFT and

quantum Monte Carlo (QMC) that ionization potentials and electron affinities of Al_n clusters follow systematic patterns consistent with experimental results.

Experimental methods complement these predictions. Photoelectron spectroscopy of Al_n^- clusters ($13 \leq n \leq 52$) confirmed icosahedral features for Al_{13}^- and revealed size-specific spectra consistent with structural transitions [198]. Ion mobility and reactivity studies have also demonstrated sharp variations in stability and reactivity near magic-number sizes [196]. These results reinforce the link between geometric structure, electronic configuration, and chemical behaviour in small aluminum clusters.

The complex potential energy surfaces (PES) of these systems, which are often populated by numerous low-lying isomers, necessitate the use of global optimization strategies. Many global optimization techniques have been employed for optimizing cluster geometries with *ab initio* energies, notably simulated annealing [193, 199], genetic algorithms [200], tabu search [201], and particle swarm optimization [202]. However, exhaustive *ab initio* searches remain computationally prohibitive for $n \gg 10$ due to the high cost of repeated energy evaluations and poor scaling with increasing n . A common compromise is a two-stage approach: an initial global search with inexpensive models, followed by DFT re-optimization and relaxation of promising candidates [201, 197].

Recently, machine learning (ML) has emerged as a powerful alternative. Neural network potentials can serve as a high-accuracy alternative to DFT, enabling rapid energy evaluations during structure searches. Yang *et al.* [194] demonstrated a deep-learning-based optimizer for platinum clusters, while Fu *et al.* [203] applied graph neural networks to screen silver clusters efficiently. Such ML-driven frameworks enable more diverse and efficient exploration of the configuration space [204].

In this work, we present an active-learning framework for global optimization for aluminum clusters, combining machine learning with density functional theory (DFT). An E(3) equivariant neural network potential 'Allegro' [174] is iteratively refined by integrating parallel tempering Monte Carlo sampling and DFT validation. Candidate structures are sampled using the neural

network potential, and their energies are compared with those obtained from DFT. New configurations with significant disagreement are incorporated into the training set to improve the potential in a closed-loop fashion. This framework systematically identifies global minima and low-lying isomers for neutral clusters ($n = 12\text{--}14$), cations ($n = 9\text{--}16$), and anions ($n = 12\text{--}14$), providing insights into size- and charge-dependent structural motifs. Thermally induced structural transitions are further analyzed by comparing high-temperature ensembles to the ground-state geometries to characterize melting-like behaviour. In addition, key electronic properties—such as atomization energies, adiabatic and vertical ionization energies, and electron affinities—are calculated and compared with available experimental and theoretical data. The following sections describe the computational methods, present the structural and electronic results, and discuss their implications. Although demonstrated on aluminum, the methodology is general and applicable to other atomic clusters.

5.2 Methodology

This section details the active-learning global optimization framework employed in this work and the algorithm used for low-energy isomer selection.

5.2.1 DFT-Accuracy Neural Network-Monte Carlo Framework

In this work, we employ a DFT-trained neural network potential (DFT-NN) framework introduced previously [36], leveraging a machine-learned potential [174] trained on DFT reference energies of diverse aluminum cluster configurations (Pearson correlation coefficient ~ 0.99 on a held-out test set) to enable efficient thermodynamic sampling. Full details of its training, validation, and implementation are available in [36]. Here, the same potential is retained to ensure consistency with DFT-level accuracy, but extended to global optimization via parallel tempering Monte Carlo (PTMC). For each system, PTMC exchanges configurations between 35 temperature replicas, each performing 1.5 million Monte Carlo steps, to overcome local minima and sample diverse regions of

the potential energy surface. In total, approximately 50 million energy evaluations were performed. The orders-of-magnitude computational speedup of the framework (approximately 100–1000 times faster than direct DFT) makes such large-scale sampling feasible due to both the inherent speedup from the surrogate machine-learned potential and the ability of the replica exchange to help configurations escape otherwise stable low-temperature minima.

This large-scale sampling provides a thermodynamic route to identify low-energy geometries, effectively achieving global optimization. As the system explores various configurations across a range of temperatures, it naturally visits deep energy minima corresponding to stable and metastable isomers. These structures, selected based on their low predicted energies and structural uniqueness, are subsequently refined through geometry optimization and harmonic frequency calculations at the TPSS/SDD level using Gaussian 16 [2]. This post-processing step enables a robust assessment of their relative stabilities and serves to validate the accuracy of the machine-learned model. Notably, many of these DFT-refined structures would have been difficult or computationally prohibitive to discover without the ML-guided sampling, highlighting both the efficiency and reliability of the framework.

5.2.2 Isomer Selection Algorithm

We employed a moment-based filtering algorithm to identify a diverse set of low-energy isomers from a large ensemble of candidate geometries. The procedure systematically removes redundant geometries while preserving energetic and structural diversity. Each geometry, defined by Cartesian coordinates and an associated energy (e.g., from Allegro), is processed as follows:

1. **Standard Orientation and Centering:** Each geometry is first translated to its center of mass (COM) and then rotated into a canonical orientation by diagonalizing its moment of inertia tensor. The COM is given by:

$$\vec{r}_{\text{COM}} = \frac{1}{M} \sum_{i=1}^N m_i \vec{r}_i, \quad M = \sum_{i=1}^N m_i \quad (5.1)$$

where m_i and $\vec{r}_i$ are the mass and position of atom i , N is the number of atoms per geometry, and M is the total mass of the system.

2. **Moment of Inertia Tensor:** After translation, the moment of inertia tensor is calculated as:

$$I_{\alpha\beta} = \sum_{i=1}^N m_i (\delta_{\alpha\beta} \|\vec{r}_i\|^2 - r_{i,\alpha} r_{i,\beta}) \quad (5.2)$$

where $\alpha, \beta \in \{x, y, z\}$, and $\delta_{\alpha\beta}$ is the Kronecker delta. Diagonalizing $\mathbf{I}$ gives the principal axes and corresponding principal moments I_1, I_2, I_3 .

3. **Energy-Based Sorting:** The geometries are sorted in ascending order based on their energy values E_j , where $j \in [1, G]$ and G is the total number of geometries.
4. **Redundancy Filtering:** For each candidate geometry j , the principal moments of inertia $I_1^{(j)}, I_2^{(j)}, I_3^{(j)}$ are compared with those of already accepted structures k . The relative moment difference is defined as:

$$\text{reldif}_{jk} = \frac{2 \sum_{\gamma=1}^3 |I_{\gamma}^{(j)} - I_{\gamma}^{(k)}|}{\sum_{\gamma=1}^3 (I_{\gamma}^{(j)} + I_{\gamma}^{(k)})} \quad (5.3)$$

and the maximum deviation criterion as:

$$\text{remadi}_{jk} = \frac{3 \cdot \max_{\gamma} |I_{\gamma}^{(j)} - I_{\gamma}^{(k)}|}{\sum_{\gamma=1}^3 (I_{\gamma}^{(j)} + I_{\gamma}^{(k)})} \quad (5.4)$$

A candidate geometry j is accepted if it satisfies both:

$$\text{reldif}_{jk} < \text{tol}_a \quad \text{and} \quad \text{remadi}_{jk} < \text{tol}_b \quad (5.5)$$

where tol_a and tol_b are user-defined tolerance parameters.

5. **Isomer Set Construction:** Accepted geometries are added to the isomer set until a maximum number (typically 40) is reached. Each geometry's atomic coordinates, energy, and moment descriptors are saved.

This filtering ensures the selected isomer set represents structurally unique and energetically favourable configurations. Parameters such as the tolerances and maximum number of saved isomers are user-configurable. These selected geometries are sent for optimization and frequency calculation using Gaussian, and the results of the energies are discussed in Section 5.3.2.

5.2.3 Principal Component Analysis of the structural distribution and Selection of Representative Geometries

At low temperature, the cluster samples distinct isomeric states. As temperature rises, atomic geometries diffuse, revealing structural evolution and melting signatures. To characterize these changes, principal component analysis (PCA) was applied to all generated geometries, using the first two components to capture the essential shape of the implied free-energy landscape in a lower-dimensional space. Input features for the PCA were chosen to balance interpretability with low redundancy. First, we include the directional sines and cosines of all possible quadruplet angles (without replacement), as well as the eigenvalues of the gyration tensor,

$$S_{xy} = \sum_{i=1}^N r_x^{(i)} r_y^{(i)}, \quad (5.6)$$

as well as a bond-order parameter defined by

$$\sum_{i < j} \frac{1}{1 + \exp [B (r_{ij} - C)]}, \quad (5.7)$$

with $C = 3.3 \text{ \AA}$ and $B = 6.0 \text{ \AA}^{-1}$. Small B values blur state separation, while large B values introduce numerical oscillations. These values were chosen for Al clusters.

Additionally, to describe anisotropy, each atom i is assigned a weight w_{ij} for neighbours j via

$$\begin{aligned} w_{ij} &= 1 & d_{ij} < d_1 \\ &= \cos(\pi(d_{ij} - d_1)/2(d_2 - d_1)) & d_1 \leq d_{ij} \leq d_2 \\ &= 0 & d_{ij} > d_2, \end{aligned} \quad (5.8)$$

leading to a coordination measure

$$c_i = \sum_{j \neq i} w_{ij}. \quad (5.9)$$

Lastly, to quantify directional anisotropy, a unit vector

$$\vec{u}_{ij} = \frac{\vec{r}_j - \vec{r}_i}{d_{ij}} \quad (5.10)$$

is defined for each pair of atoms i and j , describing the normalized bond direction from i to j . Two derived measures then characterize the local anisotropy of atom i based on these bond directions.

The first,

$$a_i = \left\| \sum_{j \neq i} w_{ij} \vec{u}_{ij} \right\|, \quad (5.11)$$

Quantifies the net asymmetry of neighbouring atoms, approaching zero for a symmetric neighbour distribution and growing as neighbours cluster preferentially on one side. The second,

$$b_i = \sum_{j \neq i} \sum_{k \neq i, k \neq j} w_{ij} w_{ik} \frac{\sqrt{d_{ij} d_{ik}}}{d_{jk}}, \quad (5.12)$$

captures the angular spread of neighbours while controlling for interatomic distance, distinguishing, for example, tetrahedral versus planar arrangements.

Atoms are consistently ordered by

$$x_i = 1000Z_i + 100c_i + D_i, \quad (5.13)$$

with Z_i the atomic number, c_i the coordination rounded to 0.1, and D_i the distance to the cluster center. This ordering preserves a consistent geometric index across configurations.

Features (trigonometric, bond-order, gyration eigenvalues, and directional metrics c, a, b) were calculated for all Al_n^+ ($n = 9\text{--}16$) and Al_n^q ($n = 12, 13, 14$ & $q = 0, 1$). A single PCA transform was applied to the features of the highest-temperature ensemble, as these configurations exhibit the most significant structural variability. This transformation is then used to project the features from each ensemble into a common, low-dimensional space defined by the first two PCA components. This ensures that the principal axes span the full range of accessible structures, enabling consistent projection across temperatures and allowing for the inspection of how the structural distribution and the atomic configurations that populate it evolve across the entire studied temperature range.

5.3 Result and Discussion

In the PTMC simulation, millions of configurations are sampled, and their energies are evaluated using a machine-learned (ML) potential. The lowest-energy configuration is denoted X_{ML} . A single-point TPSS/SDD energy calculation at X_{ML} yields $E(\text{DFT}/\text{ML})$, reported in the second column of Table 5.1. Each X_{ML} is then used as the initial guess for a TPSS/SDD geometry optimization, producing relaxed configurations X_{DFT} (see Fig. 5.1) and corresponding energies $E(\text{DFT})$, shown in the third column of Table 5.1.

5.3.1 Global Minimum Structures

This study identifies the global minimum (GM) geometries of cationic $\text{Al}_9^+ \text{--} \text{Al}_{16}^+$, neutral $\text{Al}_{12} \text{--} \text{Al}_{14}$, and anionic $\text{Al}_{12}^- \text{--} \text{Al}_{14}^-$ clusters using the framework, with subsequent refinement at the TPSS/SDD level. Figure 5.1 summarizes these geometries.

