

TEMPERATURE-DEPENDENT PHOTOIONIZATION OF METAL
NANOPARTICLES: PHASE TRANSITION, ISOTOPE, AND
QUANTUM EFFECTS

by

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Abstract

This dissertation investigates whether electronic observables can be used to probe structural, thermodynamic, and quantum phenomena in finite systems. To address this question, high-precision temperature-dependent photoionization measurements were performed on a free beam of ultrapure alkali metal nanoparticles. Near-threshold photoionization spectroscopy enabled ionization energies and work functions to be determined with sub-percent precision over a broad temperature range.

Temperature-dependent measurements of sodium and potassium nanoparticles revealed distinct discontinuities in the work function associated with melting. The observed transition temperatures were significantly reduced relative to their bulk values, consistent with finite-size thermodynamics described by Gibbs–Thomson scaling. These results demonstrate that electronic measurements can provide direct signatures of structural phase transitions in isolated nanoparticles.

The influence of lattice dynamics and quantum effects was investigated through measurements of the lithium isotopes ^6Li and ^7Li . A measurable isotope dependence of the work function was observed together with deviations from predictions based solely on thermal-expansion-driven electron-gas models. These findings indicate that electron–phonon coupling and quantum lattice effects contribute significantly to the electronic properties of lithium and reveal limitations of simplified free-electron descriptions for light alkali metals. The measurements also show that the temperature dependence of the work function progressively vanishes at low temperature, demonstrating behavior consistent with the Third Law of Thermodynamics.

Achieving the required precision involved the development of experimental and

analytical methods for accurate determination of nanoparticle ionization thresholds, including controlled thermalization, automated data acquisition, and Fowler-type analysis of near-threshold photoionization spectra.

Together, these results establish temperature-dependent photoionization spectroscopy of free nanoparticles as a quantitative tool for studying phase transitions, lattice dynamics, and quantum phenomena in finite systems. More broadly, this work demonstrates that precise electronic measurements can provide direct insight into the thermodynamic behavior of nanoscale materials that are otherwise inaccessible.

Chapter 1: Introduction

1.1 Finite Systems and Nanoscale Matter

The properties of condensed matter emerge from the collective behavior of electrons and atoms. Structural transformations such as thermal expansion, melting, and lattice vibrations alter the arrangement of atoms within a material and thereby modify its electronic structure. As a consequence, thermodynamic and electronic properties are fundamentally interconnected.

While thermodynamic phenomena are readily studied in bulk materials, their investigation becomes considerably more challenging in finite systems. To understand the intrinsic behavior of nanoparticles, experiments must ideally be performed on free particles isolated from substrates and other environmental perturbations. However, many conventional probes of structure and thermodynamics are difficult to apply to nanoparticles in flight.

In contrast, electronic properties of free nanoparticles are often readily accessible. Techniques such as photoionization spectroscopy, photoelectron spectroscopy, and mass spectrometry can be naturally integrated into molecular-beam experiments and have long served as primary tools for studying free clusters and nanoparticles. Measurements of ionization energies, electron affinities, and related electronic quantities can therefore be performed with high precision even when direct structural or thermodynamic measurements are impractical.

This raises a fundamental question: **can an electronic observable be used as a sensitive probe of structural and thermodynamic phenomena?**

For such an approach to be successful, the electronic observable must be coupled to the underlying atomic structure of the material. Thermodynamic processes such as thermal expansion, melting, and lattice vibrations modify interatomic separations and the distribution of atoms near the surface. These changes, in turn, alter the electronic environment experienced by

the conduction electrons. An observable that depends sensitively on the electronic structure may therefore contain information about the thermodynamic state of the system.

One quantity that is particularly well suited for this purpose is the work function, the minimum energy required to remove an electron from a material into vacuum. Because the work function depends on both the electron density and the surface electronic structure [1–9], it is sensitive to thermal expansion, phase transitions, and lattice vibrations. Precise measurements of the work function therefore may offer the possibility of investigating thermodynamic behavior through an electronic measurement.

The present dissertation explores this possibility through temperature-dependent photoionization measurements of free metal nanoparticles. These systems provide a unique opportunity to investigate the relationship between electronic structure and thermodynamics in the absence of external perturbations. Because thermodynamic processes such as thermal expansion, melting, and lattice vibrations modify the atomic structure of a material, they are expected to influence its work function as well. In finite systems, where surface and size effects become increasingly important, these couplings can be particularly pronounced [10–15]. By measuring the work function with high precision over a broad temperature range, it becomes possible to determine whether electronic observables can reveal structural and thermodynamic phenomena of ultra-pure elements that are otherwise difficult to access.

1.2 Magic numbers and electronic shell structure

One of the earliest and most influential discoveries in cluster physics was the observation of electronic shell structure in metal clusters. Mass-abundance measurements of sodium clusters revealed enhanced stability at particular cluster sizes, commonly referred to as *magic numbers* [10–12,15–17]. These preferred sizes arise from shell closures in the quantized

conduction-electron states of the cluster and are analogous to shell closures in atoms and nuclei.

Electronic shell structure influences both electronic and thermodynamic properties. Closed-shell clusters possess enhanced binding energies and correspondingly higher ionization energies than neighboring cluster sizes [10,11,18]. Since the ionization energy is the finite-system analogue of the bulk work function, shell effects provide a direct demonstration that electronic observables are sensitive to the quantum-mechanical structure of finite systems.

Shell closures also influence thermodynamic stability [15,17]. Clusters with enhanced binding energies exhibit reduced evaporation rates and increased resistance to fragmentation. Consequently, mass-abundance spectra contain information not only about cluster formation but also about the thermodynamic properties of finite systems. The discovery of magic numbers therefore established a fundamental connection between electronic structure, ionization energies, and thermodynamic behavior in nanoscale matter.

Although the nanoparticles investigated in the present work are substantially larger than the cluster sizes at which individual shell effects dominate, the observation of magic numbers provides an important conceptual foundation for this dissertation. It illustrates how electronic observables can reveal information about the underlying physical state of a finite system [11].

1.3 The work function and photoionization

The work function is one of the fundamental quantities characterizing the electronic structure of a metal. It is defined as the minimum energy required to remove an electron from the material into vacuum. The concept of the work function emerged from early studies of thermionic and photoelectric emission in metals during the late nineteenth century [8]. In 1887, Heinrich Hertz observed that ultraviolet illumination facilitated electrical discharge between metallic electrodes during experiments on electromagnetic waves [19]. Shortly afterward,

Wilhelm Hallwachs demonstrated that ultraviolet light could discharge negatively charged metal surfaces, providing direct evidence of light-induced electron emission [20]. More systematic investigations were later carried out by Philipp Lenard between 1899 and 1902, who measured the energies of emitted electrons and showed that their kinetic energies depend primarily on the frequency of the incident light rather than its intensity [21,22].

These experimental observations could not be explained within the framework of classical wave theory. A major breakthrough came in 1905, when Albert Einstein proposed that light consists of discrete quanta of energy, later termed photons. Einstein showed that photoemission occurs when a photon of energy $h\nu$ transfers its energy to an electron, enabling the electron to escape the material provided that the photon energy exceeds a threshold characteristic of the surface. Energy conservation implies,

$$h\nu = W + E_k$$

where W is the work function and E_k is the kinetic energy of the emitted electron [23]. Einstein's explanation established the work function as a fundamental electronic property of condensed matter systems and provided one of the earliest confirmations of quantum theory. Significantly, by plotting the stopping potential or emitted electron kinetic energy as a function of photon frequency for different metals, one could determine Planck's constant h from the slope of the resulting linear relation and the W from the intercept [24].

A variety of techniques have been developed for measuring work functions, including thermionic emission, photoelectron spectroscopy, Kelvin-probe methods, and field-emission measurements. These approaches have played a central role in the study of electronic structure and surface properties of bulk materials. However, most are inherently surface-based techniques and are typically applied to supported samples under conditions where interactions with

substrates, adsorbates, or other environmental factors can influence the measured work function [2,25]. Furthermore, the small temperature-dependent changes in the work function are often difficult to separate from surface contamination, reconstruction, and other extrinsic effects. As a result, obtaining precise temperature-dependent work-function measurements under well-controlled and minimally perturbed conditions remains experimentally challenging.

For finite metal systems such as nanoparticles, the corresponding quantity is the ionization energy (I) [11,12,26,27]. Unlike bulk solids, finite systems exhibit additional size-dependent contributions associated with electron removal from a confined conducting particle. In the present work, these quantities are determined using photoionization spectroscopy of free nanoparticles in a molecular beam. Near-threshold ionization spectra are analyzed using Fowler theory, enabling extraction of ionization energies and work functions with sub-percent precision [27–29].

For free nanoparticles, photoionization measurements possess several important advantages. Since the particles exist in vacuum for only milliseconds before detection, contamination effects are minimized even for highly reactive materials such as alkali metals. In addition, nanoparticles in a beam can be temperature controlled and size characterized independently, enabling systematic studies of both thermal and finite-size effects. As a result, free nanoparticles provide an ideal platform for investigating electronic-structural interplay.

1.4 Motivation

Despite extensive research on nanoparticle thermodynamics, direct measurements of structural phase transitions in isolated nanoparticles remain experimentally challenging [15]. Conventional structural probes such as electron microscopy are difficult to apply to free nanoparticles in flight, while supported nanoparticles may exhibit substrate-induced

modifications of their physical properties [17,30–33]. Alternative approaches capable of probing thermodynamic behavior in isolated finite systems are therefore of considerable interest.

Particular attention is given to alkali-metal nanoparticles because their relatively simple electronic structure allows subtle thermodynamic effects to be resolved experimentally with high precision. At the same time, their high chemical reactivity makes conventional surface measurements difficult, thereby highlighting the advantages of beam-based nanoparticle experiments.

The central premise of this dissertation is that electronic observables can serve as probes of thermodynamic and quantum phenomena. Because the work function depends on electron density, lattice structure, and surface electrostatics, changes in thermal expansion, melting, and lattice dynamics are expected to produce measurable shifts in the ionization threshold.

The possibility of extracting thermodynamic information from an electronic measurement provides the primary motivation for the work presented here.

1.5 Scope of the Dissertation

This dissertation presents the development and application of high-precision temperature-dependent photoionization measurements of free metal nanoparticles. The work combines nanoparticle beam generation, temperature-controlled thermalization, photoionization spectroscopy, and theoretical analysis of finite-size and thermodynamic effects.

The primary focus is the use of electronic observables to investigate structural and thermodynamic behavior in finite metallic systems. Particular emphasis is placed on temperature-dependent work functions, melting transitions in sodium and potassium nanoparticles, and isotope-dependent quantum effects in lithium.

Chapter 2: describes the experimental apparatus, nanoparticle source, thermalization

procedure, and photoionization measurements [27]. Chapter 3: presents the theoretical framework and threshold analysis methods used throughout the dissertation. Chapter 4: examines melting transitions in sodium and potassium nanoparticles through temperature-dependent work function measurements [34]. Chapter 5: investigates isotope-dependent quantum effects in lithium nanoparticles [35]. Finally, Chapter 6: summarizes the principal results and discusses future directions for studies of thermodynamic and electronic phenomena in nanoscale systems.

Chapter 2: Experimental Methods

2.1 Overview of the Experimental Approach

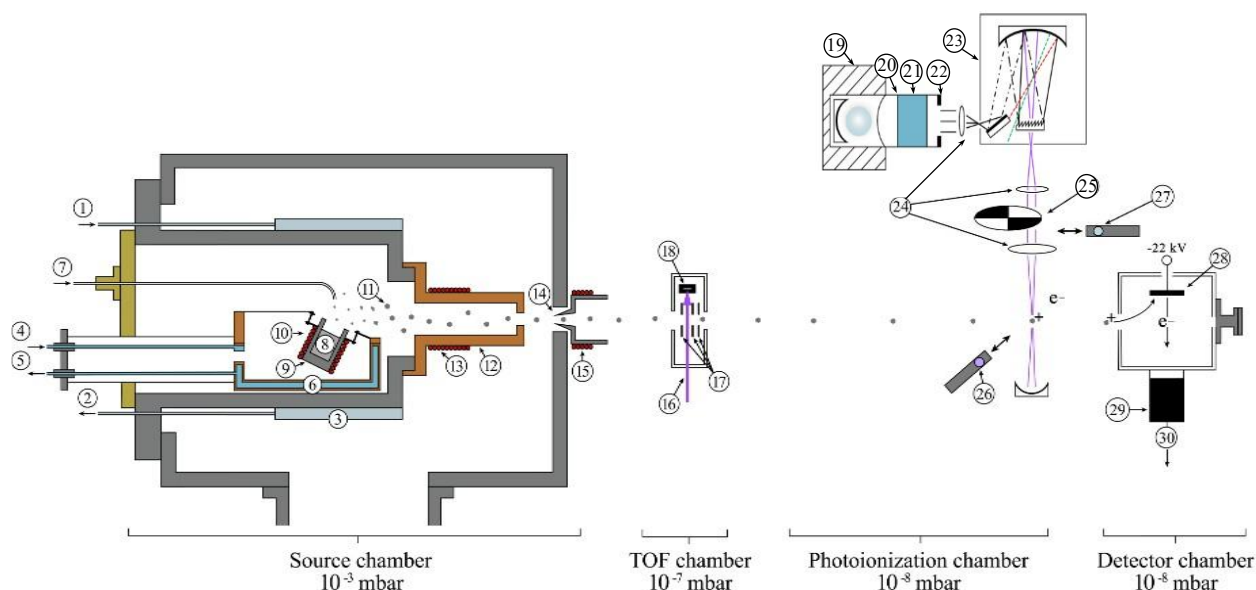


Figure 2.1. An outline of the photoionization setup (not to scale). 1, 2: Liquid nitrogen inlet and outlet, respectively; 3: liquid nitrogen jacket; 4, 5: water inlet and outlet, respectively; 6: water-cooled box; 7: helium gas inlet; 8: alkali metal in the crucible; 9: crucible; 10: crucible heater; 11: vapor-condensed nanoparticles; 12: thermalization tube; 13: thermalization tube heater; 14: skimmer (3 mm opening); 15: skimmer heater; 16: Pulsed Nd:YAG laser for TOF ionization; 17: TOF plates; 18: laser energy meter; 19: UV arc lamp; 20: cylindrical lens; 21: IR water filter; 22: iris diaphragm; 23: monochromator with automated wavelength selection; 24: focusing lenses. 25: optical chopper; 26: photodiode on a motorized linear feedthrough; 27: UV LED on a motorized stage; 28: Daly dynode; 29: scintillator (white part, inside vacuum) and photomultiplier tube (the black tube); and 30: signal pulses to computer.

Ionization energies and work functions were measured using photoionization spectroscopy of free metal nanoparticles propagating in a molecular beam. The measurements combined nanoparticle generation, temperature-controlled thermalization, UV-Vis

photoionization, time-of-flight mass spectrometry, and ion detection within a single apparatus shown schematically in Figure 2.1.

Nanoparticles were produced in a gas aggregation source and transported by a helium carrier gas through a thermalization tube, where their temperature was equilibrated over a broad range extending from approximately 60 to 390 K. The particles then expanded into vacuum, forming a directed beam that propagated through several differentially pumped chambers before entering the photoionization region. There, the nanoparticles were ionized by monochromatic ultraviolet radiation, and the resulting ions were detected as a function of photon energy to obtain near-threshold photoionization spectra.

The central experimental challenge is that the temperature dependence of the work function is typically on the order of 10^{-4} eV/K [2 – 4,7,8]. Reliable measurements therefore require precise characterization and measurement of nanoparticle temperature, size distribution, photon flux, and ionization-threshold determination.

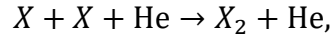
2.2 Nanoparticle Generation

2.2.1 Gas Aggregation Source

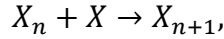
Nanoparticles were generated in a gas-aggregation source by condensation of alkali-metal vapor in a cold helium environment. The vapor was produced by resistive heating of a stainless-steel crucible mounted in a water-cooled copper housing, while helium carrier gas flowed across the crucible opening (Figure 2.2).

Nanoparticle formation in an inert-gas condensation source is governed by a complex interplay between nucleation, growth, coagulation, and evaporation processes. Although a complete quantitative description remains challenging, the essential mechanisms responsible for cluster formation are somewhat understood [11–13,36,37]. The condensation process consists of

two stages: evaporation of the metal and rapid cooling of the vapor through collisions with the helium carrier gas. Under typical operating conditions, the source pressure was maintained near 2 Torr, ensuring a sufficiently high collision rate to promote nucleation and cluster growth. The initial stage of cluster formation involves the production of dimers through three-body collisions,



where X denotes a metal atom and helium acts as a third body that removes excess energy from the collision complex [13,17,37]. Once stable nuclei are formed, cluster growth proceeds through successive addition of atoms,



where the incorporation of an additional alkali-metal atom releases approximately 1 eV of binding energy. Cluster growth may also occur through cluster-cluster coagulation,

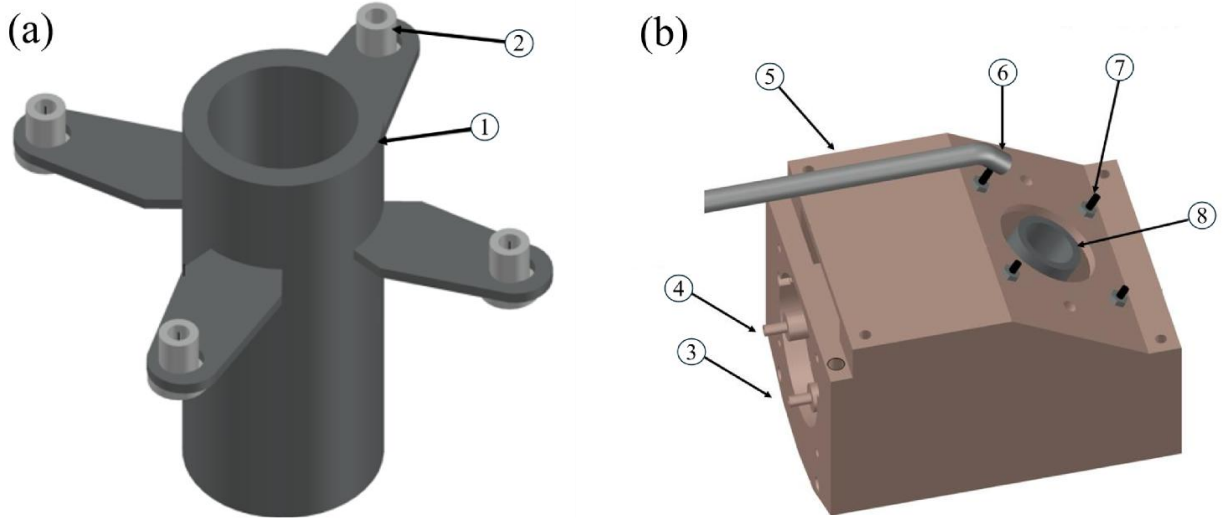
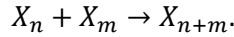


Figure 2.2. Crucible assembly used for nanoparticle generation. (a) Crucible mounted inside the water-cooled copper housing. (b) Crucible positioned at an angle of 25° relative to the beam axis. Labels: (1, 8) crucible; (2) insulating Macor shoulder washers; (3, 4) water inlet and outlet, respectively; (5) copper housing; (6) helium gas inlet tube; and (7) crucible mounting screws. The resistive heating element consisted of 24 AWG Kanthal wire electrically insulated from the crucible by ceramic sleeving and secured using high-temperature ceramic cement. Typical operating temperatures were approximately 500°C for Li, 300°C for Na, and 200°C for K.

Classical nucleation theory predicts that growth by single-atom addition is generally the

dominant mechanism under the conditions employed here. During the condensation process, clusters remain in dynamic equilibrium with the surrounding vapor and may either grow or shrink through the addition or evaporation of atoms. The competition between these processes leads to the existence of a critical cluster size, which depends on the carrier-gas pressure, gas temperature, and metal vapor pressure. Nanoparticles smaller than the critical size are more likely to dissociate, whereas nanoparticles that exceed the critical size become thermodynamically stable and continue growing as they travel through the aggregation region.

The helium simultaneously cools the metal vapor, promotes nucleation, and transports the resulting nanoparticles into the thermalization region. The helium flow rate was regulated using a mass-flow controller and was maintained at 240 sccm. The aggregation chamber can be cooled either by water or liquid nitrogen depending on the experiment. For the photoionization experiments, the condensation source was liquid nitrogen cooled to reduce the possibility of the contaminations during aggregation. Typical crucible temperatures were approximately 500 °C for lithium, 300 °C for sodium, and 200 °C for potassium.

Stable beam operation required control of crucible temperature, carrier-gas flow, and source cooling conditions. To maintain signal stability liquid nitrogen was continuously flowing. Under optimized operating parameters, the nanoparticle beam remained stable for periods exceeding 24 h, with signal variations typically below 10% over 2 hours.

A heat-shielded source geometry was later implemented (Figure 2.3) to improve thermal efficiency and long-term source stability. This modification substantially increased the usable runtime of the source to more than 36 h while maintaining highly stable beam conditions, with signal variations remaining below 10% over several hours. By reducing radiative heat losses from the crucible region, the heat shield also lowered the power required to maintain the

operating temperature. As a result, the heating elements operated at lower temperatures decreasing thermal stress and significantly improving heater lifetime.

The redesigned source also simplified routine maintenance and sample loading. Unlike earlier designs, the source could be cleaned while assembled without rebuilding the heat shield and heater assemblies (for assembly details see Appendix G:). Loading the source required only insertion of a stainless-steel crucible into the ceramic holder followed by addition of the alkali-metal sample. This substantially reduced preparation time between experiments and improved the overall reliability and reproducibility of source operation.

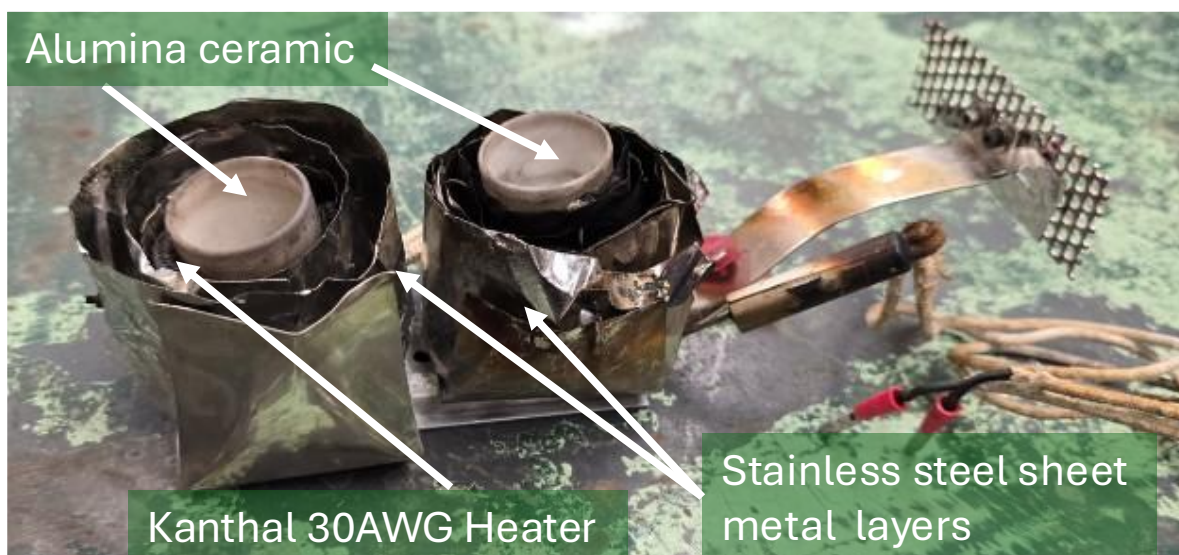


Figure 2.3. Homebuilt heat-shielded alkali-metal source constructed primarily from stainless-steel components. Alumina ceramic crucibles were used to provide electrical insulation between the heating elements and the stainless steel crucible. The heat shield was fabricated from 100 μm thick stainless-steel foil and assembled using commercially available stainless-steel threaded inserts and fasteners. The elimination of ceramic cement from the hot region substantially reduced contamination within the aggregation chamber and improved the stability of alkali-vapor discharge operation.

2.3 Thermalization of Nanoparticles

2.3.1 Temperature-Controlled Thermalization Tube

A regulated thermalization tube was attached directly to the exit of the condensation chamber to equilibrate the nanoparticles to a controlled temperature prior to photoionization. The tube was constructed from oxygen-free high-conductivity copper and had an overall length of 11

cm. Its inner diameter narrowed from 1.6 cm to a 6 mm exit aperture.

Two thermalization configurations were employed. For temperatures above approximately 190 K, the tube was resistively heated and thermally isolated from the source chamber using a Teflon spacer. The assembly was wrapped in superinsulation foil to improve temperature stability. Three resistance temperature detectors positioned along the tube length monitored the temperature profile, which remained uniform to within approximately ± 1 K.

For low-temperature operation, the thermalization tube was thermally coupled to the first stage of a closed-cycle cryocooler (Leybold COOLPAK 6000 MD with a Coolpower Model 130 cold head) using silver-coated copper braids. Additional thermal isolation from the source chamber was achieved through a reduced tube cross section and a patterned Teflon spacer, as shown in Figure 2.1. Temperature regulation was provided by a resistive heater controlled through a cryogenic temperature controller (Lake Shore 340 temperature controller), while silicon-diode sensors mounted at opposite ends of the tube monitored the temperature distribution along its length.

To maximize thermal conductance, the ends of the copper braids were coated with cryogenic thermal grease or silver paste before being firmly clamped to the cold head and thermalization tube. The braid assembly was subsequently wrapped in multilayer reflective insulation (20 layers) to reduce radiative heat transfer from the surrounding vacuum chamber. These measures substantially improved thermal stability and cooling efficiency, enabling reliable operation down to approximately 60 K while maintaining axial temperature gradients below ± 1 K along the thermalization tube.

Following condensation and thermalization, the nanoparticles and helium gas exited the source through the thermalization tube and expanded into vacuum. The nanoparticle beam was

collimated using a 3 mm skimmer positioned downstream of the thermalization tube. The beam subsequently propagated through several differentially pumped vacuum chambers over an overall beamline length of approximately 3 m before entering the photoionization chamber. Depending on helium flow conditions and thermalization temperature, the nanoparticle transit time ranged from milliseconds to a few tens of milliseconds.

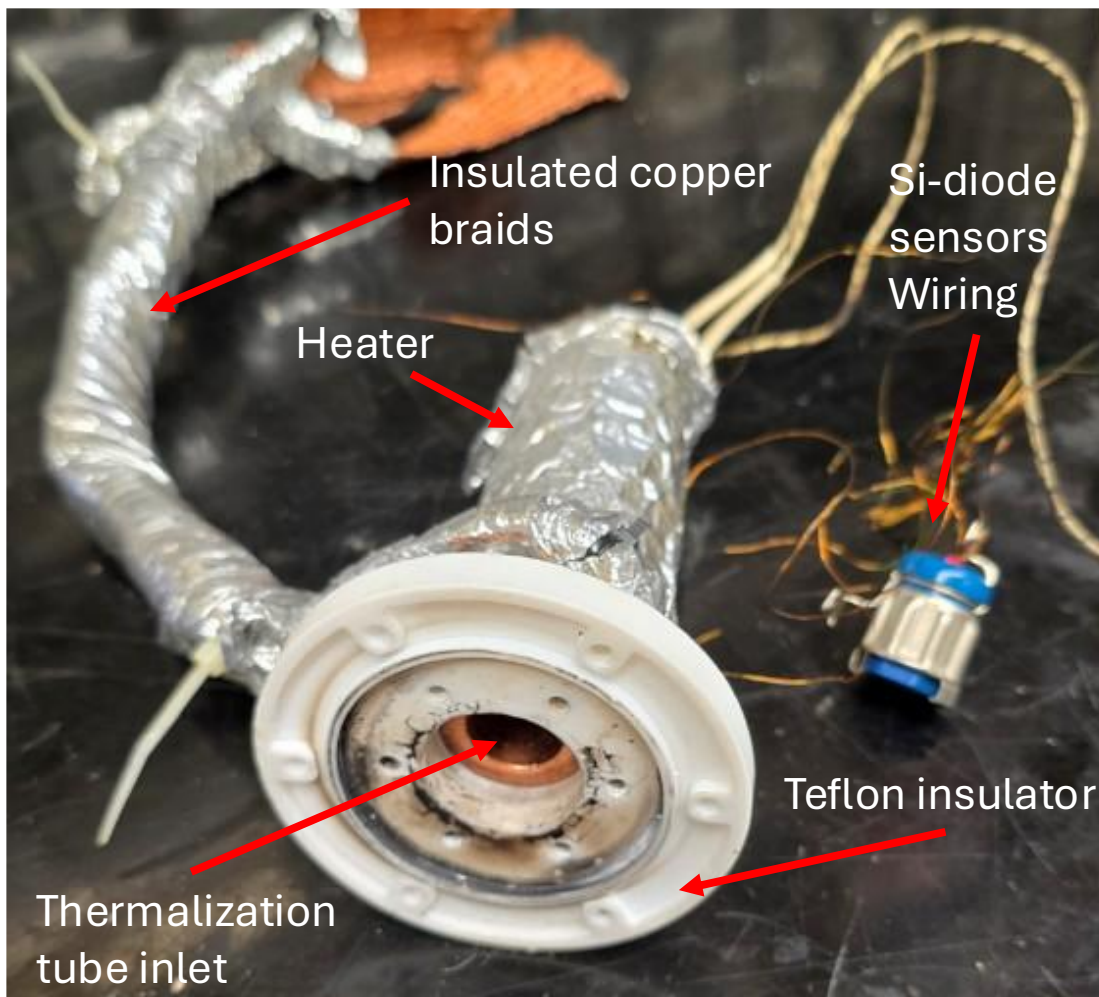


Figure 2.4. Low temperature thermalization tube ~ 60 K. The groove on the base of the Teflon mounting flange (left) aims to minimize heat transfer between the source jacket and the thermalization tube.

2.3.2 Thermal Equilibration

Reliable interpretation of the temperature dependence of the work function requires that the nanoparticles reach thermal equilibrium with the thermalization tube prior to exiting into

vacuum. Since the work function is measured as a function of temperature, any significant difference between the nanoparticle temperature and the measured tube temperature would introduce a systematic error into the experiment. It is therefore necessary to demonstrate that thermal equilibration occurs on a timescale shorter than the nanoparticle residence time inside the tube.

Thermalization occurs in two stages: first, the helium carrier gas exchanges heat with the thermalization-tube walls and equilibrates to the wall temperature; second, the nanoparticles exchange energy with the surrounding helium gas through collisions and equilibrate to the helium temperature. Because the thermal mass of the copper tube is much larger than that of either the gas or the nanoparticles, the tube temperature may be regarded as constant during the thermalization process.

Measurements performed using carefully suspended thermocouples (or Silicon diodes for low temperatures) along the tube axis demonstrated that the helium gas reaches thermal equilibrium with the tube walls within approximately 4 cm of entering the high-temperature thermalization tube. Figure 2.5 shows that the measured temperatures closely follow the controller set point throughout the high-temperature regime. The absence of significant hysteresis between heating and cooling cycles indicates stable thermal regulation, while the close agreement between TC1 and TC2 demonstrates that axial temperature gradients within the thermalization region remain small. Hence the He gas thermalizes quickly in the tube. Similar behavior was observed for the low-temperature configuration. The helium gas reached thermal equilibrium with the tube walls within approximately 4 cm of the tube entrance in the high-temperature configuration and within approximately 6 cm in the low-temperature configuration. Since these equilibration distances are substantially shorter than the total tube length, the helium

gas is fully thermalized before reaching the tube exit. Combined with the thermalization analysis presented Thermal Equilibration, this indicates that the nanoparticles are expected to reach thermal equilibrium with the surrounding helium prior to exiting the thermalization tube.

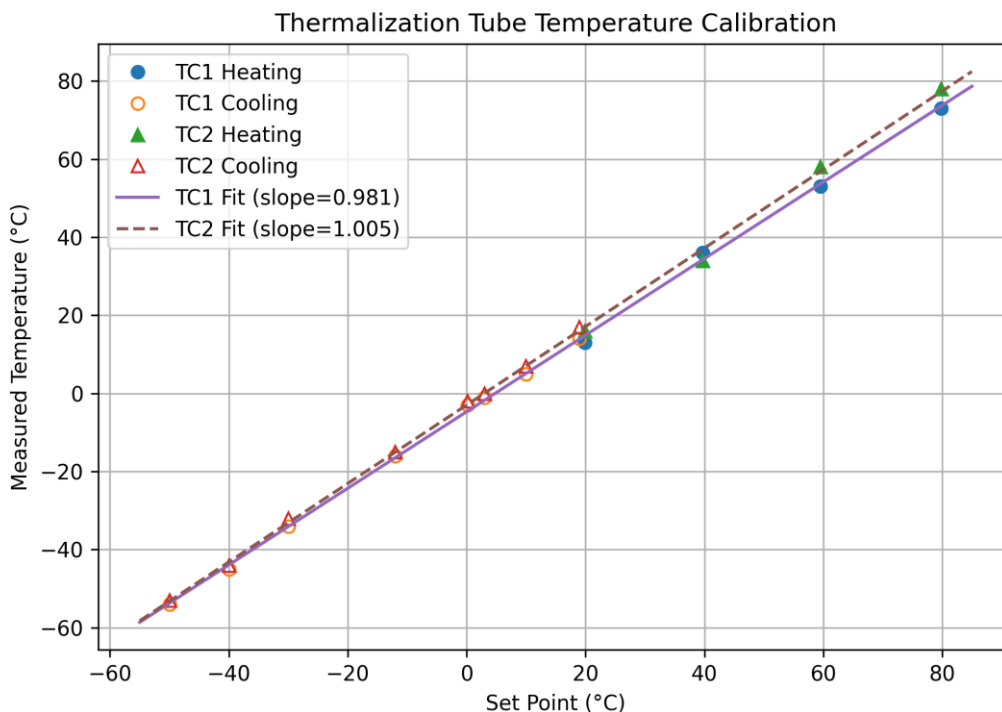


Figure 2.5. Calibration of the thermalization tube temperature measured at two locations inside separated by approximately 2 cm along the tube axis. Temperatures recorded by TC1 (2 cm) and TC2 (4 cm) are shown as functions of the controller set point during heating and cooling cycles. Linear regression lines are included as guides to the eye. The close agreement between the two thermocouples indicates that temperature gradients along the thermalization region remain small throughout the investigated temperature range. Similar measurements were performed for the low temperature thermalization tube and yielded comparable results. The helium gas reached thermal equilibrium with the tube walls within approximately 6 cm of the entrance in the low-temperature configuration, compared to approximately 4 cm in the high-temperature configuration.

The remaining question is whether the nanoparticles themselves have sufficient time to equilibrate with the thermalized helium bath. To address this issue, the helium pressure inside the thermalization tube was measured as a function of gas-flow rate using a differential pressure gauge attached to a dummy tube having identical geometry. Under normal operating conditions, the helium pressure ranged between approximately 0.2 and 1 mbar depending on temperature and flow conditions.

The efficiency of the thermalization process is governed by the ratio of the nanoparticle radius R to the mean free path of the carrier gas λ . In this experimental setup, where the Helium pressure P is approximately between 0.2 to 1 mbar and the nanoparticle radius is on the order of 3.5 nm, the Knudsen number ($Kn = \frac{\lambda}{R} \sim 10^5$) is much greater than unity, placing the system in the free-molecular-flow regime.

In this regime, the heat transfer rate $\dot{q}$ is not determined by the thermal conductivity of the gas, but by the flux of individual gas atoms striking the nanoparticle surface. The power exchange is defined by the difference between the average kinetic energy of the impinging atoms and that of the atoms reflected or re-emitted from the surface:

$$\dot{q} = a\zeta \cdot (\langle E_{\text{in}} \rangle - \langle E_{\text{out}} \rangle)$$

For a gas in local thermal equilibrium at temperature T_w , the average kinetic energy of an atom in a flux striking a surface is $2k_B T_w$. Assuming the atoms are re-emitted with an energy distribution corresponding to the nanoparticle temperature T , the expression becomes:

$$\dot{q} = a\zeta \cdot 2k_B(T_w - T)$$

The parameter a is the thermal accommodation coefficient [38,39], a semi-empirical factor that accounts for the incompleteness of energy transfer during a single collision. Physically, a represents the fraction of the incident energy that is "accommodated" by the nanoparticle's vibrational modes (phonons) before the gas atom is re-emitted.

To find the time required for a particle of N atoms to reach equilibrium, we relate the heat transfer rate to the particle's internal energy $U = Nc_{\text{at}}T$. The energy balance equation is:

$$Nc_{\text{at}} \frac{dT}{dt} = a\zeta \cdot 2k_B(T_w - T)$$

Defining the collision rate ζ as the product of the geometric cross-section πR^2 , the gas

number density n_{He} , and the mean thermal speed $\bar{v}$, we have:

$$\zeta = \pi R^2 \frac{P}{k_B T_w} \sqrt{\frac{8k_B T_w}{\pi m_{\text{He}}}}$$

Substituting this into the energy balance equation reveals an exponential relaxation of the temperature difference $\Delta T = T_w - T$

$$\frac{d(\Delta T)}{dt} = -\frac{1}{\tau}$$

The characteristic time constant τ is given by:

$$\tau = \frac{N c_{\text{at}}}{a \zeta 2 k_B}$$

This constant reveals a critical scaling law: since $N \propto R^3$ and $\zeta \propto R^2$, the thermalization time τ scales linearly with the nanoparticle radius R . Consequently, larger particles require longer residence times to reach the target temperature.