For the cationic series, a structural progression is evident: $\text{Al}_9^+ \text{--} \text{Al}_{11}^+$ favour capped polyhedral or bipyramidal structure, while $\text{Al}_{12}^+ \text{--} \text{Al}_{14}^+$ converge toward compact icosahedral or distorted decahedral structures. Al_{15}^+ and Al_{16}^+ exhibit more extended multi-shell motifs with high coordination,

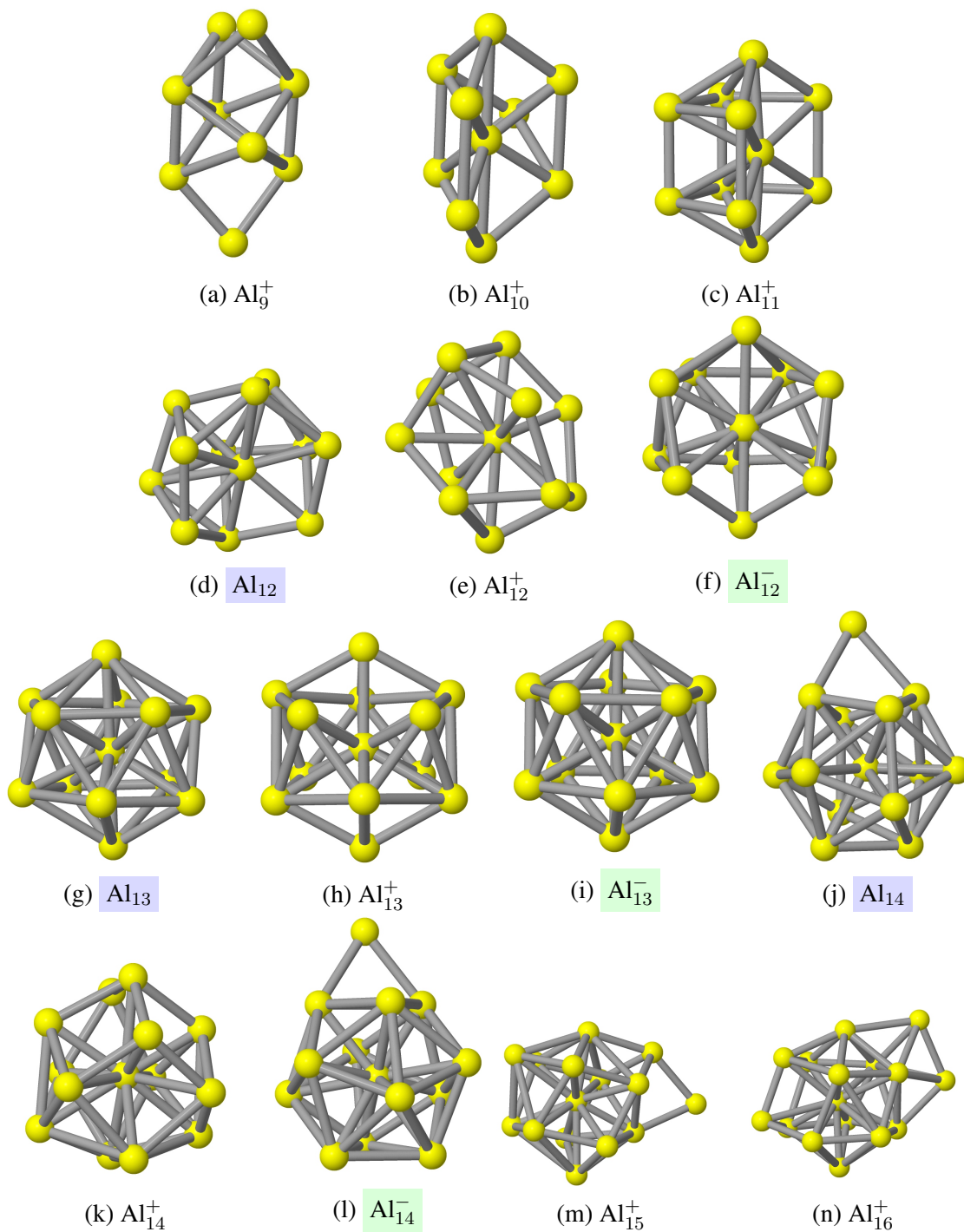


Figure 5.1: Global minimum structures identified using the DFT-NN framework and re-optimized with Gaussian 16. Blue-highlighted captions indicate neutral clusters, green-highlighted captions indicate anionic clusters, and non-highlighted captions correspond to cationic clusters.

Size	E(DFT/ML) (eV) (Present)	E(DFT) (eV) (Present)	Ladir <i>et al.</i> [197] (eV) (PBE-6-311G++(2d,2p))	Ladir <i>et al.</i> [197] (eV) (QMC)	Fournier <i>et al.</i> [201] (eV) (BPW91/LANL2DZ)	Keyampi <i>et al.</i> [205] (eV) (Gupta)	Sebetci <i>et al.</i> [209] (eV) (EAM)
Al ₉ ⁺	-17.38066	-17.63312	-17.95516	-17.9334	-17.85689	-	-
Al ₁₀ ⁺	-20.40296	-20.47223	-19.99189	-19.9677	-19.89105	-	-
Al ₁₁ ⁺	-23.18728	-23.31335	-22.0372	-22.0109	-21.93002	-	-
Al ₁₂	-26.41477	-26.76484	-24.31325	-24.2941	-24.19086	-28.2547	-28.5274
Al ₁₂ ⁺	-26.18656	-26.47039	-24.09155	-24.0633	-23.9637	-	-
Al ₁₂ ⁻	-29.42960	-29.49462	-24.41121	-24.3856	-24.27765	-	-
Al ₁₃	-30.46464	-30.63489	-26.39686	-26.3613	-26.22798	-31.6329	-32.0729
Al ₁₃ ⁺	-29.99378	-30.24103	-26.16027	-26.1237	-26.01711	-	-
Al ₁₃ ⁻	-34.03689	-34.04733	-26.51931	-24.2941	-26.34084	-	-
Al ₁₄	-33.45520	-33.44458	-	-	-28.25893	-33.9797	-34.4434
Al ₁₄ ⁺	-33.53843	-33.69047	-	-	-28.05097	-	-
Al ₁₄ ⁻	-35.82239	-36.01442	-	-	-28.34346	-	-
Al ₁₅ ⁺	-35.6269	-36.01464	-	-	-30.07236	-	-
Al ₁₆ ⁺	-38.29713	-38.67885	-	-	-	-	-

Table 5.1: Atomization energies of small aluminum clusters computed using $E_{\text{DFT/ML}}$ (DFT single-point energies at ML-predicted global minimum geometries) and E_{DFT} (fully relaxed DFT global minimum geometries), compared with literature values. Results are shown for cationic clusters ($n = 9$ –16), anionic clusters ($n = 12$ –14), and neutral clusters ($n = 12$ –14).

consistent with enhanced stabilization by a positive charge. The GM structures previously predicted by DFT-based global searches [201] were not immediately observed in Al₉⁺; however, they reappeared around 300 K in the PCA analysis (below), demonstrating the framework’s ability to explore the PES and identify deeper minima efficiently. Overall, the geometries found align with earlier first principles and empirical studies [201, 195, 205].

In the neutral clusters Al₁₂–Al₁₄, the icosahedral geometry dominates. In particular, Al₁₃ adopts a highly symmetrical icosahedron due to favourable geometric packing despite not reaching a closed-shell superatomic electron count. By contrast, Al₁₃⁻ attains a 40-electron closed-shell configuration, widely recognized as a superatom with exceptional stability [206, 196], and as highlighted in [36], it exhibits a remarkably high melting point exceeding 2200K. Al₁₄ extends the icosahedral core with a capping atom, consistent with GGA-DFT predictions [195, 207]. For the anionic species Al₁₂⁻–Al₁₄⁻, the structures retain compact high-coordination geometries closely related to their neutral counterparts but exhibit minor distortions due to the delocalization of the additional electron. These subtle relaxations are consistent with experimental photoelectron spectroscopy results [198, 208].

5.3.2 Isomers and Properties

Figure 5.2 summarizes the relative energies of the isomers with reference to the GM. Across all sizes, multiple isomers appear within modest energetic separations, reflecting a relatively flat potential energy surface. Cationic clusters (black squares) generally exhibit a dense manifold of low-lying isomers, most within 0.2 eV of the GM. This suggests a higher degree of structural flexibility and supports significant geometrical rearrangements that are accessible at finite temperatures. In contrast, specific anionic clusters, most notably Al_{14}^- , display a broader spread of isomer energies, reaching up to 0.8 eV above the GM. Such behaviour indicates a more complex potential energy landscape, likely associated with the delocalized excess electron. The neutral clusters (red circles) lie between these extremes, with moderate isomeric diversity and a smaller spread of higher-energy structures.

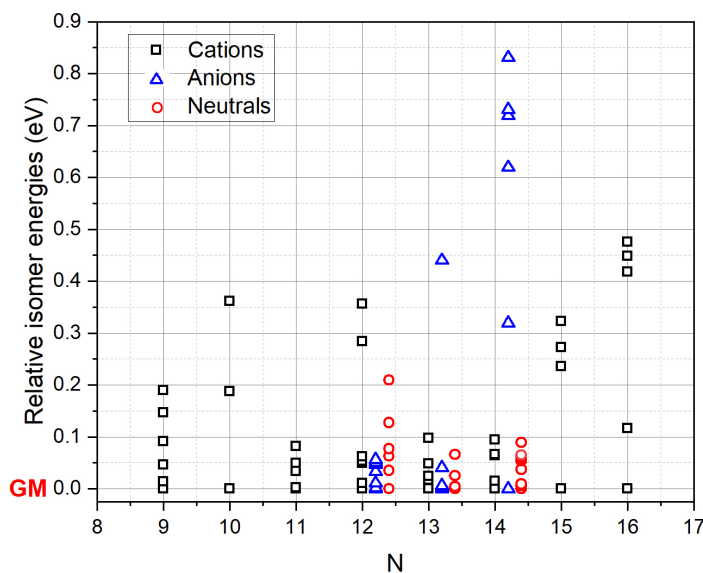


Figure 5.2: Relative energies of local isomers for aluminum clusters of varying size, for cationic (black squares), anionic (blue triangles), and neutral (red circles) charge states. All energies are referenced to the global minimum (GM), shown in red on the vertical axis.

For a more quantitative evaluation of binding characteristics, Table 5.1 compares the atomization energies from this study, $E_{\text{DFT/ML}}$, with single-point energy calculations, E_{DFT} , at identical

geometries. For cationic species, $E_{\text{DFT/ML}}$ shows systematic shifts of approximately $0.2\text{--}0.3eV$ relative to E_{DFT} , while successfully reproducing the energetic ordering. These results are consistent with previous global optimization studies [197, 201], supporting the robustness of the framework for charged clusters. Larger cations ($n > 12$) exhibit enhanced atomization energies, consistent with increased coordination and structural compactness. Overall, the energy deviation between $E_{\text{DFT/ML}}$ and E_{DFT} remains below 2%.

For both the anionic and neutral clusters, the data capture well-established stability similarly. In particular, Al_{13}^- shows a significant stabilization around $-34eV$, attributable to its closed-shell superatom nature. Comparison with previous DFT [197, 201] and quantum Monte Carlo [197] studies confirms the accuracy of these findings, while also highlighting subtle charge-specific structural effects.

Tables 5.2, 5.3, and 5.4 summarize the computed ionization energies, vertical ionization energies, and electron affinities, respectively, for Al_n clusters ($n = 12 - 14$), providing a detailed characterization of their electronic properties. These quantities are particularly relevant in assessing the ease of charge transfer processes, which can significantly impact the stability and reactivity of these clusters. The adiabatic ionization energies (IE), reported in Table 5.2, were calculated according to

$$IE = E_n^+ + ZPE_n^+ - E_n - ZPE_n \quad (5.14)$$

Where E_n^+ and E_n denote the total electronic energies of the cationic and neutral clusters at their respective optimized geometries, and ZPE_n^+ and ZPE_n are the corresponding zero-point vibrational energy corrections. The resulting values are in good agreement with prior DFT and QMC predictions as well as available experimental measurements, particularly for Al_{12} and Al_{13} . For Al_{14} , the somewhat lower calculated ionization energy is consistent with Phung et al. [207] and experimental [206]. This could be due to lower coordination of the capping atom (see. Fig. 5.1j, which may facilitate electron removal.

Size	Present	Theory (DFT) Ladir <i>et al.</i> [197]	Theory (QMC) Ladir <i>et al.</i> [197]	Theory Phung <i>et al.</i> [207]	Experiment Cox <i>et al.</i> [210]	Experiment Schriver <i>et al.</i> [206]
Al ₁₂	6.35	~6.0	~6.2	6.092	5.9–6.42	6.20
Al ₁₃	6.45	~6.4	~6.4	6.875	~6.42	6.45
Al ₁₄	5.82	-	-	6.314	-	6.16

Table 5.2: Ionization potentials (IP in eV) of aluminum clusters Al_n ($n = 12 - 14$).

Complementary to the adiabatic ionization energies (IEs), the vertical IEs were evaluated according to

$$IE_{\text{vertical}} = E_n^+ \big|_{\text{geom of neutral}} - E_n, \quad (5.15)$$

Which measures the energy cost of electron removal without structural relaxation. These are reported in Table 5.3. As expected, the vertical values are systematically higher than the adiabatic IEs due to the additional relaxation energy captured in the adiabatic process. The trends are consistent across cluster sizes, again showing best agreement with previous theoretical results for Al₁₂ and Al₁₃. At the same time, Al₁₄ continues to display a slightly reduced ionization threshold, in line with its adiabatic IE.