The total time available for thermalization is the transit time $t \sim 0.5$ ms through the tube. A significant complexity in nanoparticle beams is the velocity slip effect [40]. Because the nanoparticles are much heavier than the Helium atoms, they do not immediately reach the gas flow velocity. The aerodynamic drag force accelerates the particles, but for high-mass clusters, the particle velocity v_p is usually lower than the gas velocity v_g .

In the present study, the high estimated collision frequency ($\zeta \approx 10^9 \text{ s}^{-1}$) ensures that even without velocity slip, the minimum residence time $t \sim 0.5$ ms (worst case scenario) is at least 5 times shorter than the relaxation constant $\tau \sim 0.1$ ms. Therefore, we can confidently assume that the temperature of the nanoparticles is equal to the thermalization tube temperature.

An additional consideration is the possibility of evaporative cooling during the free flight of the nanoparticles between the thermalization tube and the photoionization region. Since the

nanoparticles are isolated from the helium bath after exiting the thermalization tube, evaporation of atoms can reduce their internal energy and potentially lower their temperature. The magnitude of this effect may be estimated from the characteristic evaporation time of a particle containing N atoms at temperature T ,

$$\tau \approx \tau_0 N^{-2/3} e^{D/k_B T},$$

where D is the surface binding energy and τ_0 is a characteristic time constant. For sodium, $D \approx 1$ eV and $\tau_0 \approx 2T^{1/2} \times 10^{-15}$ s [58], and with $N = 5000$ at $T = 400$ K, this expression yields an evaporation time of $\tau \approx 0.5$ ms. During the approximately 10 ms flight time from the thermalization tube to the photoionization region, the nanoparticle may therefore evaporate on the order of 20 atoms. Assuming a surface binding energy of approximately 1 eV per evaporated atom, this corresponds to a loss of roughly 20 eV of internal energy. Using the heat capacity of liquid sodium at 400 K, $C_p = 31.5$ J mol⁻¹ K⁻¹ [59], the resulting temperature decrease is estimated to be approximately 10 K. Although not entirely negligible, this cooling represents only a small correction relative to the temperatures investigated in the present work and does not qualitatively affect the interpretation of the photoionization measurements. Similar estimates for potassium, using the corresponding binding energies and thermodynamic parameters [60], lead to the same conclusion.

2.4 Nanoparticle Size Characterization

2.4.1 Time-of-flight mass spectrometry

Nanoparticle size distributions were measured using a homebuilt linear Wiley–McLaren time-of-flight mass spectrometer aligned collinearly with the nanoparticle beam. Nanoparticles were ionized using 355 nm laser pulses from a frequency-tripled Nd:YAG laser operating at 15 Hz repetition rate. Following extraction and acceleration, the ions propagated through a 2 m

field-free drift region before detection.

Arrival times were converted into particle masses and corresponding numbers of atoms, taking into account the Jacobian transformation associated with the conversion from time-of-flight space to mass space.

The measured size distributions were well described by lognormal functions, consistent with condensation growth processes (see Figure 2.6). Typical mean particle populations were approximately $N \sim 7500$ atoms for lithium, $N \sim 5000$ atoms for sodium, and $N \sim 4500$ atoms for potassium, with full-width-at-half-maximum values comparable to the mean sizes themselves.

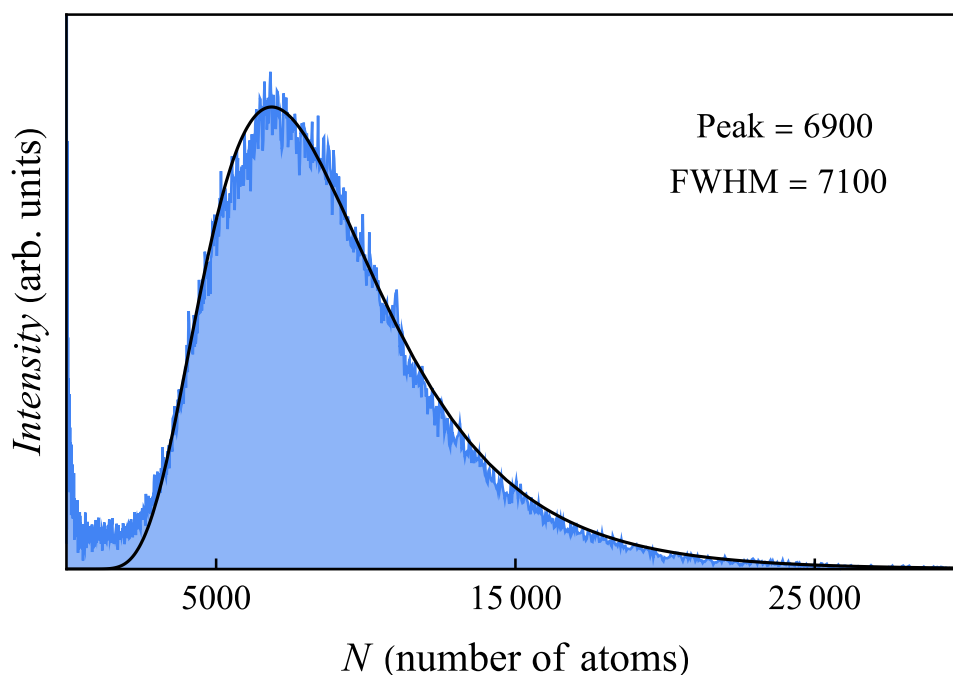


Figure 2.6. Size distribution of ^7Li nanoparticles thermalized to 80°C . The data are well described by a lognormal distribution (black envelope). The wing at the low end of the distribution is an artifact caused by TOF laser-induced fragmentation.

Mass spectra were recorded both before and after each photoionization measurement to verify that the nanoparticle distribution remained stable throughout the experiment. Accurate determination of nanoparticle size is essential because the finite-size correction to the ionization

energy scales inversely with particle radius. Errors in the size distribution therefore propagate directly into the extracted work function.

2.4.2 Multiple ionization effects in TOF mass spectra

In addition to laser-induced fragmentation, it is necessary to consider the possibility of multiple ionization during the pulsed-laser ionization used for time-of-flight mass spectrometry. Because metal nanoparticles possess relatively large photoabsorption cross sections, sequential absorption of multiple photons during a laser pulse may produce multiply charged ions. In such a case, the measured mass-to-charge ratio would differ from that of the original neutral nanoparticle population, potentially leading to systematic errors in the inferred size distribution (see Figure 2.7).

For a nanoparticle of radius R and initial charge Ze , the ionization energy may be approximated by

$$IE_Z = W + (\alpha + Z) \frac{e^2}{R},$$

where W is the work function and α is the finite-size correction coefficient discussed in Chapter 2:. Since the ionization threshold increases with each successive ionization event, only a finite number of charge states can be produced for a given photon energy.

The average number of absorbed ionizing photons is

$$n_0 = \frac{\sigma_i E_p}{E_\gamma A},$$

where σ_i is the photoionization cross section, E_p is the laser pulse energy, E_γ is the photon energy, and A is the effective laser spot area. Under the assumption of independent photon absorption events, the probability of reaching charge state Z is described approximately by a Poisson distribution,

$$P(Z) = \frac{n_0^Z e^{-n_0}}{Z!}.$$

To assess the importance of multiple ionization, mass spectra were recorded at different laser pulse energies. For example, see Figure 2.7a, large sodium nanoparticles produced under argon aggregation conditions exhibited substantial shifts in the measured mass-to-charge distribution at high laser power, indicating the presence of multiply charged ions. In contrast, the lithium, sodium, and potassium nanoparticles used for the photoionization measurements displayed negligible changes in their mass spectra when the laser power was varied over the operational range as demonstrated for Na in Figure 2.7b.

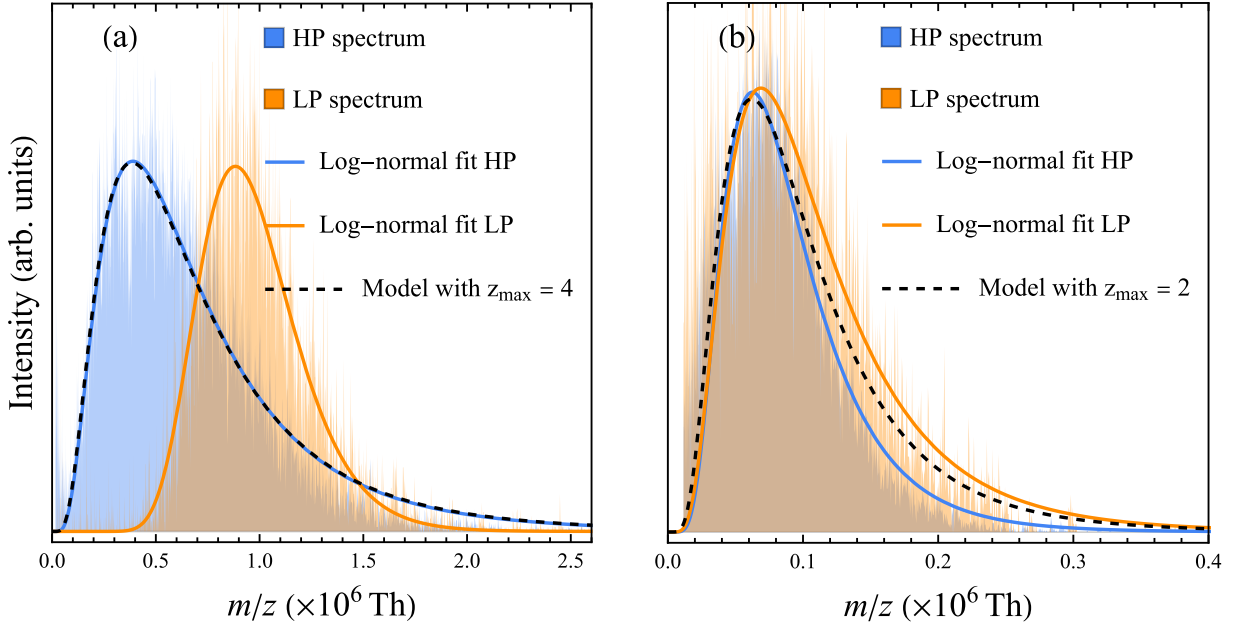


Figure 2.7. TOF mass spectra of sodium nanoparticles generated under different source conditions: (a) argon carrier gas ($Q_0 = 240 \text{ sccm}$, $T_w = 130 \text{ K}$) and (b) helium carrier gas ($Q_0 = 240 \text{ sccm}$, $T_w = 250 \text{ K}$). Nanoparticles were ionized using 355 nm Nd:YAG laser pulses, and mass spectra were recorded at low pulse energy (LP, $E_p = 0.1 \text{ mJ}$) and high pulse energy (HP, $E_p = 3.5 \text{ mJ}$). Condensation in argon produces substantially larger particles than condensation in helium. The shift of the spectra toward lower mass-to-charge ratios at higher laser intensity results from sequential absorption of multiple photons and the formation of multiply charged ions. Solid curves are fits to lognormal size distributions, while dashed curves represent model calculations based on the Poisson distribution of ionization probabilities discussed in Sec. 2.4.2.

The mass calibration measurements employed laser powers significantly lower than those required to produce appreciable multiple ionization. Furthermore, the laser beam was only

weakly focused in the ionization region. Under these conditions, corrections associated with multiply charged particles were estimated to shift the extracted work functions by less than 5 meV.

Care was also taken to evaluate the influence of laser-induced fragmentation and multiple ionization on the measured mass spectra. Measurements performed at different laser powers showed that under the operating conditions used for mass calibration, multiple ionization contributed negligibly to the extracted work functions.

2.5 Photoionization Measurements

2.5.1 Optical System

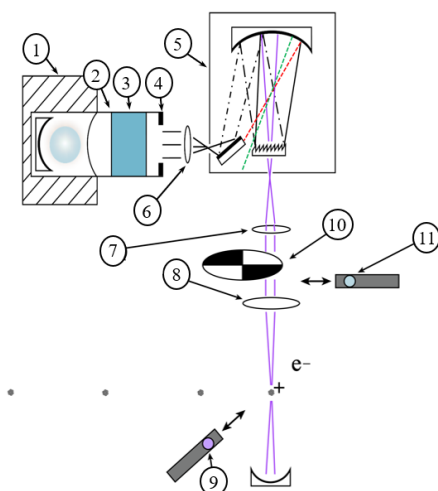


Figure 2.8. Schematic of the optical components. 1: UV arc lamp; 2: cylindrical lens; 3: IR water filter; 4: iris diaphragm; 5: monochromator with automated wavelength selection; 6: entrance focusing lenses ($d = 2''$, $f = 70$ mm); 7: exit focusing lenses ($d = 1''$, $f = 50$ mm); 8: nanocluster focusing lens ($d = 3''$, $f = 150$ mm); 9: photodiode on a motorized linear feedthrough; 10: optical chopper; 11: UV (365 nm) LED on a motorized stage.

Photoionization measurements were performed near the end of the beamline using ultraviolet and visible radiation produced by either a mercury–xenon or ultraviolet-enhanced xenon arc lamp coupled to a monochromator. The light passed through a water cooled distilled-water infrared filter, a UV grade fused silica with a 2'' diameter entrance lens for the monochromator placed a focal length (70 mm) away from the slits away from the entrance slits,

the monochromator, a UV grade fused silica with an 1" diameter collimating exit lens placed about a focal length (50 mm) away, second-order diffraction filter (300 to 650 nm band pass filter), and an optical chopper before entering the photoionization chamber. The monochromator bandwidth and wavelength calibration were better than 1 nm and 0.4 nm, respectively.

Wavelength selection was automated using a stepper motor coupled directly to the monochromator dial through a custom 3D-printed adapter. The motor resolution corresponded to 32 steps per nanometer wavelength (0.03125 nm per step), enabling highly reproducible and precise wavelength selection during automated scans.

Each light source, Hg-Xe and Xe, possesses distinct advantages and disadvantages. The Hg-Xe lamp contains numerous intense and well-defined mercury emission lines throughout the visible spectrum, making it particularly useful for accurate wavelength calibration of the monochromator. However, these same spectral lines dominate the broadband continuum emission and can introduce complications in photoionization measurements due to their exceptionally high intensities. In contrast, the Xe lamp provides a comparatively smooth and nearly uniform spectral intensity over the UV-visible range, making it more suitable for photon-flux normalization and photoionization measurements. Its principal disadvantage is the absence of strong, narrow spectral lines suitable for direct wavelength calibration.

To overcome this limitation, the monochromator was first calibrated using the Hg-Xe lamp at several well-known mercury emission lines, including 404.6 nm, 435.8 nm, and 546.1 nm. For each calibration wavelength, the corresponding position of a xenon emission feature in the near-infrared region was recorded. This is done for multiple peaks because the wavelength selection and angle of diffraction is nonlinear across the whole temperature range (a 0.3 nm shift for every 100 nm is observed). For example, when the monochromator was calibrated using the

435.8 nm mercury line, the location of the xenon peak was observed at 766.3 nm. The wavelength of this xenon feature was then used as an internal calibration reference when operating with the Xe lamp. During subsequent measurements, the monochromator calibration could therefore be verified by locating the xenon peak near 770.0 nm and adjusting the monochromator setting to reproduce the previously determined wavelength of 766.3 nm.

The accuracy of this calibration-transfer procedure was independently verified using a UV–Vis spectrometer. Repeated measurements showed that the xenon reference peak could be reproduced with excellent consistency, yielding wavelength calibrations that agreed with those obtained from the mercury emission lines to better than 0.2 nm. This approach provided a simple, reliable, and highly reproducible method for maintaining accurate wavelength calibration while benefiting from the smoother spectral output of the Xe lamp. This procedure provided a reliable method for transferring the accurate wavelength calibration obtained from the Hg–Xe lamp to the Xe lamp while retaining the superior spectral uniformity of the latter during photoionization measurements.

After passing through a rotating optical chopper, the monochromatic light was collimated and focused into the nanoparticle beam. Photon flux was monitored at the location of the cluster beam using a calibrated photodiode (see A.1, VTB1113 with a spectral range from ~310 nm to 1100 nm) connected to a lock-in amplifier referenced to the chopper frequency. The nanoparticle beam intensity was independently monitored using a stabilized ultraviolet LED aligned with the ionization region.

2.5.2 Ion Detection and Data Acquisition

Photoionized nanoparticles were detected using a Daly-type ion-counting detector consisting of an ion-conversion dynode, scintillator, and photomultiplier tube [10]. The detector

operated in pulse-counting mode and enabled sensitive measurements of near-threshold ionization yields. Typical count rates ranged from approximately 5 counts/s near threshold to 10^3 counts/s above threshold.

Because a single photoionization measurement requires repeated wavelength scans, photon-flux calibration, beam-intensity normalization, and ion counting, manual operation of the experiment would be both time-consuming and susceptible to systematic errors. To improve measurement throughput and reproducibility, a largely automated data-acquisition system was developed.

The experimental control system was implemented using LabVIEW (Appendix C:), which coordinated communication between the monochromator, photodiode calibration stage, beam-monitoring system, and data-acquisition electronics. Several motorized components were controlled using Arduino Uno microcontrollers, including monochromator wavelength selection and positioning of the photodiode and beam-monitoring LED. Communication between LabVIEW and the Arduino controllers was achieved through a serial communication protocol, allowing fully automated execution of photoionization scans without continuous operator intervention.

A typical measurement sequence consisted of recording a TOF mass spectrum, calibrating the photon flux, measuring the nanoparticle beam intensity using a 365 nm LED (Boston Electronics VC2X2C45L9-365), acquiring the photoionization yield as a function of photon energy, verifying beam stability, and finally recording a second TOF mass spectrum. Automated normalization procedures were applied throughout the acquisition process to compensate for fluctuations in lamp intensity and nanoparticle beam flux.

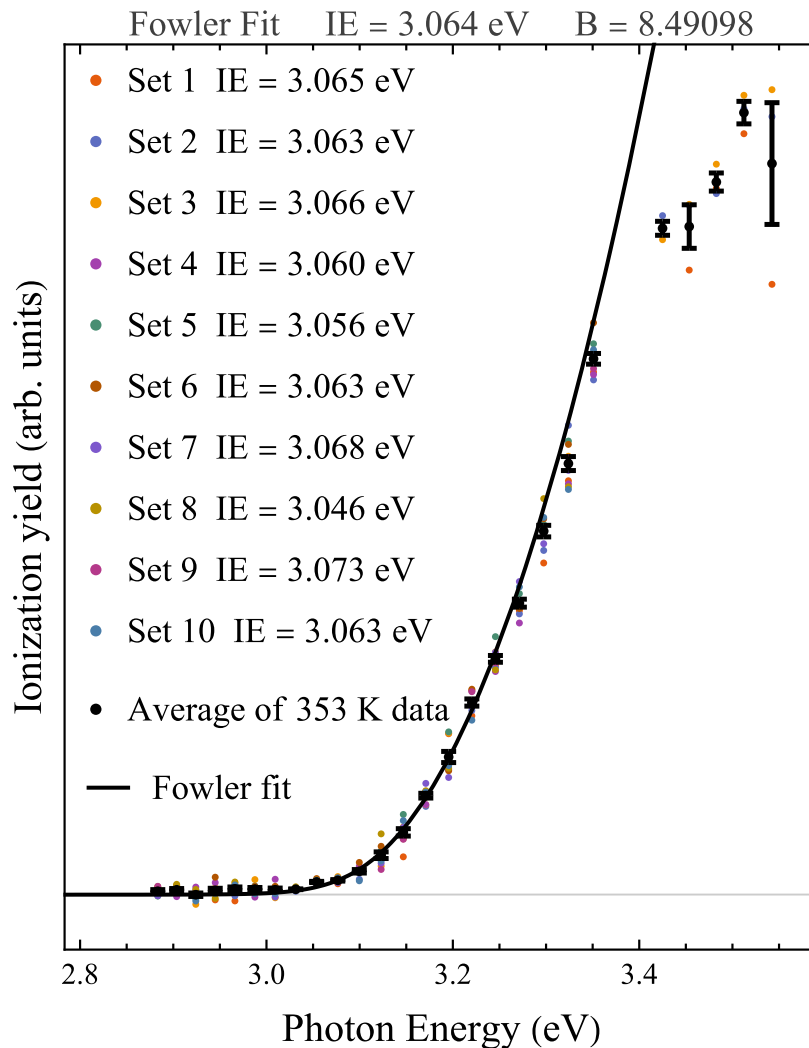


Figure 2.9. Photoionization yield data for Li nanoparticles of average size $N = 7100$ atoms at $T = 353$ K thermalization tube temperature. The points are normalized yields at different photon energies, with a wavelength step of 3 nm. The colors represent separate datasets, each one taking ~ 6 min to acquire. The black dots and their error bars are the average and standard deviation for each wavelength. The solid line is a Fowler fit (Sec. Fowler Theory of Near-Threshold Photoemission) to the black dots, and the legend tabulates the IEs determined by the Fowler fit for each individual dataset. The average value is 3.064 eV and the standard deviation is 0.007 eV. The deviation at high photon energy is due to the plasmon resonance (~ 3.5 eV) [41]. The absorbed photon can not only contribute to ionization but also to the plasmon resonance.

Automation substantially improved both measurement efficiency and reproducibility. Under normal operating conditions, approximately ten complete photoionization yield curves could be acquired per hour. Repeated measurements demonstrated excellent stability, with extracted ionization energies typically varying by less than 1% between independent scans and with statistical uncertainties generally below 0.2% (see Figure 2.9).

In addition to improving experimental throughput, automation reduced the likelihood of operator-induced errors and ensured consistent measurement conditions during the long acquisition times required for temperature-dependent studies. Particular care was taken to avoid systematic effects associated with photon-flux calibration, such as photodiode saturation near intense mercury emission lines when using the Hg–Xe arc lamp. These improvements were essential for resolving the small work-function shifts associated with thermal expansion, melting transitions, and isotope-dependent lattice dynamics discussed in later chapters.

Chapter 3: Theoretical Framework and Threshold Analysis

3.1 Theoretical Background of the Work Function

Despite the fundamental importance of the work function, there is no universally accepted theoretical framework capable of accurately predicting its value for all metals. The difficulty arises from the fact that the work function is determined by both bulk electronic properties and the detailed electronic structure of the surface. Consequently, a variety of theoretical approaches have been developed, each emphasizing different physical aspects of the problem.

One of the earliest descriptions is provided by the jellium model, in which the discrete ionic lattice is replaced by a uniform positive background charge [9,42,43]. In this picture, conduction electrons form an electron gas confined by the electrostatic potential generated by the positive background. The work function is determined by the competition between the electronic chemical potential and the electrostatic surface dipole barrier generated by electron spill-out beyond the metal surface. While the jellium model captures many qualitative features of simple metals, it often fails to reproduce accurate work function values because it neglects the discrete nature of the ionic lattice.

To improve upon this description, the stabilized jellium model introduces a pseudopotential correction that accounts for the influence of the ionic cores while retaining the simplicity of the uniform-background approximation [44,45]. This approach provides improved agreement with experimental work functions, particularly for simple metals, but still neglects crystallographic surface effects and detailed electronic structure.

An alternative physical picture is provided by image-charge models of electron emission. In these approaches, the work function is interpreted as the energy required to move an electron from a characteristic screening distance outside the metal surface to infinity [46,47]. The resulting work function depends on the image-charge potential and the electronic density of the metal. One particularly successful formulation was developed by Durakiewicz and co-workers, who related the work function to the Fermi energy and Wigner–Seitz radius [7,47,48]. This model reproduces experimental work functions of many metals with surprisingly good accuracy and forms the basis of the temperature-dependent calculations discussed later in Sec. 3.2.5.

Although these theories differ in their physical assumptions and level of complexity, they share a common conclusion: the work function depends sensitively on electron density, surface electrostatics, and lattice structure. Consequently, any temperature-induced modification of these quantities, whether through thermal expansion, lattice vibrations, or structural phase transitions, is expected to produce corresponding changes in the work function. This sensitivity forms the basis for using temperature-dependent photoionization measurements as a probe of thermodynamic and quantum phenomena in finite systems.

3.1.1 Microscopic definition of the work function

Microscopically, the work function represents the energy difference between the electronic chemical potential inside the material and the vacuum level outside the surface. It may

therefore be written as

$$W = E_{vac} - \mu$$

where E_{vac} is the vacuum energy level outside the surface and μ is the electronic chemical potential of the metal [2,5,8,9]. Equivalently, the work function may be expressed in terms of the electrostatic surface dipole barrier as

$$W = e\Delta\phi - \mu$$

where e is the magnitude of the electron charge $\Delta\phi$ is the electrostatic potential difference between the interior of the metal and the vacuum outside the surface. The origin of this surface dipole layer arises from the spill-out of conduction electrons beyond the positively charged ionic lattice at the metal surface [9]. Since the electronic charge distribution extends slightly farther into vacuum than the ion cores, a separation of charge develops near the surface, producing an electrostatic dipole barrier. This surface potential step contributes directly to the work function and depends sensitively on the electron density (ρ_e) and surface geometry. The work function therefore depends on both the bulk electronic structure and the surface.

For finite systems such as isolated nanoparticles, the analogous quantity measured experimentally is the ionization energy. The ionization energy differs from the bulk work function according to

$$I = W + \frac{\alpha e^2}{R},$$

where R is the nanoparticle radius and α is a coefficient associated with the electrostatic charging energy of the particle [6,10–13,29,49,50]. This finite-size correction becomes increasingly important at small particle sizes and forms the basis for connecting nanoparticle ionization measurements to bulk work functions.

3.1.2 Understanding the finite size correction

Classically, for finite metallic particles, the ionization energy differs from the bulk work function because electron removal leaves the particle positively charged. The additional electrostatic energy required to charge the particle increases the energy needed to remove an electron and therefore introduces a size-dependent correction to the work function. The simplest estimate of this effect is obtained by treating the nanoparticle as an isolated conducting sphere of radius R . The capacitance in Gaussian units is

$$C = R.$$

If the particle carries charge e , the electrostatic energy is

$$U_{\text{ch}}(Q) = \frac{e^2}{2C} = \frac{e^2}{2R}.$$

Therefore, the energy cost of removing one electron from a neutral sphere is

$$\Delta I_{\text{ch}} = \frac{e^2}{2R}.$$

This gives the simplest finite-size correction,

$$I(R) = W + \frac{e^2}{2R},$$

where W is the bulk work function. In SI units, the same expression is obtained by replacing e^2 with $e^2/4\pi\epsilon_0$.

Alternatively, the finite-size correction may be derived using the classical image-charge model. In this picture, the work function is interpreted as the energy required to remove an electron from a distance d outside the metal surface to infinity. Solving the image-charge problem for an isolated conducting sphere of radius R yields a size-dependent electron removal energy

$$I(R) = \frac{e^2}{4d} \frac{1 + 4(d/R) + 6(d/R)^2 + 2(d/R)^3}{(1 + d/2R)(1 + d/R)^2}.$$

In the bulk limit $R \rightarrow \infty$, the expression reduces to

$$W = \frac{e^2}{4d}.$$

Expanding the spherical result where $R \sim 1 \text{ nm} \gg d \sim 1 \text{ \AA}$,

$$I(R) = W + \frac{3}{8} \frac{e^2}{R} + O(R^{-2}),$$

leading to the familiar finite-size correction

$$I(R) = W + \frac{3}{8} \frac{e^2}{R}.$$

This expression provides the basis for converting measured nanoparticle ionization energies into bulk-limit work functions throughout the present work.

The capacitance and image-charge models are both purely classical yet predict different coefficients, $1/2$ and $3/8$, and this apparent inconsistency must be addressed. The resolution is that the two calculations include different amounts of physics:

- The **capacitance estimate** counts only the self-energy of the unit charge left behind,
 $+ \frac{1}{2} e^2/R$
- The **image-charge model** additionally accounts for the attractive work the departing electron performs against its own induced surface charge. This polarization contribution lowers the removal energy by $-\frac{1}{8} e^2/R$, so that

$$\alpha = \underbrace{\frac{1}{2}}_{\text{charging}} - \underbrace{\frac{1}{8}}_{\text{image polarization}} = \frac{3}{8}$$

The derivation above predicts a universal coefficient of $3/8$ within the image-charge

approximation. In practice, however, the finite-size correction is influenced by additional material-dependent quantum-mechanical effects that are not fully captured by the simple electrostatic model. These include the detailed electronic structure of the surface, electron spill-out beyond the positive background, exchange-correlation effects, and modifications of the surface dipole layer. Consequently, experimental determinations of the finite-size correction generally employ

$$I(R) = W + \alpha \frac{e^2}{R},$$

where the coefficient α is treated as a material-dependent parameter.

Neither classical model is rigorous, because at the relevant length scales ($R \sim 1$ nm, $d \sim 1$ Å) the very concept of a sharp image plane breaks down. A first-principles treatment is provided by density functional theory, in which the ground-state energy is a unique functional of the electron density $\rho(\mathbf{r})$. For a cluster of N atoms, each contributing w valence electrons, and carrying z excess electrons, the total energy is

$$E[\rho] = \int \left[t[\rho] + \varepsilon_{xc}[\rho] + \frac{1}{2} e^2 \phi_e(\mathbf{r}) \rho(\mathbf{r}) + V_I(\mathbf{r}) \rho(\mathbf{r}) \right] d^3r + E_I,$$

with the individual contributions defined as follows:

- $t[\rho]$ — the kinetic energy density functional (treated semiclassically through the extended Thomas–Fermi expansion);
- $\varepsilon_{xc}[\rho]$ — the exchange-correlation energy density, evaluated in the local density approximation;
- $\phi_e(\mathbf{r}) = \int \rho(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'| d^3r'$ — the Hartree potential of the electrons;
- $V_I(\mathbf{r})$ — the electrostatic potential of the uniform positive (jellium) background;
- E_I — the self-energy of that background, constant for fixed N .

The density is subject to the normalization constraint fixing the total electron number,

$$\int \rho(\mathbf{r}) d^3r = Z = wN + z,$$

where z denotes the number of **excess electrons** ($z = -1$ for the singly ionized cation, $z = 0$ for the neutral, $z = +1$ for the anion). The ionization energy and electron affinity then follow from the constrained total-energy differences $I = E(z = -1) - E(z = 0)$ and $A = E(z = 0) - E(z = +1)$, respectively. Solving this model variationally [50] establishes the correct hierarchy of coefficients:

1. In the classical (Coulomb-only) limit — retaining only the electrostatic terms and discarding the kinetic and exchange-correlation contributions — the variational solution yields $\alpha = 1/2$, and a vanishing bulk work function, $W = 0$. The nonzero work function of a real metal is therefore an entirely quantum-mechanical phenomenon, arising from the kinetic, exchange, and correlation energies and from the surface dipole created by electron spill-out.
2. The image-charge value $3/8$ does not emerge from this classical limit; it follows only from the image construction, which the authors of [50] argue is unjustified at atomic distances.
3. When the full quantum-mechanical energetics are retained, α becomes a material-dependent quantity governed primarily by r_s . For sodium ($r_s \approx 3.96 a_0$) the calculation gives $\alpha \approx 0.4$ — close to the image-charge value. The proximity of $3/8$ is coincidental rather than fundamental.

For the present work, experimentally determined coefficients are used: $\alpha \approx 0.31 - 0.33$ for lithium, $\alpha \approx 0.39$ for sodium, and $\alpha \approx 0.34 - 0.38$ for potassium are used.

3.2 Thermodynamic Properties of the Work Function

3.2.1 Thermodynamic definition of the work function

The thermodynamic behavior of the work function may be understood by considering the

dependence of the electronic free energy on temperature, entropy, and structural properties of the material. The starting point is the first law of thermodynamics,

$$dU = \delta Q - \delta W$$

where U is the internal energy, δQ is the heat transferred into the system, and δW is the work performed by the system. For reversible processes, this relation becomes

$$dU = TdS - PdV + \mu dN$$

where T is temperature, S is entropy, P is pressure, V is volume, μ is the electronic chemical potential, and N is the number of particles.

Using the relation between the work function and the chemical potential, the work function may be written as

$$W = e\Delta\phi - \left(\frac{\partial U}{\partial N}\right)_{S,V}.$$

3.2.2 Temperature dependence of the work function

The temperature dependence of the work function therefore arises from temperature-induced changes in both the electronic chemical potential and the surface dipole barrier. Taking the temperature derivative gives

$$\frac{dW}{dT} = e \frac{d(\Delta\phi)}{dT} - \frac{d\mu}{dT}$$

The first term reflects changes in the surface electrostatic potential, primarily associated with thermal expansion and modifications of the electron density near the surface. The second term describes the temperature dependence of the electronic chemical potential.

For simple metals, thermal expansion often provides the dominant contribution to the temperature dependence of the work function. As the lattice expands with increasing temperature, the average electron density decreases, generally leading to a reduction in the work

function. More generally, W can be viewed as a function $W(r_s, T)$. The temperature variation may be expressed as

$$\frac{dW}{dT} = \frac{dr_s}{dT} \left. \frac{\partial W}{\partial r_s} \right|_T + \left. \frac{\partial W}{\partial T} \right|_{r_s},$$

or equivalently

$$\frac{dW}{dT} = \alpha_{\text{th}} r_s \left. \frac{\partial W}{\partial r_s} \right|_T + \left. \frac{\partial W}{\partial T} \right|_{r_s}.$$

The first term represents the effect of thermal expansion, while the second includes additional contributions such as electron–phonon interactions and other explicit temperature depends.

3.2.3 Thermal Expansion and Heat Capacity

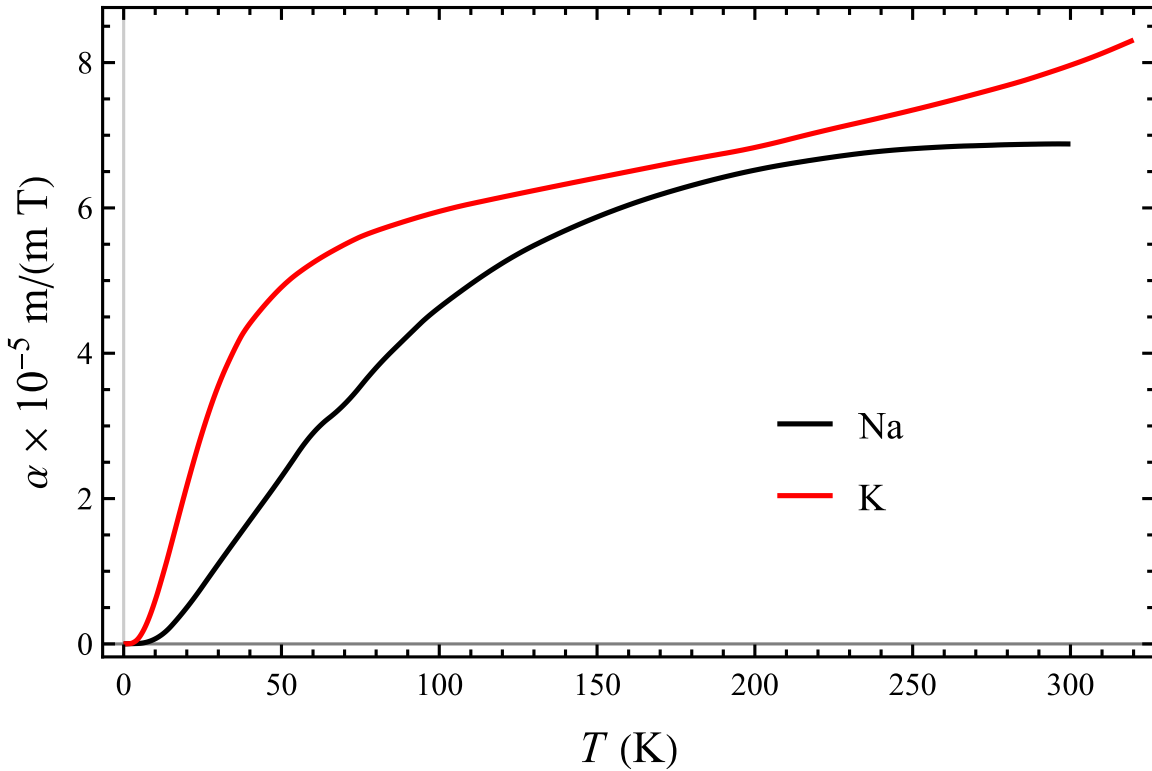


Figure 3.1 Temperature dependent data of the linear thermal expansion coefficient for K [51] and Na [52].

Figure 3.1 shows the measured thermal-expansion coefficients of Na and K as functions of temperature. From Figure 3.1 and the inset Figure 5.2, it is clear that the temperature

dependence of the thermal expansion closely resembles that of the heat capacity, with both quantities decreasing rapidly at low temperature and approaching zero as $T \rightarrow 0$. This similarity is not coincidental but reflects a fundamental thermodynamic connection between the two quantities.

The volume thermal expansion coefficient is defined as

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P.$$

Using Maxwell relations together with the cyclic identity for thermodynamic derivatives, one obtains the relation

$$\beta = \frac{C_V \gamma_G}{V K_T},$$

where C_V is the constant-volume heat capacity, γ_G is the Grüneisen parameter, and K_T is the isothermal bulk modulus. The full derivation of this relation is presented in

Figure A.4 systematic error from photodiode saturation resulting in artificial peaks in the spectrum.

Relation Between Thermal Expansion and Heat Capacity.

This relation is useful for understanding the thermodynamic origin of the temperature dependence of the work function and its connection to the Third Law of Thermodynamics. Since thermal expansion arises from anharmonic lattice vibrations and is directly linked to the heat capacity by the Grüneisen parameter, the thermal expansion coefficient, this implies

$$\beta \rightarrow 0 \text{ as } T \rightarrow 0,$$

because the heat capacity approaches zero at low temperature. Consequently, the temperature dependence of the lattice spacing and electron density also vanishes at sufficiently low temperature.