Size	Present	Theory (DFT) [197]	Theory (QMC) [197]
Al ₁₂	6.41	~6.2	~6.4
Al ₁₃	6.46	~6.8	~6.9
Al ₁₄	5.88	-	-

Table 5.3: Vertical ionization energies (VIE) of Al_n ($n = 12-14$).

Finally, the electron affinities (EAs), which characterize the tendency of the neutral cluster to accept an additional electron, were computed using.

$$EA = E_n + ZPE_n - E_n^- - ZPE_n^-, \quad (5.16)$$

with E_n^- and ZPE_n^- referring to the anionic cluster’s total and zero-point vibrational energies. The results, summarized in Table 5.4, show strong agreement with reference data, typically within $0.1 - 0.2\text{eV}$ of experimental observations. The largest EA is found for Al_{13} , consistent with its well-known superatomic stability and closed electronic shell. The reduced EA of Al_{14} again reflects its structural and relatively low binding strength.

Size	Present	Theory (DFT) Ladir <i>et al.</i> [197]	Theory (QMC) Ladiret <i>et al.</i> [197]	Experiment Li <i>et al.</i> [196]	Experiment Cha <i>et al.</i> [211]	Experiment Taylor <i>et al.</i> [208]
Al_{12}	2.74	~ 2.6	~ 2.4	2.75 ± 0.06	2.80 ± 0.10	2.53
Al_{13}	3.39	~ 3.3	~ 3.6	3.62 ± 0.06	3.75 ± 0.10	2.86
Al_{14}	2.57	-	-	2.60 ± 0.06	2.65 ± 0.10	2.47

Table 5.4: Electron affinities (EA in eV) of Al_n clusters ($n = 12-14$).

Altogether, the consistent agreement of ionization potentials, vertical IEs, and EAs with reference data is reassuring. The apparent differences between Al_{12} , Al_{13} , and Al_{14} further highlight the size- and charge-state-dependent nature of these properties, offering valuable insights into their stability and potential for applications in nanoscale materials and cluster-based functional devices.

5.3.3 Melting and Structure

Figure 5.3 shows the calculated heat capacity $C(T)$ (eV/K) of Al_{13}^+ as a function of temperature, obtained using the present framework. At low temperatures, the icosahedral ground state dominates up to approximately 500 K. A weak shoulder in $C(T)$ at this range reflects a solid–solid (or pre-melting) rearrangement, where surface atoms exchange positions while the overall structure remains intact. The prominent peak near 1700 K corresponds to the main melting-like transition to a disordered, liquid-like phase, consistent with the behaviour observed for most clusters studied here. Thus, while the dominant heat-capacity maximum is generally associated with melting, secondary smaller features may indicate structural or surface rearrangements preceding the full transition. The

structural snapshots illustrate this evolution from ordered to progressively distorted and ultimately liquid configurations. This heat-capacity profile motivates a deeper analysis of geometric evolution across temperatures, which is addressed by the PCA structural distribution analysis.

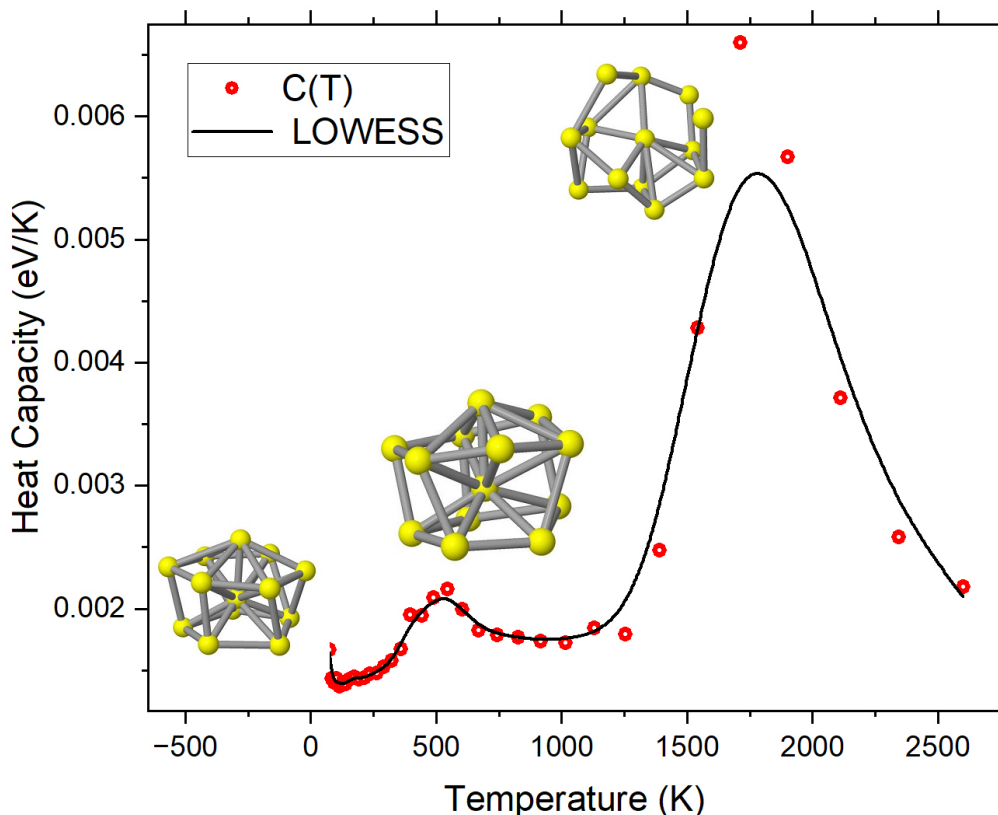


Figure 5.3: Heat Capacity $C(T)$ vs temperature (K). Shows how the structure evolve in Al_{13}^+ during melting.

Figure 5.4 presents PCA structural distribution maps for Al_9^+ through Al_{16}^+ clusters, derived from framework-sampled geometries at selected temperatures corresponding to prominent heat-capacity peaks. The first two principal components, shown on the axes, capture the dominant collective structural variations present in these finite systems. The plotted colour scale represents the relative sampling frequency of geometries in PCA space rather than a Boltzmann-weighted free energy profile. In this representation, blue indicates regions of the highest structural probability as identified by the k-means clustering scheme with *scikit-learn*. At the same time, red denotes

low-probability, sparsely visited regions.

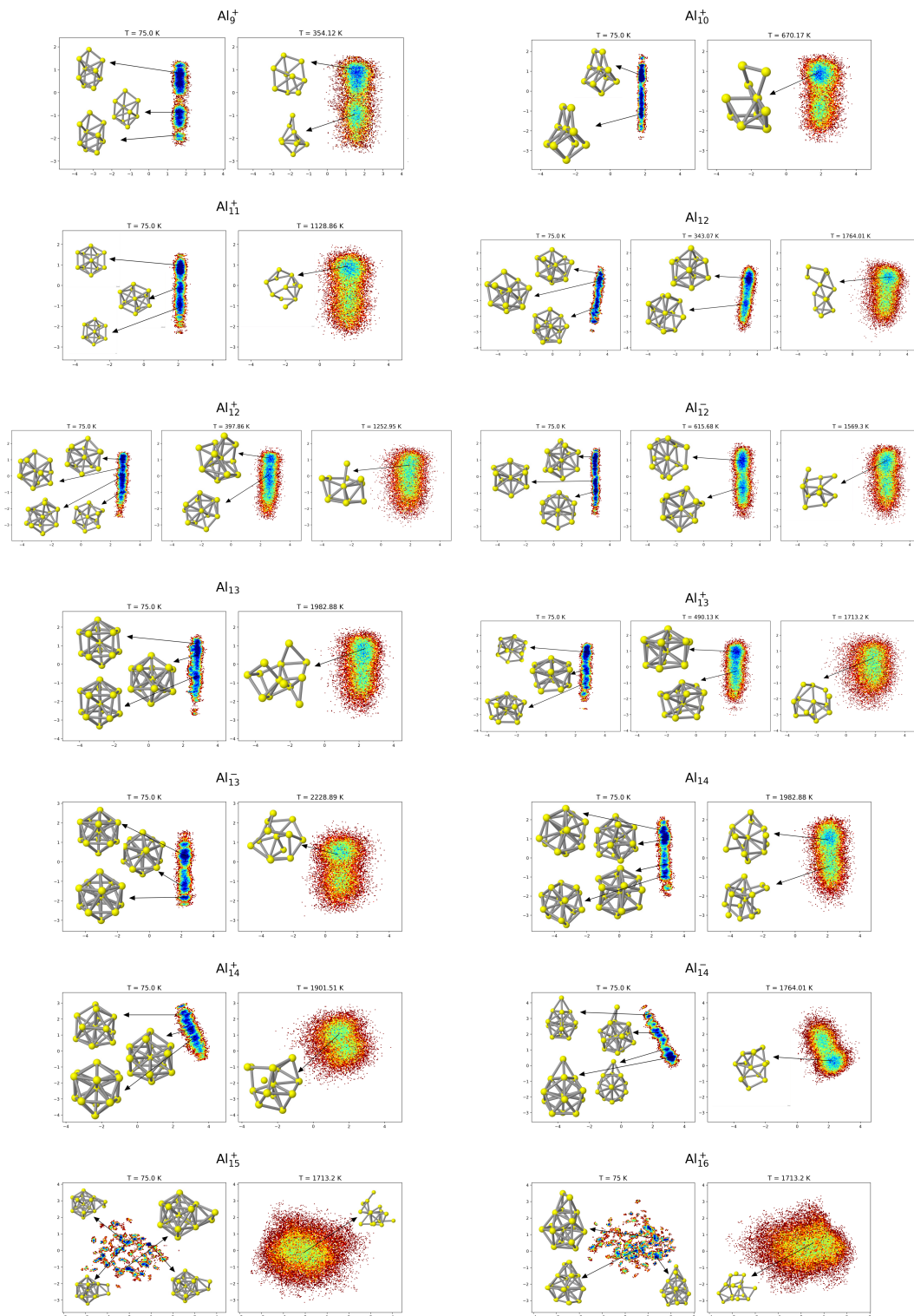


Figure 5.4: Principal component analysis (PCA) of structural distributions for aluminum clusters. Results are shown for cationic clusters (Al_9^+ to Al_{16}^+), and selected anionic and neutral clusters (Al_{12}^- to Al_{14}^- and Al_{12} to Al_{14}). Representative geometries illustrate the structural evolution during melting. The number of temperature points varies among clusters, as some systems (e.g., Al_{13}^+) exhibit premelting transitions prior to full melting, as indicated by their heat capacity behavior.

At low temperatures ($75K$), these PCA density maps display highly localized blue regions corresponding to the dominant ground state. These ground-state configurations are generally characterized by icosahedral (I_h) or near-close-packed arrangements, exhibiting high coordination numbers and stable bonding patterns, as confirmed by the representative structures shown alongside each cluster. The sharply peaked and compact distribution in PCA space underscores the rigidity and structural homogeneity of these cold-solid states.

As the temperature increases toward the melting temperature, the occupation probability broadens, populating more diffuse regions of PCA space, which appear red in the density maps. This shift reflects an increased exploration of diverse, liquid configurations with significant bond rearrangements and reduced symmetry. For example, Al_{13}^- around $2200K$ exhibits fragmentation of its icosahedral structure into amorphous, lower-coordination structures, accompanied by a pronounced spreading of its PCA density. The representative geometries from these red regions display open, dynamically disordered configurations consistent with a molten-like character. A systematic trend is apparent across the cluster series. Smaller systems such as Al_9^+ and Al_{10}^+ transition from a well-defined solid motif to a single disordered basin in PCA space. In contrast, larger clusters including Al_{15}^+ and Al_{16}^+ reveal multiple distinct high-density regions even at lower temperatures, suggesting the presence of several competing isomeric motifs and a more intricate configurational landscape. This richer structural complexity is consistent with an increasingly rugged potential energy surface that stabilizes multiple local minima as the number of atoms increases. Although not shown explicitly here, harmonic frequency analyses performed on representative geometries further support these observations. In the cold-solid regime, the structures exhibit only 0–2 imaginary frequencies, consistent with mechanical stability near local minima. As the clusters approach their melting region, the number of imaginary modes progressively rises to 4–12, reflecting the growing anharmonicity and dynamical instabilities as the system leaves the harmonic basin and enters the molten state.

5.4 Conclusion

In this work, we developed a global optimization framework combining an E(3) equivariant neural network potential with iterative DFT-level refinement, embedded within a Parallel Tempering Monte Carlo (PTMC) scheme. This strategy is broadly applicable to atomic clusters and was successfully demonstrated on aluminum systems ranging from Al_9^+ to Al_{16}^+ , including selected anionic and neutral forms of Al_{12} – Al_{14} .

Using this approach, we systematically explored the structural landscapes of the clusters, identifying low-energy isomers, relative energetics, and charge-dependent structural variations. The methodology reliably reproduced known global minima, as validated against reference structures from the literature. Many of the DFT-relaxed geometries would have been difficult to discover without the ML-guided framework. Beyond structural energetics, vertical ionization energies, electron affinities, and related electronic properties were computed to characterize the electronic structure. Principal Component Analysis (PCA) of the sampled geometries revealed how these clusters evolve from ordered, symmetric ground states to increasingly disordered, fluxional structures at elevated temperatures. This analysis offers mechanistic insight into their melting-like transitions and underscores the role of electronic shell effects in stabilizing or destabilizing specific structural motifs.

Overall, these results establish the framework as a robust and transferable strategy for probing thermodynamics, electronic properties, and structural transitions in small atomic clusters, with promising potential for application to broader classes of metallic and molecular nanoclusters.

Chapter 6

Selection of AB_2C_{10} Superatom Candidates and Investigation of Their Melting Transitions

6.1 Motivation

Superatoms are atomic clusters whose delocalized valence electrons fill quantized orbitals analogous to atomic shells, resulting in closed-shell configurations and atom-like chemical behavior [212, 11]. Within the spherical jellium framework, these valence electrons occupy angular-momentum-ordered shells in a quasi-spherical potential, stabilizing highly symmetric structures. Exceptionally stable configurations, known as *magic numbers* [213], are exemplified by the 13-atom aluminum anion (Al_{13}^-), which adopts an icosahedral geometry and a filled 40-electron jellium shell ($1s^2 1p^6 1d^{10} 2s^2 1f^{14} 2p^6$). This closed-shell superatom exhibits remarkable stability. The neutral superatom Al_{13} behaves chemically like a halogen, reacting similarly to iodine [214, 27]. Such findings have motivated the idea of a **periodic table of superatoms** [215], where stable clusters serve as artificial atoms, offering tunable building blocks for new materials with tailored properties.

Recent research has extended these ideas to heteroatomic systems, where substitution or doping modulates valence electron counts and cage rigidity. For example, substituting an Al atom in Al_{13}^- by a boron atom gives $iB@Al_{12}^-$ which preserves the 40-electron configuration while improving stability [216]. Doping transition metals into 12-atom cages, such as $Mn@Sn_{12}$ [217] and $An@Al_{12}$ (where An denotes actinide elements) [218], has been shown to induce novel magnetic properties while preserving the underlying structural symmetry. Other studies have explored gold- or silver-based clusters with ligand stabilization [219, 220], and platinum clusters confined in zeolites have shown superatomic orbitals and superdiamagnetism [221]. More recently, Piotrowski *et al.* [222] systematically compared group IVB endohedral and exohedral 13-atom clusters, demonstrating tunable magnetic and electronic properties while preserving icosahedral structures. These developments suggest that 13-atom superatoms are ideal systems to probe the relationships among electronic shell closure, cage rigidity, and vibrational stability. Notably, Al_{13}^- exhibits an exceptionally high melting point of approximately 2200K (see Chapter 4), motivating further exploration of heteroatomic 13-atom superatoms for enhanced thermal stability.

In this thesis, we investigate whether significant HOMO-LUMO gaps, robust cage geometries, and lowest vibrational frequencies correlate with elevated melting temperatures. Using the DFT-

trained neural network framework introduced in Chapter 4, we selected candidate clusters with quasi-spherical shapes, minimal icosahedral distortion and relatively high thermodynamic stability. These features are expected to support the design of thermally stable superatom clusters, enabling further studies of phase transitions and melting behaviour.

6.2 Different AB_2C_{10} Superatom Candidates

The AB_2C_{10} cluster family consists of a single central atom A, two B atoms placed at opposite poles, and ten C atoms completing a quasi-icosahedral shell. These highly symmetric (D_{5h} point group) 13-atom clusters were selected as candidates for superatomic behaviour due to their ability to sustain closed-shell electron configurations and their geometric compatibility with spherical jellium models.

	Atomization Energy (eV)	HOMO-LUMO Gap (eV)	Lowest Frequency (LF)	Rigidity
$\text{Zr}_1\text{K}_2\text{Cu}_{10}$	31.070	0.735	36	77112
$\text{Zr}_1\text{Rb}_2\text{Au}_{10}$	33.605	1.247	23.58	99193
$\text{Zr}_1\text{Sr}_2\text{Cu}_{10}$	33.219	0.735	38.82	101873
$\text{Sn}_1\text{Sn}_2\text{Y}_{10}$	38.852	0.277	46.08	199384
$\text{Sn}_1\text{Sn}_2\text{Ca}_{10}$	22.103	0.834	63.24	212683
$\text{Cr}_1\text{Li}_2\text{Ag}_{10}$	22.861	1.290	54.85	273926
$\text{Cr}_1\text{Sn}_2\text{Ti}_{10}$	41.287	0.724	104.1	646958
$\text{Cr}_1\text{Sn}_2\text{Zr}_{10}$	55.308	0.864	98.93	937608

Table 6.1: Atomization energies, HOMO–LUMO gaps, lowest vibrational frequencies, and rigidity measures for heteroatomic 13-atom superatom candidates.

Table 6.1 reports atomization energies and vibrational frequencies obtained from Gaussian 16 [2]. The rigidity parameter was computed as $f(M) \times (\text{LF})^2$, where $f(M) = (M_B + 5M_C)/6$ is the weighted average mass of surface atoms. Higher rigidity corresponds to a larger effective spring constant associated with the lowest-frequency vibrational mode, typically attributed to surface atom displacements and indicative of enhanced structural stability. Based on these data, $\text{Zr}_1\text{Rb}_2\text{Au}_{10}$

was selected because it has a high HOMO-LUMO gap and a relatively simple electronic structure. Sn_3Y_{10} was chosen because it has three Sn atoms in a colinear arrangement and a rigid Y_{10} shell.

6.3 Results

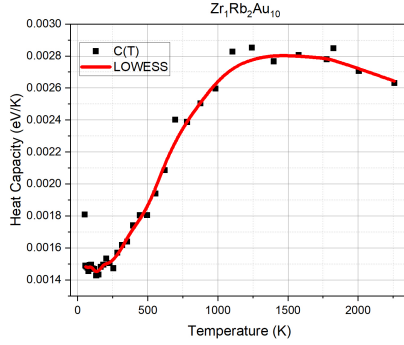
The DFT-NN-PTMC framework explained in Chapter 5 is used to study melting like transition in both $\text{Zr}_1\text{Rb}_2\text{Au}_{10}$ and Sn_3Y_{10} . As shown in Chapter 6, this approach can also facilitate global optimization. Two methodological updates are noted. First, the melting criterion based on the derivative of δ with respect to temperature, previously obtained via a LOWESS fit to δ , is now evaluated using a spline fit implemented in *scipy*. The spline’s continuous representation permits smoother and more reliable differentiation with reduced numerical noise. Second, the protocol for generating the initial training dataset has been revised to allow clusters of more than one element.

The weighted mean of the elements’ melting points serves as a helpful reference point. They are 1240 K ($\text{Zr}_1\text{Rb}_2\text{Au}_{10}$) and 1500 K (Sn_3Y_{10}). Small elemental clusters often melt at temperatures 10% to 40% below the bulk melting point.

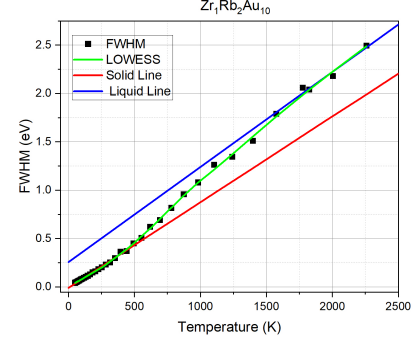
	T_c from $C(T)$ (K)	T_f, T_m from W_U (K)	T_c from $d\delta/dT$ (K)	T_c from $d^2G(T)/d^2T$ (K)	T_f, T_m from F_s (K)	U_0 (eV) (Allegro)	U_0 (eV) (DFT)	MAE (meV/atom) Model Accuracy	R^2
$\text{Zr}_1\text{Rb}_2\text{Au}_{10}$	1349	578, 1790	1205	1305	820, 1724	-34.6933	-34.7374	6.06	0.994
Sn_3Y_{10}	2029	1310, 2567	2243	2220	1291, 2459	-42.6443	-42.6026	4.99	0.997

Table 6.2: Melting temperatures of $\text{Zr}_1\text{Rb}_2\text{Au}_{10}$ and Sn_3Y_{10} clusters in K, T_c (from $C(T)$), T_f and T_m (from W_U), T_c (from $d\delta/dT$), T_c (from $d^2G(T)/d^2T$), T_f and T_m (from F_s) global minimum energy U_0 (Allegro and DFT), mean absolute errors (MAE) of the trained model(in meV/atom) and Pearson correlation coefficient R^2 between Allegro and DFT energies.

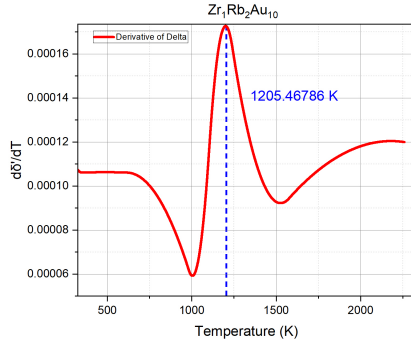
The system $\text{Zr}_1\text{Rb}_2\text{Au}_{10}$ was modeled using a two-layer architecture with a cutoff radius of $r_{\text{cut}} = 9 \text{ \AA}$, spherical harmonics up to angular momentum $l = 3$, edge encodings, and a batch size of 32. The training objective employed a per-atom mean-squared-error (MSE) loss on the total



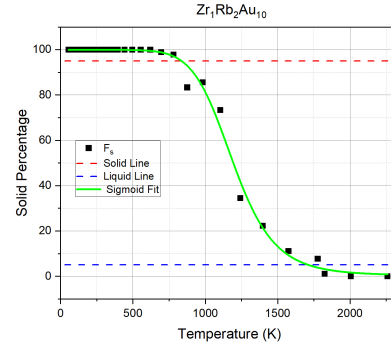
(a) Heat capacity ($C(T)$) vs. temperature (K). The solid red line is a LOWESS fit.



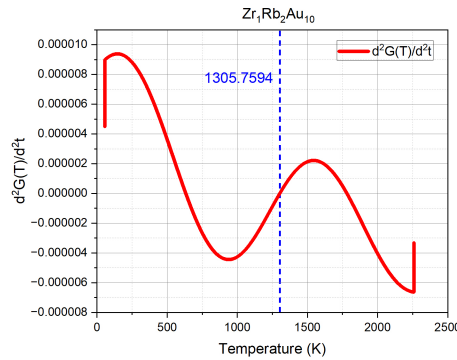
(b) Width W_U of the probability function of the potential energy vs temperature (K). The red and blue dashed lines are straight-line fits at low (red) and high (blue) temperatures. The green solid line is a LOWESS fit.



(c) Derivative of δ ($d\delta/dT$) vs. temperature (K). The vertical blue dashed line shows the peak.



(d) Percentage of configurations classified as solid F_s vs temperature (K). The red and blue dashed lines are the [95%, 5%] cutoffs, respectively. The green line is a sigmoid fit.



(e) Second derivative of $G(T)$ ($d^2G(T)/dT^2$) vs temperature (K). The vertical blue dashed line shows the inflection point.

Figure 6.1: Temperature dependence of properties used to detect melting for $Zr_1Rb_2Au_{10}$: $C(T)$, W_U , $d\delta/dT$, solid fraction F_s , and the inflection point in d^2G/dT^2 .

energy. The transition temperatures—(T_c), freezing temperature (T_f), and melting temperature (T_m)—were extracted according to multiple criteria, with numerical values summarized in Table 6.2 and corresponding plots in Figure 6.1. The melting temperature was determined by averaging the T_c values from $C(T)$, $d\delta/dT$, and the inflection point $d^2G(T)/dT^2$. In addition, the median of the T_f and T_m estimates from W_U and the solid fraction F_S was incorporated. The average of these five estimates of melting points is 1263 K. This is quite close to the weighted mean of the experimental melting points of the elements. As such, the 1263 K melting point is only slightly higher than typical for a small cluster and does not give strong support for the view that $\text{Zr}_1\text{Rb}_2\text{Au}_{10}$ is a superatom. The global minimum-energy geometry (Figure 6.2(a)) corresponds to an icosahedron with the Zr atom at a highly coordinated central site, while the Rb atoms occupy top and bottom positions.