The Grüneisen parameter may therefore be interpreted as a measure of lattice anharmonicity, while the vanishing of both C_V and β at low temperature provides a thermodynamic basis for the flattening of the experimentally measured work function curves.

3.2.4 Low-temperature limit and the third law of thermodynamics

An important thermodynamic limit emerges as $T \rightarrow 0$. Using the Maxwell relation

$$\left(\frac{\partial \mu}{\partial T}\right)_{N,P} = -\left(\frac{\partial S}{\partial N}\right)_{T,P},$$

together with the Third Law of Thermodynamics, the entropy approaches a constant at zero temperature, implying

$$\frac{d\mu}{dT} \rightarrow 0 \text{ as } T \rightarrow 0.$$

At the same time, thermal expansion vanishes, causing the surface dipole contribution to become temperature independent. Therefore,

$$\frac{dW}{dT} \rightarrow 0 \text{ as } T \rightarrow 0.$$

Thus, the low-temperature behavior of the work function constitutes a direct manifestation of fundamental thermodynamic principles [8].

3.2.5 Modeling the temperature dependence of the work function: electron gas model

To model the temperature dependence of the work function, the nanoparticle is approximated as a free-electron gas characterized by a temperature-dependent Wigner–Seitz radius $r_s(T)$ [7]. The thermal expansion of the lattice modifies the average electron density and therefore alters both the electronic chemical potential and the work function.

the linear thermal expansion coefficient $\alpha_{th}(T)$ by

$$\frac{1}{r_s} \frac{dr_s}{dT} = \alpha_{th}(T),$$

Then,

$$\frac{dr_s}{r_s} = \alpha_{th}(T) dT.$$

Integrating from T_0 to T ,

$$\ln \left(\frac{r_s(T)}{r_s(T_0)} \right) = \int_{T_0}^T \alpha_{th}(T') dT',$$

which gives the exact form

$$r_s(T) = r_s(T_0) \exp \left[\int_{T_0}^T \alpha_{th}(T') dT' \right].$$

Since the thermal expansion is small, which is the case over the temperature range of interest for most metals, then

$$r_s(T) \approx r_s(T_0) \left[1 + \int_{T_0}^T \alpha_{th}(T') dT' \right].$$

The linear thermal expansion coefficient $\alpha_{th}(T)$ was obtained from tabulated experimental data and interpolated over the measured temperature range. Taking $T_0 = 300$ K as a reference temperature, the temperature dependence of the Wigner–Seitz radius is written as

$$r_s(T) = r_s(T_0) \left[1 + \int_{T_0}^T \alpha_{th}(T') dT' \right],$$

The electronic energy was modeled using the semi-empirical expression

$$E(r_s) = \frac{h^2}{8m} \left(\frac{9}{4\pi^2 a_0^3} \right)^{2/3} \frac{1}{r_s^2} - \frac{16.6}{r_s} + \frac{7.8}{12r_s} \left(1 + \sqrt{\frac{3(r_s + 7.8)}{r_s}} \right),$$

which includes both the free-electron kinetic-energy contribution and effective interaction corrections. The temperature dependence was calculated through the electronic chemical potential $\mu(T)$, initialized at the reference temperature according to

$$\mu(T_0) = E_F(T_0),$$

where E_F is the free-electron Fermi energy.

The chemical potential was propagated numerically using

$$\mu(T_{n+1}) = \mu(T_n) + \alpha_{th}(T_n) r_s(T_n) \left(\frac{dE}{dr_s} \right)_{r_s=r_s(T_n)} \Delta T,$$

with $\Delta T = 1$ K.

The derivative entering the propagation equation is

$$\frac{dE}{dr_s} = -\frac{h^2}{4m} \left(\frac{9}{4\pi^2 a_0^3} \right)^{2/3} \frac{1}{r_s^3} + \frac{16.6}{r_s^2} + \frac{1}{12(r_s + 7.8)^2} + \frac{(r_s - 7.8)}{4(r_s + 7.8)^3}.$$

The numerical integration was performed both above and below T_0 , yielding the chemical potential over the full experimental temperature range.

The work function was then calculated from

$$\phi(T) = \frac{C}{[E_F(T)/\text{eV}]^{1/2} r_s(T)^{3/2}},$$

where $C = 37.4$ for alkalis.

3.3 Fowler Theory of Near-Threshold Photoemission

The photoelectric effect in metals occurs when absorption of a photon transfers sufficient energy to an electron to overcome the surface potential barrier and escape into vacuum. Fowler argued that the electrons capable of escaping from a metal surface are those whose kinetic energy component normal to the surface, after photon absorption, exceeds the work function [53,54]. Electrons satisfying this condition are commonly referred to as *available electrons*.

If the photoelectron yield is proportional to the number of available electrons, the yield may be expressed as

$$Y \sim \int N(T; u, v, w) dw$$

where u , v , and w are the velocity components of the electron, with w defined as the component normal to the surface.

The number of electrons having velocity components within the intervals $(u, u + du)$, $(v, v + dv)$, and $(w, w + dw)$ follows the Fermi–Dirac distribution and may be written as

$$n(T; u, v, w) \, dudvdw = 2 \left(\frac{m}{h} \right)^3 \frac{dudvdw}{e^{\left[\frac{1}{2} m(u^2 + v^2 + w^2) - E_F \right] / k_B T} + 1}$$

where m is the electron mass, E_F is the Fermi energy, and k_B is Boltzmann's constant.

Transforming the velocity components parallel to the surface into polar coordinates and integrating over those degrees of freedom yields the number of electrons per unit volume possessing normal velocity components between w and $w + dw$:

$$N(T; w) \, dw = \frac{4\pi m k_B T}{h^3} \ln \left[1 + e^{\left(E_F - \frac{1}{2} m w^2 \right) / k_B T} \right] dw$$

The condition for electron escape is that the normal kinetic energy after photon absorption exceeds the surface barrier. This requirement may be written as

$$\frac{1}{2} m w^2 + h\nu = W + E_F$$

substituting the distribution of available electrons into the expression for the yield gives

$$Y \sim T^2 \int_0^\infty \frac{\ln[1 + e^{-y + (h\nu - W)/k_B T}]}{\sqrt{y + (E_F - h\nu + W)/k_B T}} dy$$

Near threshold, where $h\nu \approx W$, the integral may be simplified by neglecting the y -dependence in the denominator. Expanding the logarithm and integrating term by term yields Fowler's result:

$$Y \sim T^2 \operatorname{Li}_2(e^{(h\nu - W)/k_B T})$$

or equivalently,

$$\ln\left(\frac{Y}{T^2}\right) = B + \ln[Li_2(e^{(h\nu - W)/k_B T})]$$

where Li_2 is the dilogarithm (Jonquière) function and B is a temperature-independent constant containing experimental prefactors. The latter expression is particularly convenient for threshold analysis because it effectively separates the two fitting parameters, B and W , onto orthogonal axes. Specifically, the work function determines the horizontal displacement of the Fowler curve through the argument $(h\nu - W)/k_B T$, while the constant B contributes only as a vertical offset. This decoupling substantially improves the numerical stability and robustness of the fitting procedure, reducing correlations between fitting parameters and enabling more precise extraction of ionization thresholds from experimental data.

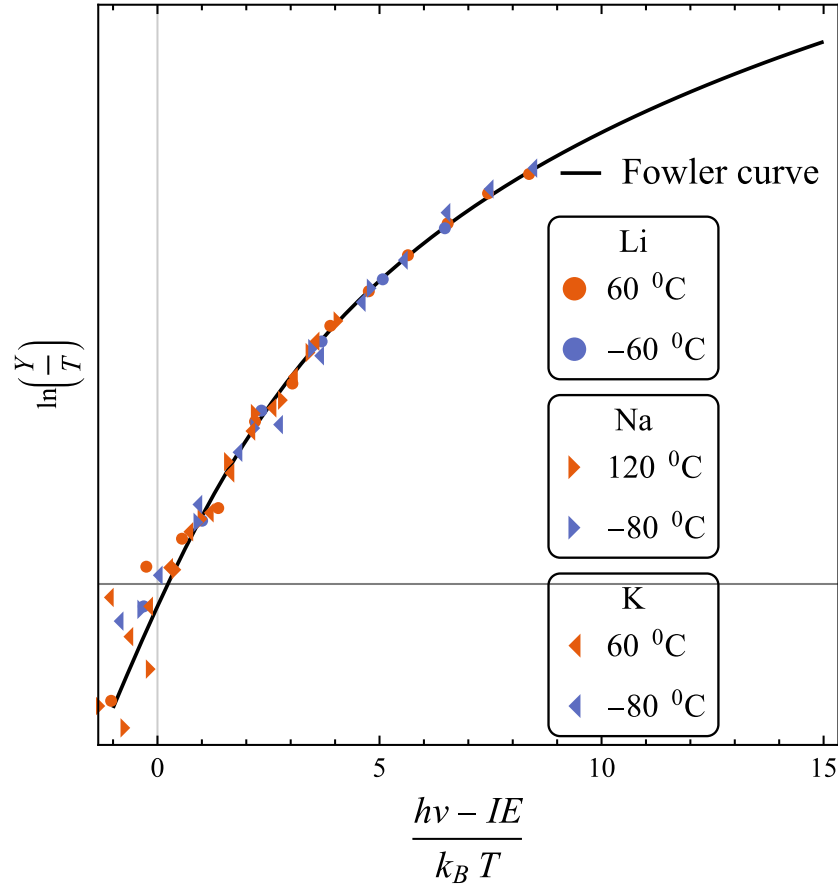


Figure 3.2. Near-threshold universal Fowler fit of different nanoparticles elements and different temperatures.

An important feature of Fowler theory is that the thermal broadening of the ionization threshold emerges naturally from the Fermi–Dirac distribution without introducing arbitrary fitting parameters. Although originally derived for bulk metal surfaces, the Fowler formalism has been found experimentally to describe near-threshold photoionization spectra of metallic nanoparticles with remarkable accuracy, making it particularly suitable for the present work (see Figure 3.2).

Much of the material presented in Chapters 4 and 5, including portions of the text, figures, tables, and analysis, is adapted from Refs. [2–4] and from the doctoral dissertation of A. O. Haridy. The material has been reorganized and revised for consistency with the present dissertation.

Chapter 4: Melting Transitions in Sodium and Potassium Nanoparticles

4.1 Introduction

One of the most significant consequences of nanoparticle systems is the modification of phase transitions relative to bulk materials [17]. As the dimensions of a particle decrease to the nanometer scale, the surface-to-volume ratio increases substantially, causing surface energy contributions to become increasingly important. Among the resulting finite-size effects, the suppression of the melting temperature is one of the most extensively studied manifestations of nanoscale thermodynamics [15,31,32,55–61]. This behavior is commonly described by the Gibbs–Thomson relation and has been observed in a wide variety of metallic nanoparticles and clusters [17,62,63].

Experimentally probing melting transitions in isolated nanoparticles presents significant challenges. For nanoparticles supported on substrates, electron microscopy techniques can directly visualize structural transformations, although interactions with the substrate and beam-

induced effects may complicate interpretation. In contrast, free nanoparticles in a molecular beam provide contamination-free and substrate-free systems, but direct structural imaging of nanometer-scale particles in flight remains impractical. Alternative approaches therefore rely on indirect probes of phase transitions, including calorimetry [15,64] and magic number measurements [58]. Here we propose a new approach using the work function.

Historically, the temperature dependence of metallic work functions has received relatively limited attention because the expected variations are small, typically on the order of k_B . For highly reactive alkali metals, precise measurements are additionally complicated by surface contamination [2,65,66], which can strongly alter photoemission properties. The use of free nanoparticles largely eliminates these difficulties because the particles remain isolated in vacuum for only milliseconds before detection, thereby maintaining effectively uncontaminated surfaces throughout the measurement process.

This chapter addresses the central question of whether electronic observables can reveal thermodynamic phenomena in finite systems. Temperature-dependent measurements of sodium and potassium nanoparticles reveal distinct discontinuities in the work function associated with melting. The observed transition temperatures are substantially reduced relative to their bulk values, in agreement with finite-size thermodynamics described by the Gibbs–Thomson equation. These results demonstrate that electronic measurements can provide direct signatures of structural phase transitions in isolated nanoparticles.

4.2 Melting signature via precise ionization energy measurements

4.2.1 Temperature Dependence of the Work Function

The experimentally determined work functions of Na and K nanoparticles are shown in Figure 4.1. The data reveals two distinct temperature regimes separated by a discontinuity in

both the magnitude and slope of the work function.

Table 4-1. Work functions and their temperature coefficients in the solid phase, derived from the data in Figure 4.1, and comparison with the image charge model [7] and earlier literature. $T \rightarrow 0$ K and $T \rightarrow 293$ K temperature values were extrapolated from the linear fit of the solid phase (see Figure 4.1).

	Extrapolated W (eV), this work		W (eV) in reviews [2]	dW/dT (eV/K), this work	dW/dT (eV/K), from model [7]	dW/dT (eV/K) in [67,68]
	W (eV) at $T \rightarrow 0$ K	W (eV) at $T \rightarrow 293$ K				
Na	2.802 ± 0.009	2.743 ± 0.016	2.54 – 2.75	-1.7×10^{-4}	-2.0×10^{-4}	-5.1×10^{-4} , -4.0×10^{-4}
K	2.390 ± 0.012	2.317 ± 0.023	2.29 – 2.30	-2.5×10^{-4}	-2.7×10^{-4}	-2.6×10^{-4} , -5.3×10^{-4}

The work function decreases approximately linearly with increasing temperature. This behavior is attributed primarily to thermal expansion of the lattice which decreases the electron density. The measured slopes of the solid-phase work functions are summarized in Table 4-1. These values are in reasonable agreement with phenomenological image-charge model (Sec. 3.2.5) and earlier experimental measurements of alkali-metal work functions. At higher temperatures, the work functions exhibit abrupt downward shifts accompanied by changes in slope (see Figure 4.1).

The observed transition temperatures occur at approximately 280 K for sodium nanoparticles and 240 K for potassium nanoparticles. Both temperatures are significantly (~ 100 K) below the bulk melting temperatures of the corresponding metals.

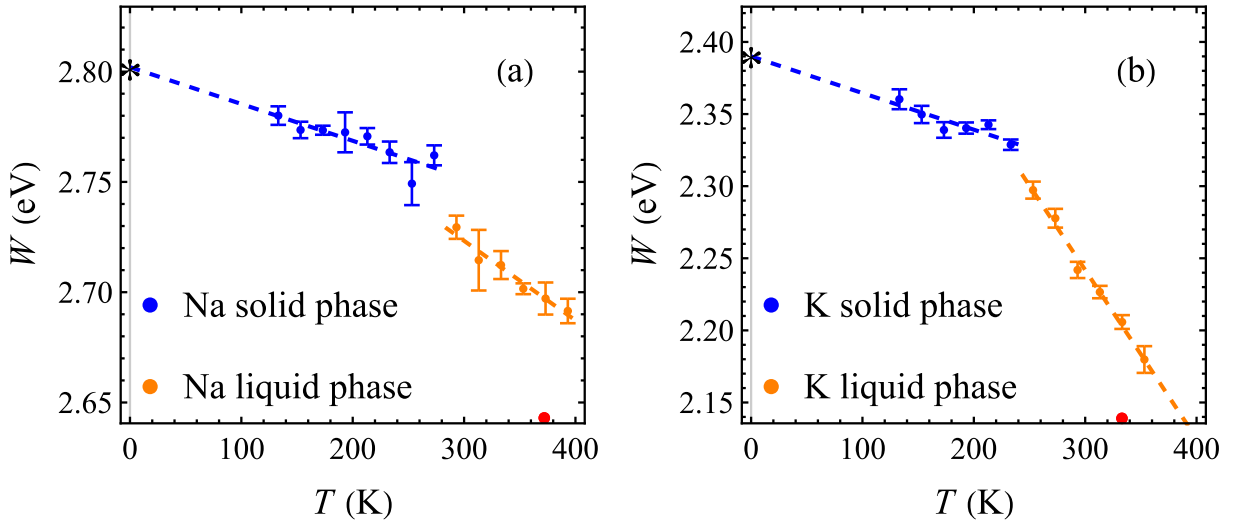


Figure 4.1. Temperature-dependent work functions of sodium and potassium nanoparticles. The figure is reproduced from Ref. [34]. Note the slope change between the solid phase (blue dashed line) and the liquid phase (orange dashed line). The dots on the x-axis indicate the bulk melting point for each metal. The asterisks mark the linear extrapolation of the experimental data points to $T = 0$ K.

4.2.2 Finite-Size Melting and the Gibbs–Thomson Relation

The suppression of the melting temperature in nanoparticles arises from the increasing importance of surface energy as the particle size decreases. In bulk systems, the contribution of surface atoms to the total free energy is negligible compared to the bulk cohesive energy. This is why, for example, a 1 kg block of Na melts at the same temperature as 1 g. In nanoparticles, however, the large surface-to-volume ratio causes surface effects to significantly modify thermodynamic equilibrium conditions. And since the surface the surface-to-volume goes as $1/R$, the depression from the bulk melting the expected to also go as $1/R$.

For a spherical nanoparticle of radius R , the melting temperature is commonly described by the Gibbs–Thomson relation [31,34,63]

$$T_m(R) = T_m \left(1 - \frac{c\sigma_{sl}}{H_f R} \right),$$

where $T_m(R)$ is the melting temperature of the nanoparticle, T_m is the bulk melting temperature, σ_{sl} is the solid–liquid interfacial energy per unit area, H_f is the enthalpy of fusion per unit

volume, and c is a geometric factor. For bulk thermodynamic equilibrium, $c = 2$ is commonly used, whereas values closer to $c = 3$ have been suggested for isolated nanoparticles in the gas phase [62].

The physical origin of the Gibbs–Thomson relation may be understood by considering the free-energy balance between the solid and liquid phases. Because the liquid phase generally possesses a lower surface energy, melting becomes energetically favorable at lower temperatures for small particles. As the particle radius decreases, the surface contribution to the total free energy increases approximately as $1/R$, producing a corresponding reduction in the melting temperature [17].

To estimate the magnitude of the melting-point depression, the solid–liquid interfacial energy may be approximated using Turnbull’s empirical relation [69,70]

$$\sigma_{sl} \approx \sigma_0 H_f d_m,$$

where d_m is the characteristic atomic spacing given by $\sqrt[3]{4\pi/3}(a_0 r_s)$ and $\sigma_0 \approx 0.45$ for many metals. Substituting this relation into the Gibbs–Thomson equation yields

$$T_m(N) \approx T_m \left(1 - \frac{1.6c\sigma_0}{N^{1/3}} \right),$$

where N is the number of atoms in the nanoparticle.

For the sodium and potassium nanoparticles investigated in the present work, the average particle populations were approximately $N \sim 5000$, corresponding to diameters of 7 nm for Na and 8 nm for K. The experimentally observed transition temperatures were approximately 280 K for sodium and 240 K for potassium, corresponding to $T_m(N) \approx 280$ K for sodium and $T_m(N) \approx 336.7$ K for potassium. These values are consistent with the expected finite-size suppression predicted by the Gibbs–Thomson model.