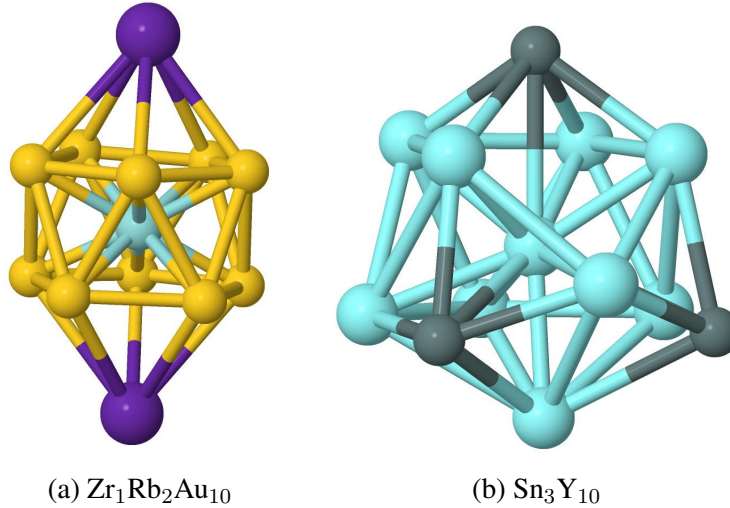
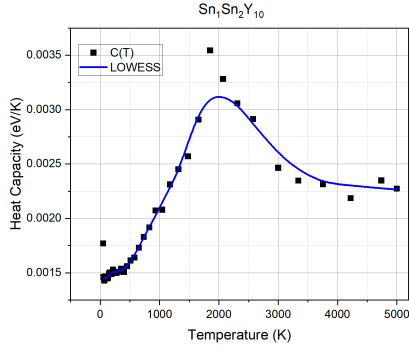
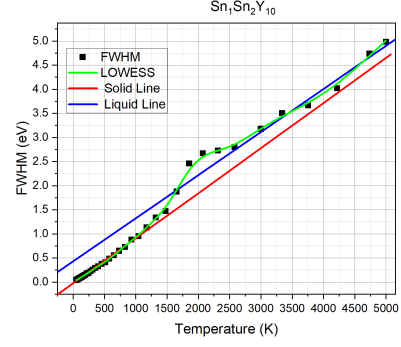


Figure 6.2: Global minimum-energy geometry identified using the DFT-NN framework.

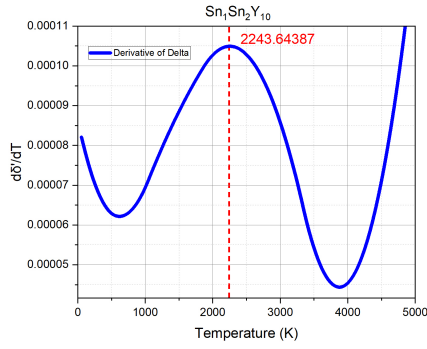
Fig. 6.3 shows the melting criteria for the Sn_3Y_{10} candidate. The results from all criteria are well-converged. The mean of the five determinations of the melting point is 2061 K. This is significantly higher than the mean of the elements' melting points (1500 K) and supports the view that Sn_3Y_{10} is a superatom. The model architecture was slightly modified with a cutoff radius of $r_{\text{cut}} = 8 \text{ \AA}$. An interesting insight is that, although an icosahedron was expected, global optimization (GO) instead identified a structure (Fig. 6.2(b)) where the central atom is Y (not Sn). In insight, it is logical: Y has a higher cohesive energy than Sn (4.37 vs 3.14 eV/atom).



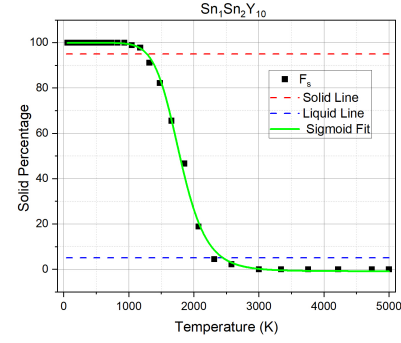
(a) Heat capacity ($C(T)$) vs. temperature (K). The solid blue line is a LOWESS fit.



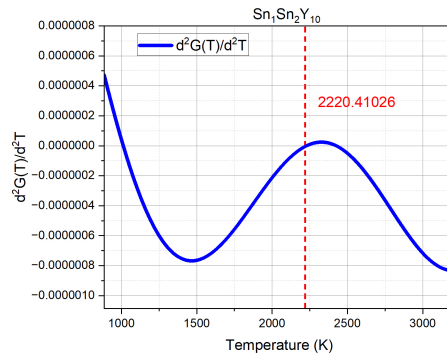
(b) Width W_U of the probability function of the potential energy vs temperature (K). The red and blue dashed lines are straight-line fits at low (red) and high (blue) temperatures. The green solid line is a LOWESS fit.



(c) Derivative of δ ($d\delta/dT$) vs. temperature (K). The vertical red dashed line shows the peak.



(d) Percentage of configurations classified as solid F_s vs temperature (K). The red and blue dashed lines are the [95%, 5%] cutoffs, respectively. The green line is a sigmoid fit.



(e) Second derivative of $G(T)$ ($d^2G(T)/dT^2$) vs temperature (K). The vertical red dashed line shows the inflection point.

Figure 6.3: Temperature dependence of properties used to detect melting for Sn_3Y_{10} : $C(T)$, W_U , $d\delta/dT$, solid fraction F_s , and the inflection point in d^2G/dT^2 .

These early results motivate further examination of possible superatomic behaviour in these two clusters and the six other clusters of Table 6.2. We are currently collaborating with Mauricio Piotrowski and coworkers to examine the electronic structure and the results of ab initio molecular dynamics (AIMD) simulations for these clusters. We hope to characterize in detail the **possible** superatomic character of these clusters by looking at several indicators of stability: thermodynamic stability (relative atomization energies), thermal stability (melting points found with DFT-NN-PTMC Framework and by AIMD), mechanical stability (with measures of icosahedral symmetry and rigidity), and chemical stability (with the HOMO-LUMO gap and binding energies of small molecules to the clusters).

Chapter 7

Conclusion and Future work

7.1 Conclusion

This thesis examined melting transitions in atomic and superatomic clusters. We developed computational tools combining geometric metrics, density functional theory, and machine-learned interatomic potentials, all integrated with parallel tempering Monte Carlo (PTMC). Four investigations advanced the approach from geometric melting criteria to a broadly transferable framework for diverse elements and bonding types.

Chapter 3 introduced four temperature-dependent indicators to identify melting transitions with improved efficiency over traditional heat capacity $C(T)$ calculations. These functions, defined by the width of the potential energy distribution (f_1) and statistics of ordered interatomic distances (f_2, f_3, f_4), offered a direct measure of the transition. Their behaviour near the melting temperature aligned consistently with that predicted by conventional $C(T)$ calculations, while reducing simulation time by up to three orders of magnitude. Additionally, an artificial neural network classifier using the (f_2, f_3, f_4) features was constructed to estimate the solid fraction $F_S(T)$ and to delineate the solid-liquid coexistence region between freezing and melting temperatures. Inflection points in $d^2G(T)/dT^2$ and $F_S(T)$ emerged as sensitive and robust markers of phase transitions, fulfilling the initial goal of identifying geometric features capable of signalling melting without million-step sampling.

Chapter 4 introduced a framework for fast calculation of energies with an accuracy approaching that of DFT. It involves making a dataset of geometries and DFT energies with a global optimization algorithm; fitting the data accurately with an equivariant deep learning method (Allegro); and doing a few iterations of exploratory PTMC simulations to add more configurations to the data set and refit the Allegro potential. This computational method reproduced experimental and theoretical melting features of Na_{20} and further characterized Al_n clusters, showing that their melting points depend strongly on size and charge state. Notably, $\text{Al}_{11}^+ - \text{Al}_{16}^+$ clusters melted above the bulk melting point of aluminum, while smaller charged clusters such as Al_9^+ and Al_{10}^+ showed lower melting temperatures. These results confirmed the non-monotonic dependence of melting temperatures on cluster size and charge, supporting the idea that small-cluster thermodynamics are highly system-specific.

The computational framework we introduced enables DFT-quality melting point predictions for arbitrary clusters with $n < 20$ –30 atoms within practical computational time frames.

Chapter 5 developed an active-learning global geometry optimization (GO) protocol tested on aluminum clusters. This protocol extended the framework of Chapter 4, enabling the exploration of tens of millions of DFT-accurate energies at a reduced computational cost and accelerating the identification of low-energy candidates (Global minimum and isomers). Systems included Al_n^+ ($n = 9$ –16) and neutral or anionic Al_n ($n = 12$ –14). Low-energy structures were refined by TPSS/SDD-level geometry optimization in Gaussian and validated with harmonic frequency analysis. Ionization energies, electron affinities, and vertical ionization potentials were calculated, demonstrating agreement with previous studies. Structural transitions during melting were analyzed using bond-orientational order parameters and principal component analysis of atomic density distributions, which distinguished partial from complete melting transitions. This approach can be extended to other systems with appropriate training data.

Chapter 6 currently in progress, extends these methods to heteroatomic 13-atom superatom clusters, as tested on $\text{Zr}_1\text{Rb}_2\text{Au}_{10}$ and Sn_3Y_{10} . It uses the same PTMC-based framework developed in Chapter 4, combined with the melting criteria introduced in Chapter 3, to analyze these heteroatomic systems. The melting criteria converged to melting temperatures of 1263 K for $\text{Zr}_1\text{Rb}_2\text{Au}_{10}$ and 2061 K for Sn_3Y_{10} , both above bulk references, suggesting enhanced thermal stability due to superatomic bonding patterns. DFT optimizations showed stable icosahedral and showed that the preferred geometry of Sn_3Y_{10} has a Y atom at the center. We are currently investigating other possible superatoms with a variety of computational methods, including melting point determinations.

Collectively, these studies establish a unified, extensible platform for studying cluster melting. Many critical technical improvements were made to the PTMC code in the course of this study: (1) we added the option to call an external program for calculating the energy; (2) we added a checkpoint option, which allows to break down long simulations into segments (this is important on the Digital Research Alliance Canada computers where there is a time limit of one week); (3)

changes to the input and output format to make the program more straightforward to use.

Initially, the goal of this thesis was to develop indicators of melting that give converged melting points with shorter simulations, and then use the methodology to study the physics of a few specific clusters. These two goals were achieved in the work described in Chapters 3 and 4. As this work was nearing completion, we became acquainted with a deep learning approach (Allegro) for highly accurate fits of potential energy functions. We seized the opportunity to incorporate this into a general approach, described in Chapter 4, for clustering melting simulations. Interfacing Allegro to our other computer codes was time-consuming, but well worth it. It was, in a way, the last piece of our **simulation puzzle**. With the framework described in Chapter 4, extended with methods of Chapters 5 and 6, we now have a general tool for simulating melting in clusters with up to roughly 30 atoms of any chemical composition at the level of accuracy of DFT. This is a significant improvement over previous work, where potentials had to be designed laboriously, one at a time, for every new cluster. It opens the door for possible systematic studies of cluster melting over a wide range of sizes and chemical compositions.

7.2 Future Work

The first immediate priority for future work is to expand and complete the study of superatomic clusters described in Chapter 6. This includes analyzing additional structural and dynamical properties of these systems and comparing them to results obtained from ab initio molecular dynamics simulations. That effort is ongoing and is expected to be finalized in the coming months.

Beyond this, the development of a transferable and scalable simulation framework combining density functional theory, machine-learned interatomic potentials, and parallel tempering Monte Carlo (DFT-NN PTMC) enables systematic studies of melting-like transitions in clusters formed from nearly any element in the periodic table. The primary constraint is the availability of computational resources. Interesting candidates for simulations include clusters that have shown potential in nanotechnology, such as gold, platinum, silicon, silicon oxide, aluminum oxide, and

ferromagnets (Fe, Co, Ni, and their alloys). Liquid metals are another class of systems that are interesting for fundamental reasons: mercury, gallium, and gallium alloys. *Galinstan*, an alloy of Ga, In and Sn, is of particular interest: with a melting point of 254 K and a low toxicity, it is considered a safer liquid metal alternative to mercury.

Several technical enhancements could further improve performance and extend the accessible cluster sizes. The current Allegro model is version 0.6.00; upgrading to version 0.7.00, which offers higher inference accuracy and throughput, would help support larger-scale simulations. The PTMC code uses a Python-based flash server, with Gunicorn managing multiple workers. Although Gunicorn has improved stability, occasional overload still occurs, so additional server-side optimization is likely needed. In addition, reducing the frequency of checkpoint writes from every simulation step to every 15–20 steps could lower input/output overhead on high-performance computing systems.

Reducing latency between PTMC and external program calls is another area of potential improvement. Currently, the framework utilizes Python-based interprocess communication, which introduces a performance bottleneck. One option is to apply the *TorchScript C++ API*, which compiles models trained in PyTorch for native execution in $C++$, thereby reducing Python overhead. Another possibility is to experiment with Fortran bindings for PyTorch models; tools such as *Ftorch* are emerging and could offer additional speedups, though they will need rigorous testing. Rewriting critical subroutines in $C++$ or using *Cython* to compile selected Python components could also improve performance. Finally, streamlining data exchange between PTMC and the neural-network model by using shared memory or direct socket communication may help reduce latency on large-scale computing resources.

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Appendices

Appendix A

XYZ Coordinates of Rare Gas, Covalent, and Metallic Clusters Studied — Supplementary to Chapter 3

The global minimum geometries presented below were identified through Parallel Tempering Monte Carlo (PTMC) simulations, which cover clusters with metallic, covalent, and van der Waals bonding characteristics across the entire size range considered.

<i>Ar₇</i>			
Ar	-0.124987	2.929618	-1.394526
Ar	2.936564	0.650738	-1.233790
Ar	-1.717315	-2.232335	1.631854
Ar	0.532323	0.834253	1.686478
Ar	-3.016627	1.152753	0.394486
Ar	1.935003	-2.526209	0.623348
Ar	-0.544961	-0.808818	-1.707850

Ar_8			
Ar	-1.490600	2.429460	0.689294
Ar	1.452438	0.013868	0.723560
Ar	-2.029299	-1.068836	-0.681133
Ar	0.127860	-3.503832	1.224136
Ar	2.010400	3.665298	-0.179352
Ar	0.182420	1.336030	-2.592366
Ar	-1.471006	-0.532884	3.063295
Ar	1.217787	-2.339104	-2.247434

Ar_{10}			
Ar	-2.339225	-0.585364	-3.186018
Ar	-2.215134	-0.750234	3.277581
Ar	1.104443	3.869189	0.061806
Ar	0.840303	1.639926	-3.106202
Ar	1.013666	1.473572	3.145298
Ar	0.903766	-2.027824	-1.958914
Ar	0.966769	-2.091192	1.800956
Ar	-0.910106	0.695762	0.042296
Ar	2.927025	0.558757	-0.055137
Ar	-2.291506	-2.782590	-0.021668

Ar_{13}

Ar	-2.056038	-1.230868	-2.770991
Ar	2.072294	1.233638	2.755055
Ar	0.012822	0.010285	0.012546
Ar	-0.294543	-3.641009	-0.303197
Ar	2.996060	-1.978987	0.826168
Ar	-1.819928	1.566384	2.812592
Ar	3.241222	1.468612	-0.909328
Ar	-2.985808	1.961350	-0.822058
Ar	-3.238036	-1.476937	0.928365
Ar	1.787800	-1.592801	-2.848858
Ar	0.083555	1.918353	-3.140489
Ar	0.338698	3.674867	0.300213
Ar	-0.138098	-1.912887	3.159982

 Ar_{18}

Ar	-0.041620	-3.332871	-2.964755
Ar	0.076795	-1.405520	0.142785
Ar	1.980629	3.890650	2.182718
Ar	-2.006502	3.714280	2.541432
Ar	2.943275	3.553624	-1.625955
Ar	-3.070675	-3.199755	-0.467991
Ar	-0.155711	2.159295	-0.245513
Ar	-2.089653	-0.089204	-2.555803
Ar	3.233538	-2.934087	-0.919962
Ar	-1.567553	-2.775062	3.154719
Ar	-0.370971	3.238661	-3.770695

Ar	0.220165	0.683385	3.246213
Ar	-3.528699	3.209132	-1.189238
Ar	3.130440	0.531348	0.726642
Ar	1.716958	0.133498	-2.809701
Ar	-3.060059	0.227288	1.194267
Ar	2.296523	-2.573247	2.818523
Ar	0.293122	-5.031415	0.542312

Ar_{19}

Ar	-0.506128	-3.378380	-3.161774
Ar	1.083094	-0.184155	-4.542700
Ar	0.704276	2.635413	-1.816291
Ar	-3.414682	2.936997	3.014352
Ar	-2.179671	0.074043	-2.486058
Ar	-2.979991	3.491521	-0.874870
Ar	0.133856	1.729503	4.308427
Ar	-4.643524	0.236799	0.482315
Ar	1.356649	-4.457246	0.023287
Ar	3.355923	-2.995056	-3.013442
Ar	4.223988	-1.868634	0.653962
Ar	-2.707969	-0.838050	3.744470
Ar	-0.068262	4.433419	1.556156
Ar	-1.107733	0.976718	0.985668
Ar	4.059958	0.815096	-2.207964
Ar	0.927605	-1.650277	2.695794
Ar	-1.983483	-2.571982	0.274836
Ar	2.609507	1.561605	1.344175

Ar	1.136587	-0.947334	-0.980342
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Ar_{20}

Ar	-1.621163	-2.283856	1.171381
Ar	4.478973	-1.075404	1.561105
Ar	-2.317864	1.641048	1.040792
Ar	-4.701148	-0.762076	2.568893
Ar	-1.217067	-0.062158	4.236378
Ar	-2.307991	-0.714946	-4.822992
Ar	0.574681	3.266594	-0.774316
Ar	-1.596298	-3.638045	-2.450520
Ar	0.596318	1.945737	-4.387833
Ar	-2.769094	2.538968	-2.618610
Ar	3.743669	2.736761	1.399271
Ar	0.311844	3.433231	3.095089
Ar	1.753385	-2.886703	-0.529485
Ar	1.553677	-2.752341	3.420241
Ar	3.083112	0.472339	-1.723299
Ar	1.379783	-1.896688	-4.267532
Ar	2.670000	0.825937	4.638701
Ar	1.081290	0.249290	1.411362
Ar	-4.146071	-0.844671	-1.292607
Ar	-0.550035	-0.193016	-1.676020

Si_7

Si	-0.0371176	0.1255618	2.0265679
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Si	0.8954205	0.7093649	-1.6723056
Si	-0.9409070	1.0365436	-0.0748316
Si	-0.8485621	-0.9047675	-1.6041471
Si	1.4047308	1.3192951	0.5711559
Si	-1.4343489	-1.2490324	0.6709351
Si	0.9422953	-1.0329888	0.0776552

Si_8

Si	3.6833038	2.4291627	-1.2343413
Si	1.6271970	3.2772764	-0.8182809
Si	3.7048398	2.1661672	-3.7765424
Si	0.0912269	2.0077110	-2.4203782
Si	1.5863862	0.9165071	-1.1192784
Si	1.4977610	2.8150371	-4.4069096
Si	1.6324200	0.6850389	-3.6550812
Si	3.0260247	4.0924972	-2.8030137

Si_{10}

Si	0.2711155	1.8018200	-1.2767374
Si	-1.0860128	-1.7042527	-0.9728945
Si	1.2293813	-1.7919441	-0.5760436
Si	-1.7119692	0.5302173	-1.3935779
Si	-0.2726191	-1.8425906	1.2813382
Si	1.1157149	1.7461582	0.9509260
Si	-2.0931697	-0.4084727	0.7751534

Si	1.6748924	-0.5184355	1.3941361
Si	-1.2152760	1.7755141	0.5909887
Si	2.0961917	0.4054374	-0.7688377

Si_{13}

Si	-6.1217644	-6.0863768	7.9921092
Si	-6.1814990	-2.5611126	5.1279270
Si	-5.6548904	-4.0024898	6.9427925
Si	-8.4838794	-6.2655434	7.7791460
Si	-7.1308410	-3.8794999	3.4620012
Si	-5.3055019	-6.0836528	5.7902256
Si	-9.7470916	-3.1752983	6.0163515
Si	-7.5956757	-2.7307991	7.0485754
Si	-9.1158993	-4.8490812	4.3994445
Si	-9.2737195	-4.0434941	8.1215553
Si	-10.2043349	-5.4778803	6.4329754
Si	-7.1786771	-6.1271672	4.3000347
Si	-7.0746298	-7.4768758	6.2849519

Si_{18}

Si	2.679906	0.754932	-1.081121
Si	-0.183058	2.432525	-2.929623
Si	-0.290423	3.308839	-0.677919
Si	1.275878	-0.923082	-2.062690
Si	-1.960259	1.853873	-1.485687

Si	-1.848326	-2.309796	2.478803
Si	-1.474416	0.048987	3.000000
Si	0.226245	-1.542702	3.406468
Si	1.759875	-1.655321	1.642675
Si	-1.599188	-2.320519	0.084458
Si	0.705544	-2.452291	-0.320247
Si	1.346535	1.971351	0.485683
Si	2.923604	-1.502115	-0.413017
Si	-2.871442	-0.608674	1.234074
Si	-0.742153	0.123830	-2.648400
Si	-2.434282	-0.425598	-1.074497
Si	1.796143	2.823466	-1.732393
Si	0.689816	0.422295	2.093433

Si_{19}

Si	1.7777752	-0.2119687	-1.0152306
Si	-1.7132531	4.1531877	-2.4613875
Si	2.0770502	4.1616440	-2.5427939
Si	2.1244936	-0.7851902	1.2518256
Si	0.2553808	0.8032000	-2.4582501
Si	1.4165924	3.9097236	-0.2498935
Si	3.2103491	2.8307639	0.7899966
Si	-1.6175257	1.9391160	-1.5283456
Si	3.7036983	-1.4844987	-0.4138513
Si	4.4880830	-0.6710144	1.6920192
Si	0.1880207	5.3139837	-1.7301183
Si	3.0056549	1.0767182	2.3580557

Si	-0.9427838	3.8046501	-0.2347511
Si	3.5914270	2.4292745	-2.9503067
Si	4.7340336	2.1392214	-0.8486899
Si	1.3731874	2.3299771	-3.8606375
Si	5.1568641	1.5685909	1.3990165
Si	3.9161922	0.2719378	-1.9760567
Si	-0.9832979	2.3526796	-3.8171322

Si_{20}

Si	-2.7069270	9.9713648	-7.0195449
Si	-1.2670706	10.8610067	-12.6730084
Si	-3.1795314	7.8606432	-7.8435843
Si	0.7097466	9.5794757	-12.6906068
Si	0.3640377	6.6311158	-9.1475953
Si	0.9028791	8.0521002	-7.4136614
Si	1.6899230	9.9334290	-10.5082384
Si	-2.4582053	10.1908504	-10.7210710
Si	0.7605709	10.2466147	-8.3361560
Si	-2.9466329	7.9726492	-10.2380478
Si	-0.1010374	7.9459996	-5.2355918
Si	-1.2610248	12.2638974	-10.7514395
Si	-2.4148492	8.0177515	-5.6077272
Si	0.9858856	7.8179807	-11.1363384
Si	-1.9778082	6.1821099	-8.9417212
Si	-1.0997560	6.6946696	-11.0404503
Si	-1.3905795	11.0030530	-8.7422035
Si	-1.2556377	10.0517282	-5.1438827

Si	0.9070960	9.9924894	-5.9856540
Si	0.7730929	11.7492224	-11.7450405

Ag_8

Ag	-0.502783	1.533078	0.964295
Ag	0.506425	-1.797821	0.141842
Ag	-1.675871	-0.325717	-0.666379
Ag	1.277519	-0.165215	2.105032
Ag	-1.346486	-0.849307	1.904055
Ag	1.698506	0.610419	-0.413855
Ag	-0.342855	1.763004	-1.710873
Ag	0.385544	-0.768441	-2.324117

Ag_{12}

Ag	0.430376	-1.028614	-0.667831
Ag	-1.654962	0.131179	-1.943022
Ag	-0.425122	-0.670570	1.874397
Ag	-0.565947	2.018137	1.440854
Ag	-2.775270	0.569694	1.379329
Ag	1.834040	-2.033747	1.399668
Ag	-2.152536	2.439083	-0.677760
Ag	0.384502	1.670424	-1.096444
Ag	2.730936	-2.408678	-1.112568
Ag	1.707337	0.692528	1.010486
Ag	-2.107426	-1.643354	0.040918
Ag	2.594072	0.263919	-1.648027

Ag_{16}			
Ag	0.956178	0.235697	-0.415527
Ag	-1.539224	-0.196017	0.649847
Ag	-0.847541	1.493579	2.692188
Ag	-3.111380	-1.344111	-1.381285
Ag	1.608339	1.906241	1.622915
Ag	1.187131	-0.128847	3.392022
Ag	-0.472132	-1.948570	-1.148652
Ag	3.400231	-0.681098	-1.282863
Ag	1.278269	-0.598820	-2.930361
Ag	-2.593838	1.288322	-1.447471
Ag	0.650161	-1.840373	1.302358
Ag	2.931611	-0.401831	1.346362
Ag	-1.405770	-0.592403	-3.325221
Ag	-0.663849	2.294174	0.182058
Ag	-0.148316	1.647094	-2.442035
Ag	-1.229868	-1.133038	3.185668

Ag_{20}			
Ag	-0.005033	0.058559	-0.115703
Ag	-0.268412	-2.727496	0.115310
Ag	1.974787	0.323214	1.866138
Ag	-0.289405	-1.170568	2.354145
Ag	0.762821	2.666071	-1.940950
Ag	-2.674164	-1.942889	1.227749

Ag	-2.566838	-2.951423	-1.271718
Ag	-0.508459	-1.519378	-2.315136
Ag	-1.575633	2.281739	-0.571464
Ag	-1.527110	3.302690	1.929393
Ag	0.803974	2.531744	0.770924
Ag	-2.144106	0.653218	1.534106
Ag	1.425824	0.235612	-3.025114
Ag	-0.059707	1.428137	3.182099
Ag	1.989590	-2.398822	1.520246
Ag	2.534755	0.999603	-0.676878
Ag	-2.592311	-0.236137	-1.022914
Ag	-1.170423	1.032335	-2.949904
Ag	1.918548	-1.637865	-1.127816
Ag	3.971305	-0.928345	0.517485