The agreement between the experimentally observed transition temperatures and the

Gibbs–Thomson scaling strongly supports the interpretation of the observed discontinuities in the work function as signatures of nanoparticle melting. The measurements therefore establish that structural phase transitions in finite systems can be detected through high-resolution electronic threshold measurements. Having established that the observed transition temperatures are consistent with finite-size melting, the next question is how the melting transition modifies the electronic work function itself.

4.2.3 Work Function Change Upon Melting

Table 4-2: Magnitudes of melting-induced work function drops estimated from the data in Figure 4.1 and from the equation below.

	Measured $ \Delta W $ (eV)	Calculated $ \Delta W $ (eV)
Na	0.025-0.03	0.033
K	0.02-0.03	0.046

The melting transition is typically accompanied by a reduction in density due to the less compact atomic arrangement of the liquid phase relative to the solid phase. Assuming that the dominant contribution to the temperature dependence of the work function arises from thermal expansion, the change in the work function associated with melting may be estimated from the density discontinuity as

$$\Delta W \approx \frac{dW}{d\rho} \Delta\rho,$$

where ρ is the mass density. Using the relation between density and thermal expansion, this expression may be rewritten as

$$\Delta W \approx \frac{dW}{dT} \frac{1}{\beta} \frac{\Delta\rho}{\rho}.$$

dW/dT is the experimentally measured slope of the solid phase (see Table 4-1). The values for

β and ρ were also of the bulk solid phase values. The results are summarized in Table 4-2.

Physically, the drop in density during melting decreases the average electron density within the nanoparticle. Since the electrostatic surface dipole barrier and electronic chemical potential both depend on electron density, the work function correspondingly shifts to lower values. The drop observed experimentally therefore reflects the structural transformation accompanying the melting transition.

In addition to the discontinuity in magnitude, the slope of the work function becomes steeper in the liquid phase. This behavior reflects the increase in thermal expansion following the phase transition [71]. Upon melting, the atomic structure becomes more disordered and more compressible, resulting in a more rapid increase of the average interatomic spacing with temperature. This behavior highlights the intimate connection between thermal expansion and the slope of the work function.

The effect is particularly pronounced for potassium, which exhibits a larger increase in thermal expansion upon melting than sodium. Because the thermal expansion coefficient of liquid K exceeds that of liquid Na, the temperature dependence of the work function becomes correspondingly steeper in the liquid phase for K. This observation further supports the close relationship between thermal expansion and the temperature-dependent behavior of the work function.

4.2.4 Thermal expansion estimate of nanoparticles from the work function

Let's attempt to quantify this relationship. Recall that for simple metals the dominant factor of the thermal effect of the change of the work function is [8]

$$\frac{dW}{dT} = \alpha_{\text{th}} r_s \left. \frac{\partial W}{\partial r_s} \right|_T$$

Let us assume that for the simplest case

$$\frac{\partial W}{\partial r_s} = -\frac{W}{r_s}.$$

This is the case, for example, in the image charge approximation. And its agreement with experiment motivates its use here. Then,

$$\frac{dW}{dT} = \alpha_{\text{th}} r_s \left. \frac{\partial W}{\partial r_s} \right|_T = -\alpha_{\text{th}} r_s \frac{W}{r_s},$$

or,

$$\frac{d \ln(W)}{dT} = \alpha_{\text{th}}.$$

Hence, the slope of $\ln(W)$ vs. T should give an estimate of the thermal expansion coefficient of the nanoparticle. The resulting values for the solid phase are $60. \pm 15 \mu\text{m}/(m \cdot K)$ and $108. \pm 27 \mu\text{m}/(m \cdot K)$ for Na and K, respectively. These values are in good agreement with the data in Figure 3.1. For liquid $133. \pm 32 \mu\text{m}/(m \cdot K)$ and $522. \pm 39 \mu\text{m}/(m \cdot K)$ for Na and K, respectively.

Existing theoretical estimates of the liquid-phase temperature dependence of the work function remain limited. Calculations based either on a transposition of the image charge model [7] to the liquid-state densities [72] or on a variational DFT treatment of a two-component model [73], are within an order of magnitude of the data in Figure 4.1 but mostly not in numerical agreement. The present measurements therefore suggest that a more complete theoretical description of temperature-dependent work functions in liquid alkali metals would be of considerable interest.

4.3 Discussion

4.3.1 The work function value at $T = 0$ K.

A common approximation in the literature is to describe the work function using a linear

dependence on temperature [2,4,7,67],

$$W(T) = W_0 + aT.$$

While this representation may provide a reasonable fit over a wide temperature interval, it cannot be valid over the full temperature range. According to the third law of thermodynamics, the heat capacity vanishes as $T \rightarrow 0$, causing the thermal expansion coefficient to vanish as well. As discussed in Sec. Low-temperature limit and the third law of thermodynamics this implies

$$\frac{dW}{dT} \rightarrow 0 \text{ as } T \rightarrow 0.$$

Consequently, the work function cannot remain linear down to zero temperature. The apparent linear behavior frequently observed experimentally arises because measurements are often performed at temperatures that are not small compared to the Debye temperature. Over such temperature intervals, the true dependence may be approximated by a straight line, even though the slope must ultimately approach zero at sufficiently low temperature.

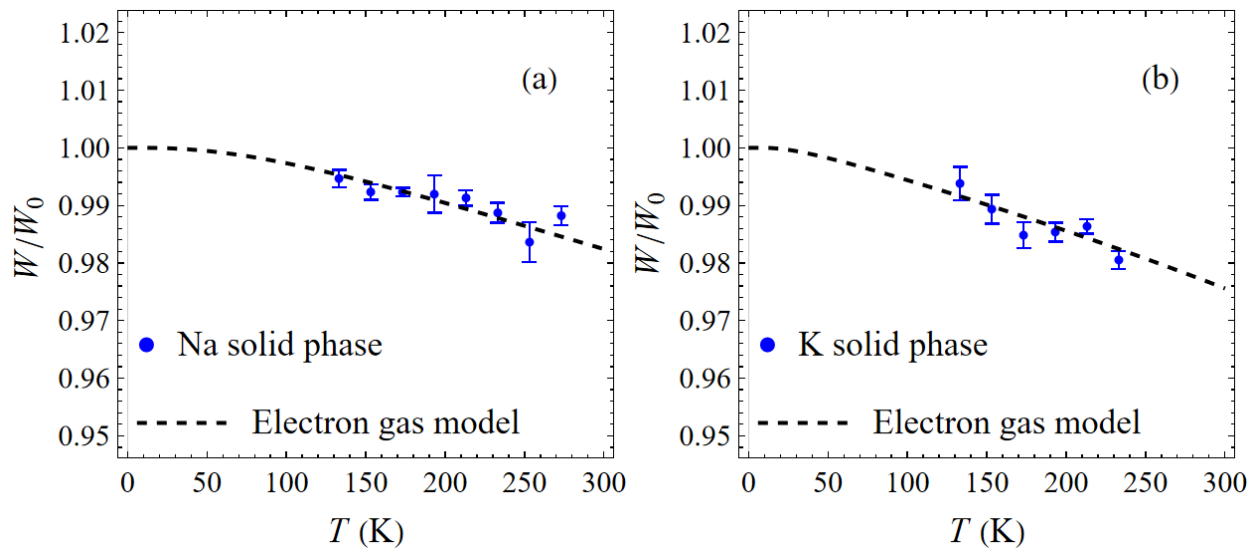


Figure 4.2. Temperature variation of the metal work function predicted by the electron gas model (dashed line) compared to the experimental data for Na and K at temperatures below the nanoparticles' melting points. $W(T)$ is plotted relative to its value at 0 K, W_0 . Fitting the model electron gas curve to the data yields $W_0 = 2.795$ eV for Na and $W_0 = 2.375$ eV for K, which is 0.3% and 0.6%, respectively, below the straight-line extrapolation of the data points. As mentioned in Temperature Dependence of the Work Function, the $W(T)$ plots for these metals retain their nearly straight-line shapes to much lower because of the low debye temperatures of Na (160 K) and K (90 K).

The electron-gas model introduced naturally satisfies this thermodynamic constraint through the temperature dependence of the thermal expansion coefficient. By combining experimental thermal-expansion data [51,52] with the image-charge model of the work function, it becomes possible to calculate $W(T)$ over the full temperature range and to extract a physically meaningful value of the zero-temperature work function $W(0)$ (Figure 4.2).

4.3.2 Direct Determination of the Solid–Liquid Interfacial Energy

One of the principal quantities governing finite-size melting is the solid–liquid interfacial energy σ_{sl} . This parameter plays a central role in determining the stability of the solid phase and appears explicitly in the Gibbs–Thomson relation. Despite its importance, direct experimental measurements of σ_{sl} are relatively uncommon because the solid–liquid interface is difficult to access experimentally for reactive metals such as Na and K.

The melting temperatures measured in the present work provide a means of estimating σ_{sl} directly. Rearranging the Gibbs–Thomson relation,

$$T_m(R) = T_m \left(1 - \frac{c\sigma_{sl}}{H_f R} \right),$$

gives

$$\sigma_0 = \frac{\sigma_{sl}}{H_f d_m} = \frac{1}{1.6c} \left(1 - \frac{T_m(R)}{T_m} \right),$$

where $T_m(R)$ is the experimentally measured melting temperature of a nanoparticle of radius R , T_m is the bulk melting temperature, and H_f is the enthalpy of fusion per unit volume. Using the measured transition temperatures and nanoparticle sizes, values of σ_{sl} can be calculated for both Na ($\sigma_0 \sim 1.1$) and K ($\sigma_0 \sim 0.8$).

This analysis demonstrates that temperature-dependent photoionization measurements provide not only a means of identifying melting transitions but also a method for determining

thermodynamic quantities associated with phase coexistence. In this sense, the electronic work function serves as an indirect probe of the solid–liquid interfacial energy through its sensitivity to melting-induced structural changes.

4.4 Conclusions

Temperature-dependent photoionization measurements of sodium and potassium nanoparticles reveal distinct discontinuities in the work function associated with the onset of melting. The observed transition temperatures are significantly reduced relative to the bulk values, consistent with finite-size melting described by the Gibbs–Thomson relation.

The measurements demonstrate that the work function is sensitive not only to gradual thermal expansion but also to abrupt structural transformations accompanying phase transitions. The experimentally observed melting-induced shifts in the work function and changes in slope are quantitatively consistent with density changes occurring during melting. Moreover, relevant thermodynamic quantities such as melting temperature, thermal expansion, and the solid liquid interfacial energy can be calculated directly,

These results establish temperature-dependent photoionization spectroscopy as a powerful experimental tool for probing structural and thermodynamic properties in isolated nanoparticles. The methods developed here provide a framework for future investigations of phase transitions, thermal expansion, and finite-size thermodynamics in nanoscale systems.

Chapter 5: Isotope Effects and Quantum Lattice Dynamics in Lithium

Nanoparticles

5.1 Why Lithium?

Lithium occupies a unique position among the alkali metals because of the unusually strong influence of quantum lattice effects on its physical properties. Its low atomic mass,

relatively high Debye temperature, and substantial zero-point motion produce deviations from the nearly free-electron behavior that successfully describes heavier alkali metals such as sodium and potassium. As a consequence, Li exhibits anomalous structural, thermodynamic, and electronic properties, including enhanced electron–phonon interactions, unusual structural transitions, and pronounced isotope effects. The work function provides a particularly sensitive probe of these phenomena because it depends on both the electronic chemical potential and the electrostatic surface barrier.

The existence of two stable isotopes, ^6Li and ^7Li , provides a unique opportunity to isolate the role of lattice dynamics experimentally. Since the isotopes possess identical electronic charge configurations but different ionic masses, any measurable isotope dependence in the work function must originate from differences in lattice dynamics rather than electronic structure.

An additional motivation for studying lithium is the substantial disagreement among previously reported work-function values. As shown in Figure 5.1, published measurements span a remarkably broad range. Much of this variation likely arises from the extreme sensitivity of the work function to surface contamination and oxidation. Since many measurements were performed using conventional surface-science techniques and often without reporting the sample temperature, direct comparison between experiments is difficult. These considerations motivate the use of isolated nanoparticles, whose short flight times through vacuum minimize contamination and allow accurate temperature control.

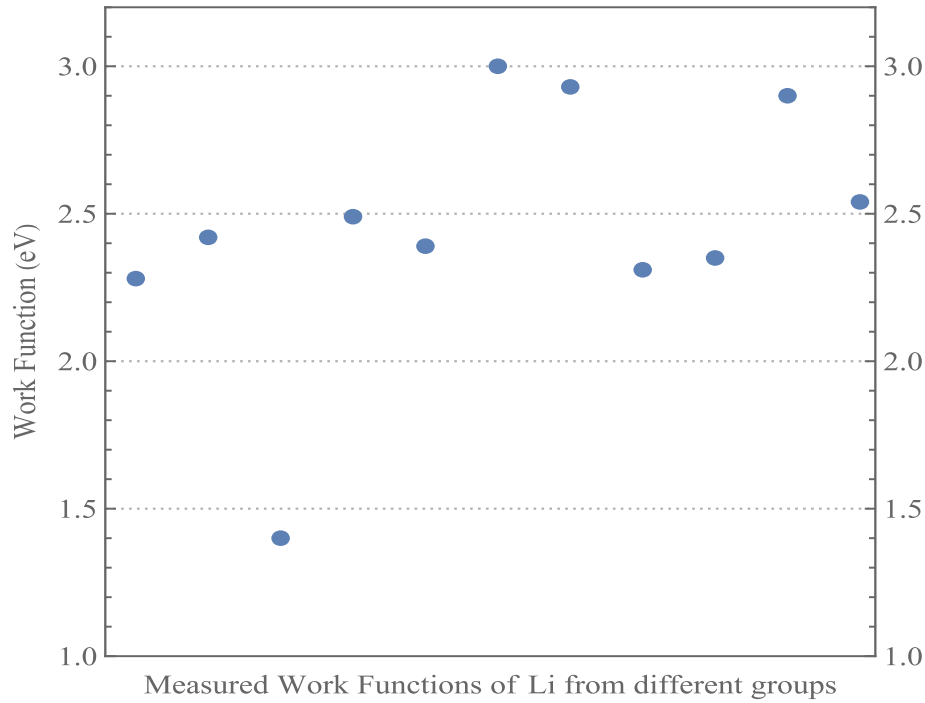


Figure 5.1. Experimental values of Li's work function. Work function values are taken from reference [74] and references therein. Values are in chronological order.

5.2 The Work function temperature dependence of Li

5.2.1 Experiment results

The temperature dependence of the work functions of ^6Li and ^7Li is shown in Figure 5.2. Several important features are immediately apparent. First, the work function decreases with increasing temperature for both isotopes. Second, the temperature dependence is strongly nonlinear over the investigated temperature range. Third, a clear isotope dependence is observed, with the two work function curves separating as the temperature increases.

Within a simple free-electron description, one would expect the work functions of the two isotopes to be nearly identical. Since the isotopes possess the same electronic structure and differ only in ionic mass, any observed splitting between the curves must originate from lattice-dynamical effects. These effects clearly reveal themselves in the thermal expansion.

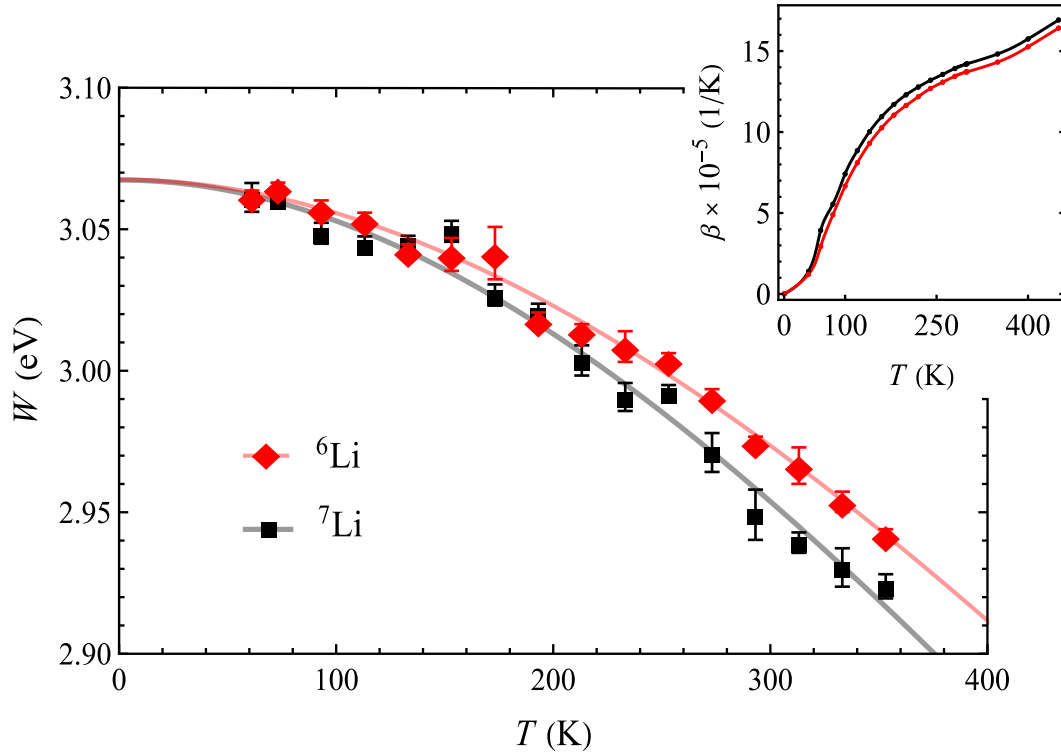


Figure 5.2. Experimentally determined work functions of lithium isotopes, ^7Li (squares) and ^6Li (diamonds). The error bars represent the standard error, typically $\sim 0.3\%$, derived from three individual photoionization measurements at each temperature. (Below 150 K, where the variation of W becomes small, five individual measurements at each temperature were performed.) The solid lines are least-squares polynomial fits to the data. The inset shows the volume thermal expansion coefficients of ^7Li (black top line) and ^6Li (red bottom line) based on data from Ref. [75]. The large error bars of ^6Li at ~ 180 is due to a leak in the source chamber.

The work function of ^7Li decreases more rapidly with temperature than that of ^6Li , producing a measurable isotope splitting. The inset of Figure 5.2 shows the corresponding thermal expansion data. Consistent with the behavior observed for sodium and potassium, the isotope with the larger thermal expansion also exhibits the larger temperature dependence of the work function, reinforcing the strong relationship between thermal expansion and work-function behavior. Remarkably, however, the larger thermal expansion is observed for the heavier isotope, ^7Li . This counterintuitive result cannot be understood within a purely classical picture and points to the importance of quantum effects in the lattice dynamics of lithium.

From a thermodynamic viewpoint, remember that

$$\beta = \frac{C_V \gamma_G \kappa_T}{V}$$

where γ is the Grüneisen parameter and κ_T is the compressibility. The isotope dependence of β and the work function therefore depends not only on atomic mass but also on how the phonon frequencies modify C_V , γ , and the anharmonic free energy. In Li, quantum effects are sufficiently large that the heavier isotope ends up having the larger measured thermal expansion.