Appendix B

Confusion Matrix from ANN Classifier — Supplementary to Chapter 4

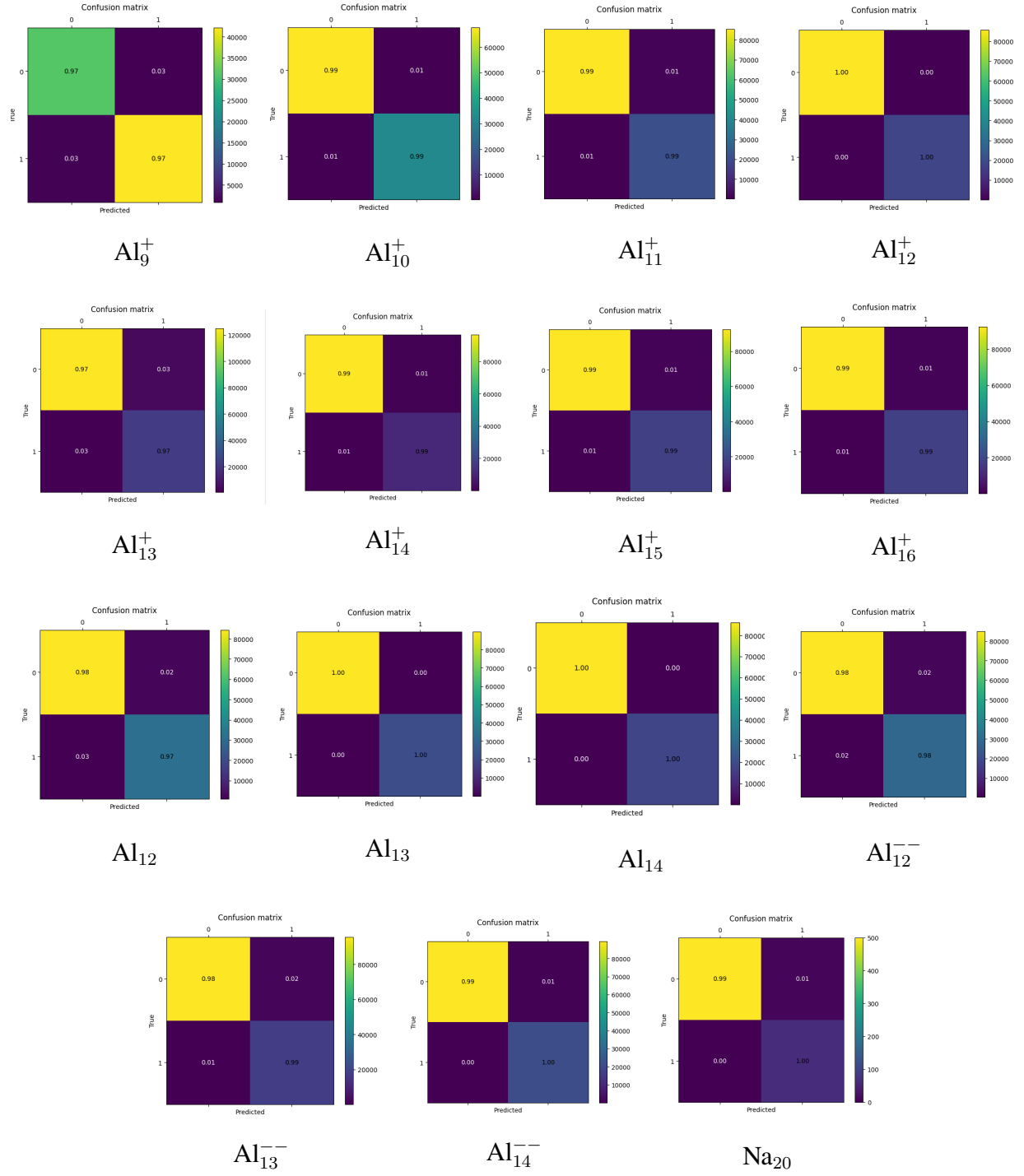


Figure B.1: Confusion matrices of the ANN classifier for all studied clusters.

Cluster	TN	FP	FN	TP	AUC
Al_9^+	31217	978	1192	42134	0.971
Al_{10}^+	67705	563	311	32115	0.991
Al_{11}^+	85380	1075	291	21141	0.987
Al_{12}^+	85789	361	84	18057	0.996
Al_{13}^+	124972	4050	735	22387	0.968
Al_{14}^+	96627	518	74	10668	0.994
Al_{15}^+	92472	1160	178	17673	0.989
Al_{16}^+	92415	1217	164	17687	0.989
Al_{12}	84314	2072	1003	31287	0.973
Al_{13}	89745	302	105	21331	0.996
Al_{14}	86090	60	20	18121	0.999
Al_{12}^{--}	84935	1486	431	28227	0.984
Al_{13}^{--}	95574	1677	250	17578	0.984
Al_{14}^{--}	89491	556	95	21341	0.995
Na_{20}	500	6	0	64	0.994

TN = True Negatives (solid correctly classified as solid); FP = False Positives (solid incorrectly classified as liquid); FN = False Negatives (liquid incorrectly classified as solid); TP = True Positives (liquid correctly classified as liquid); AUC = Area Under the Receiver Operating Characteristic curve.

Table B.1: Summary of confusion matrix elements and AUC for each cluster

B.1 Global Minimum Geometry Structure XYZ for Al_{16}^+ and

Na_{20}

	Al_{16}^+		
Al	0.6204930	-1.6996957	1.1473453
Al	-0.5120207	0.3420647	-0.0447187
Al	-2.8083493	1.3568909	1.0930229
Al	-1.8499475	-1.8014474	-1.3043432
Al	-2.1998390	-1.4683408	1.3351503
Al	3.1129884	-2.9471694	-0.4637827
Al	-3.0822846	0.5433498	-1.5956136
Al	-0.1404940	0.3878616	-2.6530487
Al	-1.4541219	2.7614603	-1.4368396
Al	-0.3661560	2.7489866	1.2927970
Al	2.2260693	-0.1147632	-0.8783958
Al	1.7069420	0.9406060	1.6142163
Al	0.7108776	-2.3357228	-1.7343334
Al	3.4784950	-1.3541937	1.7269129
Al	-0.6570663	0.2750886	2.8835070
Al	1.2144138	2.3650243	-0.9818761

 Na_{20}

Na	2.2271194	2.4734519	0.6466535
Na	-0.7372100	0.0880439	1.2917946
Na	0.2890787	-0.1408444	-1.4568581
Na	2.1856326	-2.3272273	0.9925529
Na	-1.1023631	-3.4703201	-0.1516511
Na	-3.5023026	-0.1065582	-1.2990552
Na	1.6622864	-3.3882912	-2.3354738
Na	-0.3495115	-2.9317873	3.2963328
Na	3.7045252	-0.1445681	-1.6171993
Na	-3.6190738	2.0879778	1.5141713
Na	1.7180770	0.3057646	3.6544336
Na	-3.6515630	-1.8548669	1.7707323
Na	-1.7142345	-2.2281913	-3.4920069
Na	-1.1008793	3.4605499	-0.6857769
Na	-1.6416914	1.7352502	-3.7158353
Na	-1.8918157	0.3509212	4.3784836
Na	4.6903877	0.0805402	1.7280205
Na	1.7486730	2.9432887	-2.7489389
Na	-0.3799017	3.4071214	2.8006811
Na	1.4647667	-0.3402550	-4.5710607

B.2 Training Curves of the converged final model after training and retraining

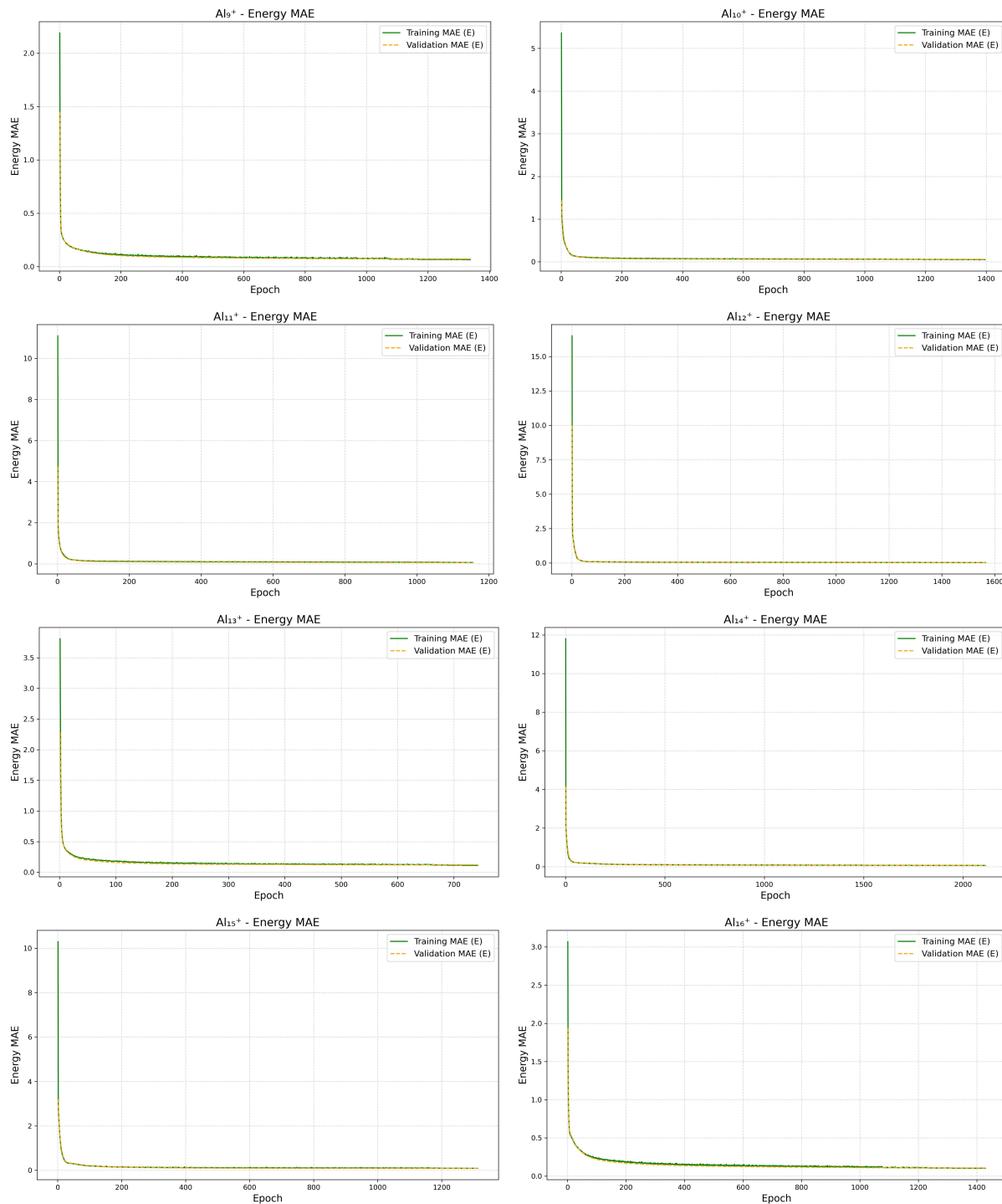


Figure B.2: Training and validation energy MAE curves for cationic clusters (Al_9^+ to Al_{16}^+).

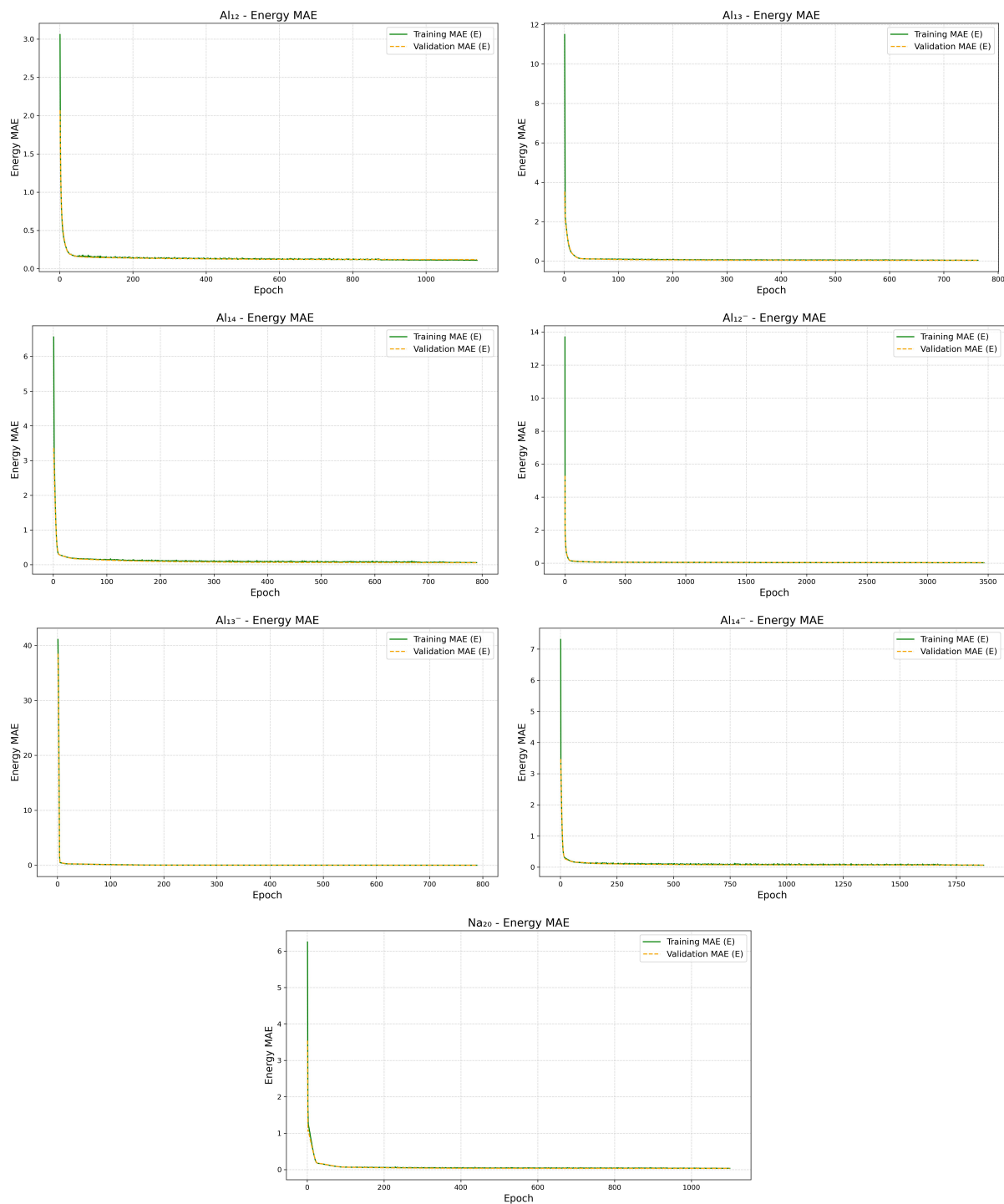


Figure B.3: Training and validation energy MAE curves for neutral (Al_n ($n=12,13,14$)) (including Na_{20}) and anionic (Al_n^- ($n=12,13,14$)) clusters .

Appendix C

XYZ Coordinates of Global Minimum found from Framework — Supplementary to Chapter 5

The global minimum geometries presented below were identified using the GO using the DFT-NN
framework.

	Al_9^+		
Al	-2.213149896	-0.047201914	-1.688357702
Al	3.286436004	-0.053612065	-0.417120267
Al	0.038349328	0.002292810	1.658017607
Al	0.444042612	-0.009361351	-1.269473810
Al	-1.154705332	-2.023123294	-0.049608120
Al	-1.112947899	2.031196001	-0.109697848
Al	1.723222943	2.112690062	0.316561701
Al	1.647043721	-2.088375769	0.361312115
Al	-2.658291480	0.075495522	1.198366325

	Al_{10}^+		
Al	-1.562847909	2.700451732	-0.008214060
Al	2.879350539	0.679520046	0.139648120
Al	0.159879009	-2.695804269	-0.178431590
Al	-0.031937413	0.538536242	0.029462843
Al	1.637866514	-0.984067895	-1.611734452
Al	1.504902954	-1.131998659	1.630920208
Al	1.277555448	2.903573044	-0.030866125
Al	-1.455372312	-1.087620693	-1.646627534
Al	-1.432011596	-1.301906656	1.574098620
Al	-2.977385234	0.379317107	0.101743970

	Al_{11}^+		
Al	0.006584917	0.016156008	-0.685176006
Al	1.598717643	2.322487816	-1.004165347
Al	-1.519458784	-2.296292144	-1.084283402
Al	-0.722887730	-1.854589609	1.505049111
Al	-1.207884374	2.526019400	-0.608045065
Al	0.577590561	1.810653144	1.561115494
Al	-1.898139696	0.597790320	1.509920853
Al	1.806680668	-0.667970000	1.528242940
Al	-2.814774497	0.203166670	-1.121392452
Al	1.271688205	-2.507262452	-0.619206042
Al	2.901883087	-0.150159153	-0.982060085

$$A_{l_{12}}$$

Al	-1.652206573	2.247832819	0.879423435
Al	0.011130785	-0.077461371	0.671708327
Al	0.176224268	-1.150233404	-1.704799994
Al	-2.561244638	-0.239709331	1.655692994
Al	2.640733346	-1.612452336	-0.159228502
Al	2.183317179	0.807530807	-1.287219915
Al	0.432287545	-2.865341665	0.882425769
Al	-1.996468382	-2.225913480	-0.276629615
Al	0.980635428	2.645855660	0.719918109
Al	-0.254743226	1.746339474	-1.778931334
Al	-2.381228218	0.272496251	-1.282933298
Al	2.421562485	0.451056576	1.6805740245

$$A_{l_{12}}^{-}$$

Al	0.008112294	0.031292830	0.328043422
Al	-2.284302935	1.282839993	1.458679841
Al	1.803885618	1.790822498	1.526478203
Al	-2.418244926	0.520751392	-1.158680189
Al	0.206581370	-2.606444323	1.212554677
Al	-0.408264424	2.834832489	0.167722743
Al	1.561922210	-1.669072832	-1.278673314
Al	-2.208052564	-1.433394813	1.163364054
Al	-1.087337904	-1.825044192	-1.485734535
Al	2.437587969	0.979308305	-1.109051231
Al	-0.028193566	1.023613469	-2.142946548
Al	2.416306858	-0.929504816	1.318242877

Al_{12}^+			
Al	2.643205966	0.398386777	-1.208702197
Al	0.029357111	0.017543912	0.440164623
Al	0.923249103	-1.696341631	-1.616626191
Al	-2.628698427	-0.451893802	1.305831135
Al	-1.578683075	2.114114616	1.247728823
Al	-0.781144712	-2.448375824	1.213135815
Al	-1.712185952	-1.561057039	-1.324378520
Al	2.500256089	0.633446229	1.506125112
Al	0.213979672	1.237713006	-1.947478479
Al	-2.370454741	1.091588835	-1.239132758
Al	1.839750619	-1.956456292	1.061605231
Al	0.921368348	2.621331214	0.561727406

Al_{13}			
Al	1.274026662	0.897092422	2.285996388
Al	0.023815174	0.032030141	-0.006583124
Al	1.484570531	2.406435013	-0.168168530
Al	-1.409702811	0.783070616	2.252212383
Al	2.830834993	-0.067234616	0.113092701
Al	-1.205916640	0.867601395	-2.339176149
Al	-1.200854351	2.525320006	0.006005684
Al	1.157135590	-1.947803857	1.682969209
Al	1.307196976	-2.179305273	-1.184796275
Al	-1.372066788	-1.835839312	-1.513575513

Al	-2.813155174	0.099907208	-0.123483083
Al	1.455912603	0.367988677	-2.337204267
Al	-1.531796764	-1.949262419	1.33271057

$$Al_{13}^{-}$$

Al	1.480665909	2.279186613	-0.586116358
Al	2.754754120	-0.134212324	0.501873668
Al	-2.720464460	0.077073916	-0.420880089
Al	0.000453844	-0.039675478	-0.024700047
Al	0.838398713	-1.369816109	2.211465062
Al	1.276048004	-2.405432568	-0.525253294
Al	-1.409292042	-2.302353713	0.683652908
Al	-1.268157509	2.407620411	0.396103430
Al	-1.660440821	0.136430200	2.160033147
Al	-0.968570161	-1.497234102	-2.067631297
Al	1.640857412	-0.111931865	-2.224812137
Al	0.910280609	1.557640534	2.110087349
Al	-0.874533618	1.402704482	-2.213822343

$$Al_{13}^{+}$$

Al	0.197286384	0.052291931	-2.247176573
Al	2.291534269	-0.068865239	1.749570369
Al	1.750493751	2.135963517	-0.897796839
Al	-1.511911700	-2.137128626	-1.176271782
Al	-0.009729740	-0.035853566	0.317498189

Al	2.762078172	-0.399003645	-0.952709784
Al	0.660488349	2.217594318	1.643329670
Al	-1.972326521	1.434739723	1.500003279
Al	-2.197055938	-1.304729674	1.392555466
Al	1.150179859	-2.510033412	-0.861054906
Al	-2.577376354	0.382773897	-1.212136063
Al	-0.958553333	2.508449721	-0.984349185
Al	0.414892800	-2.276198946	1.728538161

Al_{14}

Al	-1.464077049	-0.385268392	-2.377470097
Al	-0.263121218	2.192516572	-1.746263465
Al	2.042143712	1.854296319	-0.243870009
Al	1.731369784	0.361761959	2.263489932
Al	-0.045311814	-0.006919529	-0.047082582
Al	2.669584753	-0.867415424	-0.111237635
Al	-1.347214070	-2.534070404	0.291065461
Al	-2.129695126	1.968123496	0.132801994
Al	0.022674528	2.369289458	1.642730532
Al	1.423329660	0.156659411	-2.492546338
Al	0.878395615	-2.117886218	1.678220975
Al	-1.205016471	-0.219253937	2.483166869
Al	-2.974741224	-0.507682103	0.106747814
Al	0.661678920	-2.264151208	-1.579753450

$$A_{l_{14}}^{-}$$

Al	1.023931989	1.767478720	-2.011671496
Al	-0.180296831	2.702516220	0.448387651
Al	-4.186830429	-0.017610353	-0.087853632
Al	0.670875768	0.931807980	2.540629891
Al	-1.934955887	0.627192917	1.531581765
Al	-1.785406421	-1.642284500	-0.494346248
Al	-0.428395259	-1.716503844	2.023502798
Al	0.337763210	0.016621311	0.015502520
Al	2.535176353	-0.610651568	-1.462854872
Al	0.794238370	-2.747892086	-0.395183656
Al	-0.009846700	-0.869688612	-2.586184748
Al	2.536242547	1.574493391	0.448938047
Al	-1.752030449	1.141293767	-1.403585455
Al	2.379533740	-1.156773343	1.433137434

$$A_{l_{14}}^{+}$$

Al	-1.681936649	0.000545580	-2.363172004
Al	-1.506160033	0.236887205	2.400054896
Al	-0.431690192	-2.267355090	-1.835273592
Al	1.460563996	0.302434985	2.227441304
Al	-0.404695261	2.412670855	1.301645124
Al	-0.408815310	2.279660400	-1.576198048
Al	1.301751188	0.052593647	-2.325526102
Al	-2.536040028	1.106326066	0.056428423
Al	1.871667350	2.198518049	-0.115039843
Al	1.570813418	-2.387536366	-0.026529772

Al	-2.159535010	-1.631417669	0.274595194
Al	0.001151030	-0.049897179	0.013738543
Al	3.036895335	-0.178243928	-0.088365096
Al	-0.113969835	-2.075186555	2.056200973

$$Al_{15}^+$$

Al	-0.573361383	0.004772830	-0.003936114
Al	-0.580318444	1.328242887	-2.516205466
Al	-0.558981837	-1.578855155	-2.345196400
Al	0.827889274	-2.318169223	0.141856392
Al	1.534639598	0.145945568	1.538204574
Al	1.646975891	-0.081239962	-1.528560403
Al	-0.673156607	-1.264070520	2.494925969
Al	-1.890790259	-2.387064586	0.216667646
Al	0.874634739	2.356289209	-0.206137773
Al	3.830184040	1.367603042	0.030915807
Al	-2.837983935	0.155554381	1.397638836
Al	-1.953833260	2.313501936	-0.168660230
Al	-0.638395425	1.642004133	2.299854268
Al	-2.752901498	-0.211696626	-1.474799555
Al	3.745399108	-1.472817915	0.123432450

$$Al_{16}^+$$

Al	0.235130665	2.040391778	-2.038071863
Al	0.727984111	-1.764538067	1.908552022

Al	0.753791289	-2.592044446	-1.096068925
Al	-1.585150112	-2.451609019	0.174734234
Al	-1.142344615	2.274409661	0.302465280
Al	-1.735934830	-0.015268000	1.662989001
Al	-1.688955218	-0.022558135	-1.395355539
Al	1.587288775	2.481572685	0.368387663
Al	-3.865989550	1.458579470	-0.087607662
Al	3.057192583	-1.778375649	0.052534830
Al	0.742410843	-0.552990152	-2.830711168
Al	0.587953273	-0.032532505	-0.072192063
Al	0.507501950	1.089229152	2.521767622
Al	3.000463201	0.339339679	1.759295407
Al	-4.117341613	-1.246498924	0.115758246
Al	2.935999248	0.772892473	-1.346477083