5.2.2 Comparison with the electron gas model

A natural question is whether the observed temperature dependence can be explained solely through thermal expansion of the electron gas as is the case for Na and K. To investigate this possibility, the measurements were compared with the electron gas model introduced in Section 3.2.5.

In this model, the work function depends on temperature only through the temperature dependence of the Wigner–Seitz radius $r_s(T)$. As temperature increases, thermal expansion reduces the electron density, producing a corresponding decrease in the work function. The model therefore predicts both the magnitude and temperature dependence of $W(T)$ from independently measured thermal expansion coefficients.

Figure 5.3 compares the model predictions with the experimental data. The model reproduces the overall decrease of the work function with increasing temperature. However, it significantly underestimates both the curvature of the experimental $W(T)$ curves and the magnitude of the isotope splitting.

The disagreement demonstrates that thermal expansion alone is insufficient to describe the electronic properties of lithium. Although changes in electron density clearly contribute to the observed behavior, they cannot fully account for the measured temperature dependence of the work function. Additional mechanisms, which are not yet fully understood, must also influence

the work function.

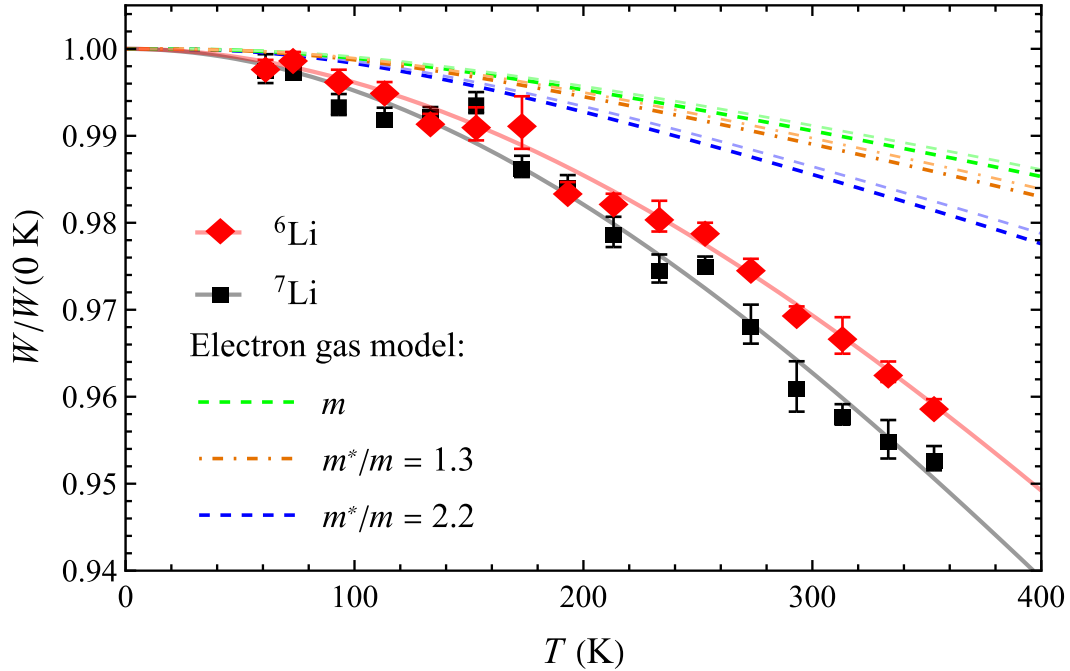


Figure 5.3. Comparison of the experimental work functions with the electron-gas model. The dashed lines follow the formalism of the electron-gas model [7] computed using the thermal expansion data from the inset of Figure 5.2 (each close-lying pair of lines corresponds to the two lithium isotopes) and three potential options for the electron mass parameter.

One possible source of discrepancy is the effective mass of the conduction electrons. The electron-gas model described in Section 3.2.5 implicitly assumes free electrons with mass m . However, Li is known to deviate from simple free-electron behavior because its valence electrons experience relatively weak shielding from the $1s$ core electrons. The resulting nonlocal pseudopotential enhances electron-ion interactions and produces an effective mass m^* that differs from the free electron value [76–78].

Experimental studies of Li clusters and bulk Li have reported effective masses significantly larger than m , indicating that electron-lattice interactions play a more important role than in the heavier alkali metals. Since the electron-gas model contains the Fermi energy,

$$E_F \propto \frac{1}{m^*},$$

modifications of the effective mass alter the predicted temperature dependence of the work

function.

To investigate this possibility, the electron-gas calculations were repeated using a range of effective-mass values m^*/m . The plot in Figure 5.3 shows two additional possibilities [33]: band effective mass $m^*/m \approx 1.3$, [76,77] and thermal effective mass $m^*/m \approx 2.2$ [78]. Increasing the effective mass improves the agreement between the calculated and experimental work-function curves by enhancing the overall thermal response and increasing the curvature of $W(T)$. However, even for values of m^*/m substantially larger than unity, the model is unable to reproduce either the magnitude of the observed isotope splitting or the full temperature dependence of the experimental data.

The inability of an effective-mass correction alone to account for the measurements indicates that the discrepancy cannot be explained solely through modifications of the electronic density of states. Instead, the results suggest that additional temperature-dependent contributions associated with quantum lattice dynamics, electron-phonon interactions, and modifications of the surface dipole barrier must contribute directly to the work function.

5.2.3 Beyond thermal expansion: quantum lattice effects

The failure of the electron-gas model indicates that the work function of lithium depends on more than the average electron density. In particular, lithium is distinguished by relatively weak shielding of the valence electrons by the 1s core electrons, causing the conduction electrons to experience a stronger and more nonlocal ionic pseudopotential than in the heavier alkali metals.

As a result, lithium exhibits enhanced electron–phonon coupling and a significantly modified effective electron mass. Numerous measurements on lithium clusters and bulk lithium have demonstrated deviations from simple free-electron behavior that are absent in sodium and

potassium.

In general, the work function depends on both electron density and temperature,

$$W = W(r_s, T),$$

so that

$$\frac{dW}{dT} = \alpha_{\text{th}} r_s \left. \frac{\partial W}{\partial r_s} \right|_T + \left. \frac{\partial W}{\partial T} \right|_{r_s}.$$

The first term represents the effect of thermal expansion and is the only contribution included in the electron-gas model. The second term incorporates all other temperature-dependent effects, including electron–phonon interactions, and other quantum lattice effects which explicitly depend on temperature.

For Na and K, the second term appears to be comparatively small, explaining the good agreement between experiment and the electron-gas model observed in Chapter 4:. In Li, however, the measurements indicate that this term is substantial and cannot be neglected.

The observed isotope dependence provides particularly strong evidence for this interpretation. Since the isotopes differ only in ionic mass, the isotope splitting must originate from lattice dynamics. The work function therefore contains information regarding quantum-mechanical lattice behavior that is not captured by purely electronic models.

5.2.4 Illustration of the 3rd Law of Thermodynamics in $W(T)$

At low temperatures, the temperature dependence of the work function gradually weakens for both isotopes (see Figure 5.2 or Figure 5.3). This behavior is consistent with the thermodynamic considerations discussed in Sec. 3.2.4.

As $T \rightarrow 0$, the heat capacity and thermal expansion coefficient vanish in accordance with the Third Law of Thermodynamics. Since thermal expansion provides one of the principal contributions to the temperature dependence of the work function, the temperature derivative

correspondingly approaches zero,

$$\frac{dW}{dT} \rightarrow 0 \text{ as } T \rightarrow 0.$$

The observed flattening of the work function curves at low temperature therefore reflects the vanishing of thermal lattice excitations and provides a direct manifestation of fundamental thermodynamic behavior.

Chapter 6: Conclusions and Outlook

6.1 $W(T)$ as a probe of lattice dynamics

This dissertation set out to investigate whether electronic observables can be used to probe structural, thermodynamic, and quantum phenomena in finite systems. To address this question, high-precision temperature-dependent photoionization measurements were performed on free alkali-metal nanoparticles under well-controlled conditions. The results demonstrate that the work function is sensitive to thermal expansion, melting transitions, and isotope-dependent lattice dynamics, establishing a direct connection between electronic properties and the thermodynamic state of a nanoparticle. More broadly, this work shows that precise electronic measurements can provide access to thermodynamic information that is otherwise difficult to obtain in isolated finite systems.

Furthermore, the significance of these results extends beyond the observation of thermodynamic phenomena. The measurements enabled quantitative determination of nanoparticle melting temperatures and provided estimates of thermal-expansion behavior and solid–liquid interfacial energies. Such quantities are generally inaccessible for isolated nanoparticles, where conventional thermodynamic measurements are difficult or impossible. These results demonstrate that electronic observables can serve not only as qualitative indicators of thermodynamic behavior, but also as a source of quantitative thermodynamic information in

finite systems.

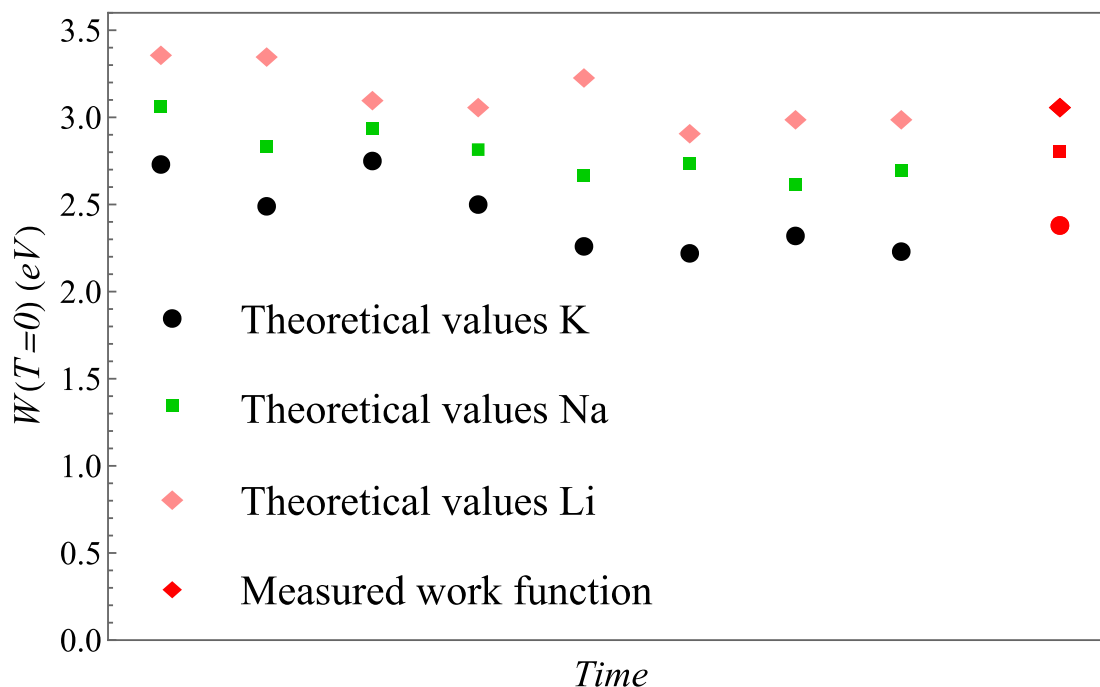


Figure 6.1 The work function values of Li, Na, K at $T = 0$ K compared to theories. Older to new theories from left to right respectively. The red dots are the measured work functions from this work.

Finally, the results presented here provide a valuable benchmark for theoretical descriptions of the work function and its temperature dependence. From something as fundamental as the third law of thermodynamics to as practical as the work function value. Figure 6.1 compares several recent theoretical predictions of the zero-temperature work function with the experimentally extrapolated values obtained in this work. The ability to resolve subtle effects associated with thermal expansion, melting, and isotope-dependent lattice dynamics places strong constraints on competing theoretical models and provides new insight into the quantum and thermodynamic mechanisms that govern electron-removal energies in metals.

6.2 Future work

Future work could extend these measurements to lower temperatures, smaller nanoparticles, and more complex materials. Particularly promising directions include studies of structural phase transitions in lithium at cryogenic temperatures [79], these phase changes are

isotope dependent.

Additionally, metals such as Gallium and Bismuth are particularly interesting. Since they expand upon solidification. This means, from the point of view of electron gas model, the work function would decrease when cooled down to lower than the melting point in contrast to the work discussed here. But one must always remember that the experimentally measured quantity is

$$\frac{dW}{dT} = \alpha_{\text{th}} r_s \frac{\partial W}{\partial r_s} + \left. \frac{\partial W}{\partial T} \right|_{r_s}.$$

Therefore, other effects could contribute that are not due to the thermal expansion but from latter terms which leads to an overall decrease in the work function.

6.3 Conclusion

More generally, the combination of temperature controlled photoionization spectroscopy and high-resolution threshold analysis provides a versatile experimental approach for exploring the coupling between electronic structure and lattice dynamics in finite systems.

The principal conclusion of this dissertation is therefore that the work function is not merely a measure of the energy required to remove an electron from a material. Rather, **from its temperature dependence, the work function is a sensitive electronic observable that encodes information about the thermodynamic and quantum state of the lattice.** As demonstrated here, precise measurements of the work function can reveal thermal expansion, melting transitions, isotope effects, and quantum lattice dynamics, establishing photoionization spectroscopy as a powerful tool for probing the fundamental behavior of nanoscale matter.

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Appendices

Appendix A: Optical calibration

A.1 Photodiode calibration

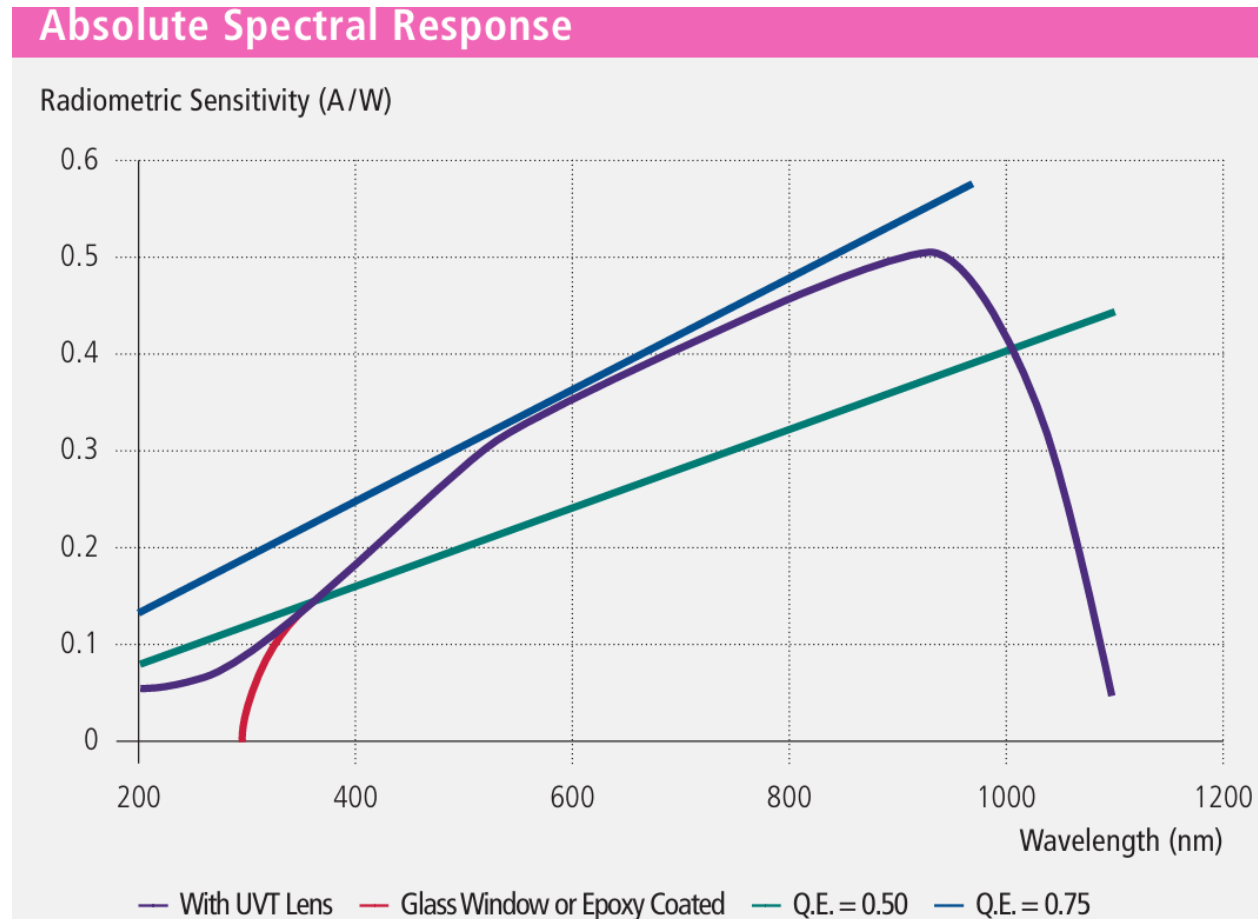


Figure A.1. The plot is taken from the data sheet in ref [80]. The red curve is the optical response of the VTB 1113 photodiode used in the experiment.

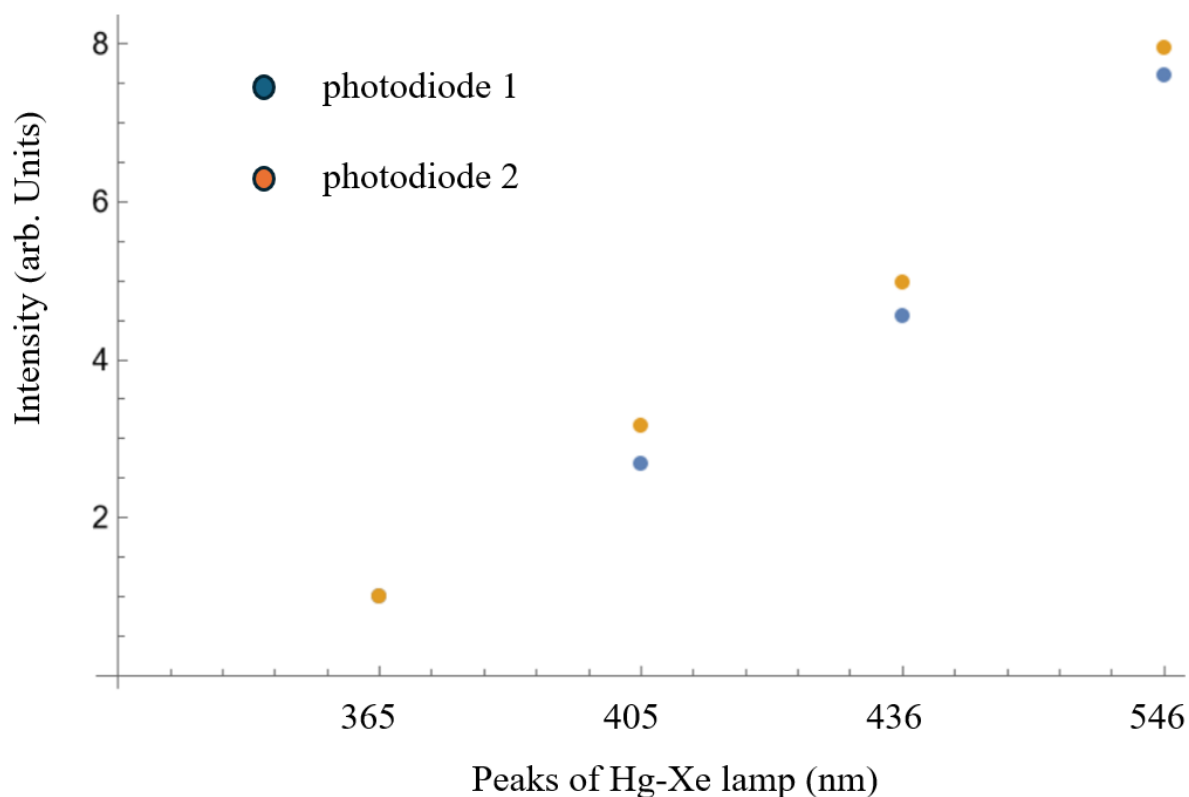


Figure A.2 calibration of photodiode using a Hg-Xe lamp peaks calibrated with another VTB 1113 photodiode.

A.2 Photocurrent calibration

Special care must be taken when performing photoionization measurements using the Hg–Xe arc lamp. In addition to the broadband continuum emission, the lamp contains several intense mercury spectral lines whose optical intensities are substantially larger than the surrounding background. When these lines are focused onto the photodiode used for photon-flux normalization, the resulting photocurrent can approach or exceed the linear response range of the detector and associated electronics.

Under these conditions, the measured photocurrent becomes smaller than the true photocurrent generated by the incident light. Consequently, the photon flux is underestimated during normalization of the photoionization yield. Since the measured yield is divided by the recorded photon flux, this underestimation produces artificial enhancements in the normalized

photoionization signal; they appear as peaks in both the photoionization yield curve and the corresponding Fowler plot, as illustrated in Figure A.4.

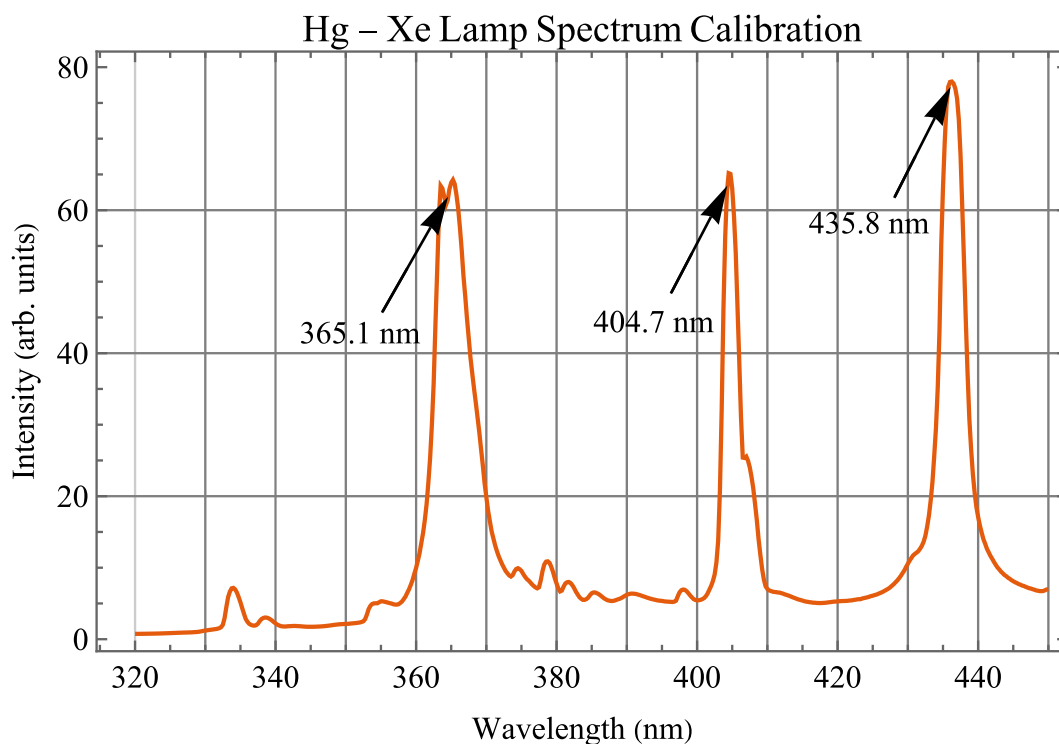


Figure A.3 Measured spectrum of the Hg-Xe lamp using the monochromator and photodiode.

The effect is purely instrumental and does not reflect any physical feature of the photoionization process. To remove this source of systematic error, measurements were preferentially performed using the Xe arc lamp, which produces a smoother spectral output. When the Hg-Xe lamp was used, photon energies corresponding to the strong mercury emission lines are skipped so to avoid artificial structure into the ionization threshold determination.

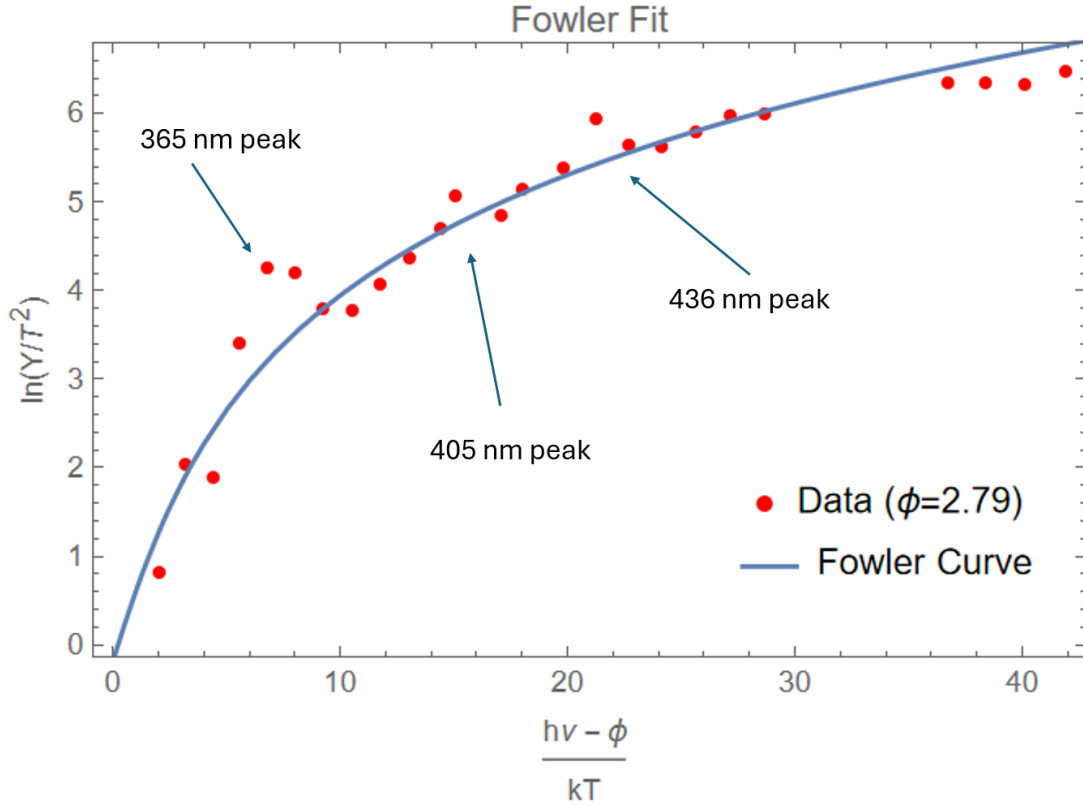


Figure A.4 systematic error from photodiode saturation resulting in artificial peaks in the spectrum.

Appendix B: Relation Between Thermal Expansion and Heat Capacity

The volume thermal expansion coefficient is defined as

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P.$$

Using the cyclic identity for thermodynamic derivatives,

$$\left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial T}{\partial P} \right)_V \left(\frac{\partial P}{\partial V} \right)_T = -1,$$

one obtains

$$\left(\frac{\partial V}{\partial T} \right)_P = - \frac{\left(\frac{\partial V}{\partial P} \right)_T}{\left(\frac{\partial T}{\partial P} \right)_V}.$$

Substituting into the definition of β gives

$$\beta = -\frac{1}{V} \frac{\left(\frac{\partial V}{\partial P}\right)_T}{\left(\frac{\partial T}{\partial P}\right)_V}.$$

Introducing the isothermal compressibility,

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T,$$

yields

$$\beta = \kappa_T \left(\frac{\partial P}{\partial T}\right)_V.$$

To relate this quantity to thermodynamic response functions, consider the Helmholtz free energy,

$$F = E - TS,$$

whose differential is

$$dF = -S dT - P dV.$$

From the equality of mixed second derivatives of F ,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V.$$

Therefore,

$$\beta = \kappa_T \left(\frac{\partial S}{\partial V}\right)_T.$$

Applying the cyclic identity again,

$$\left(\frac{\partial S}{\partial V}\right)_T = -\frac{\left(\frac{\partial S}{\partial T}\right)_V}{\left(\frac{\partial V}{\partial T}\right)_S},$$

gives

$$\beta = -\kappa_T \frac{\left(\frac{\partial S}{\partial T}\right)_V}{\left(\frac{\partial V}{\partial T}\right)_S}.$$

Using the definition of the constant-volume heat capacity,

$$C_V = T \left(\frac{\partial S}{\partial T}\right)_V,$$

one obtains

$$\beta = -\kappa_T \frac{C_V}{T \left(\frac{\partial V}{\partial T}\right)_S}.$$

Using the reciprocal derivative relation,

$$\left(\frac{\partial V}{\partial T}\right)_S = \left[\left(\frac{\partial T}{\partial V}\right)_S\right]^{-1},$$

this becomes

$$\beta = \kappa_T \frac{C_V}{T} \left(\frac{\partial T}{\partial V}\right)_S.$$

Now consider the differential form of the internal energy,

$$dE = T dS - P dV.$$

From the equality of mixed derivatives of $E(S, V)$,

$$-\left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S.$$

Substituting this relation gives

$$\beta = -\kappa_T \frac{C_V}{T} \left(\frac{\partial P}{\partial S}\right)_V.$$

Since at constant volume,

$$dE = T dS,$$

it follows that

$$\left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial P}{\partial E}\right)_V \left(\frac{\partial E}{\partial S}\right)_V = T \left(\frac{\partial P}{\partial E}\right)_V.$$

Therefore,

$$\beta = \kappa_T C_V \left(\frac{\partial P}{\partial E}\right)_V.$$

Introducing the Grüneisen parameter,

$$\gamma_G = V \left(\frac{\partial P}{\partial E}\right)_V,$$

one finally obtains

$$\boxed{\beta = \frac{C_V \gamma_G \kappa_T}{V}}$$

or equivalently,

$$\boxed{\beta = \frac{C_V \gamma_G}{K_T V}}$$

where

$$K_T = \frac{1}{\kappa_T}$$

is the isothermal bulk modulus.

This relation demonstrates that thermal expansion is directly connected to the heat capacity and the Grüneisen parameter, which characterizes lattice anharmonicity. Since $C_V \rightarrow 0$ as $T \rightarrow 0$ in accordance with the Third Law of Thermodynamics, it follows that

$$\beta \rightarrow 0 \text{ as } T \rightarrow 0.$$

Consequently, the temperature dependence of the lattice spacing and electron density also vanishes in the low-temperature limit, providing a thermodynamic basis for the experimentally observed flattening of the work function at low temperature.

Appendix C: Photoionization automation code; LabVIEW and Arduino

C.1 Arduino-Based Motion Control of the Optical Components

The monochromator wavelength stage, the LED alignment stage, the photodiode translation stage, and the entrance slit stage were controlled by an Arduino Uno board running a custom serial program. The program communicates with the LabVIEW acquisition software through a standard serial connection at 9600 baud. Each motion command consists of four numerical values sent in a single line, separated by spaces, in the following order:

monochromator LED stage photodiode slits.

The values transmitted from LabVIEW were interpreted as physical coordinates and converted internally into motor steps using calibration constants defined in the Arduino code. The monochromator position was converted using a wavelength-to-step calibration factor determined experimentally. Although the software retained provisions for automated slit control, this functionality was not used during the measurements reported here. The photodiode was mounted on a rigid stainless-steel translation arm whose position was determined directly by the stepper motor, allowing reproducible placement of the detector at the optical focus for photon-flux calibration. The LED stage was used primarily for beam-intensity normalization and possessed an optical acceptance angle of approximately 90° . Consequently, the measured LED signal was insensitive to small angular positioning errors, and sub-degree motor precision was not required for reliable operation.

To execute a move, the user sends a command of the form

mono led photodiode slits

for example:

365.0 60.0 20.0 0.0

where the numbers correspond to the desired monochromator setting, LED angle, slit position, and photodiode position, respectively. After receiving the command, the Arduino converts the inputs to step counts, updates the target positions of all four stepper motors, and moves them simultaneously until all axes reach their final positions. The Arduino then returns the message completed to indicate that the motion sequence has finished.

A special calibration command is implemented to redefine the current motor positions without physical motion. If the string

1.00 1.00 1.00 1.00

is sent, the program enters calibration mode and responds with calibrate followed by calibrated. The next four numbers sent after this command are interpreted as the current physical positions of the four stages, and the Arduino resets its internal step counters accordingly. This feature is useful after manual alignment or after powering the system on, when the absolute position of the stages must be re-established.

The control logic was designed so that a new command should be sent only after the previous move has completed and the “completed” response has been received. This prevents command overlap and ensures that the motion sequence remains synchronized with the data-acquisition software. In practice, the serial protocol provides a simple and robust interface for automated wavelength scans, photodiode positioning, and beam-alignment routines.

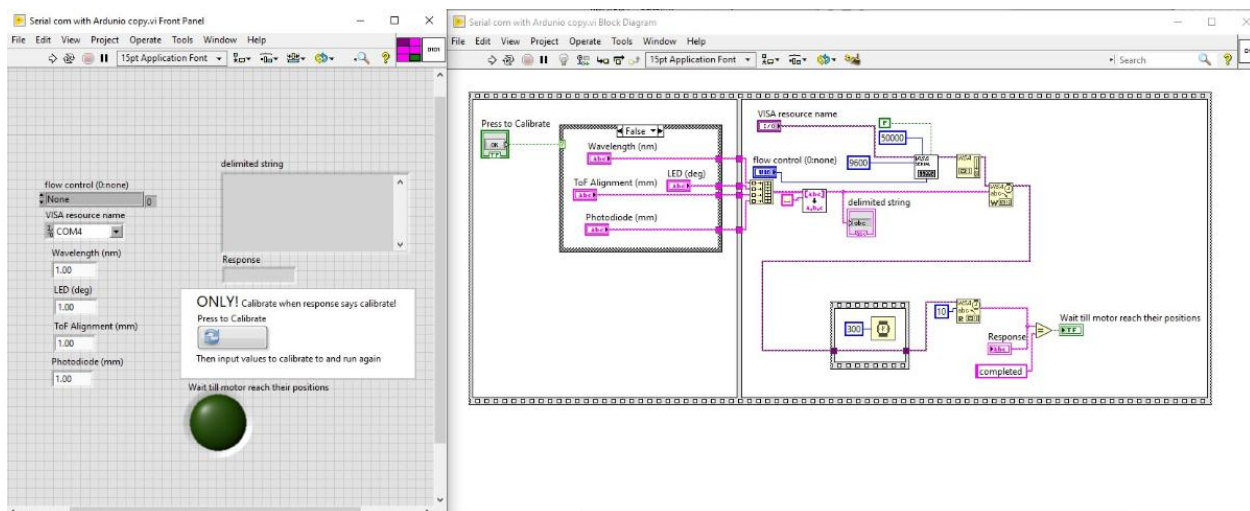


Figure C.1. Serial communication LabVIEW interface. Left is the front panel and right is the block diagram.

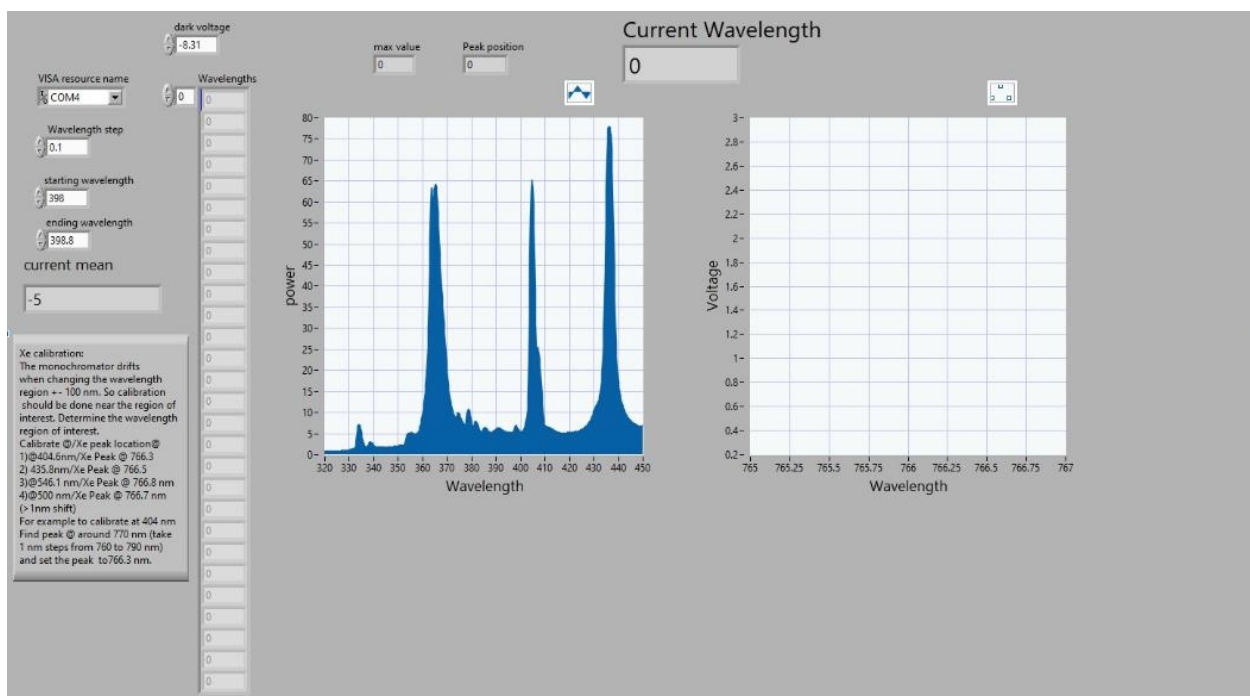


Figure C.2. Wavelength calibration front panel.

C.2 The Automation LabVIEW code:

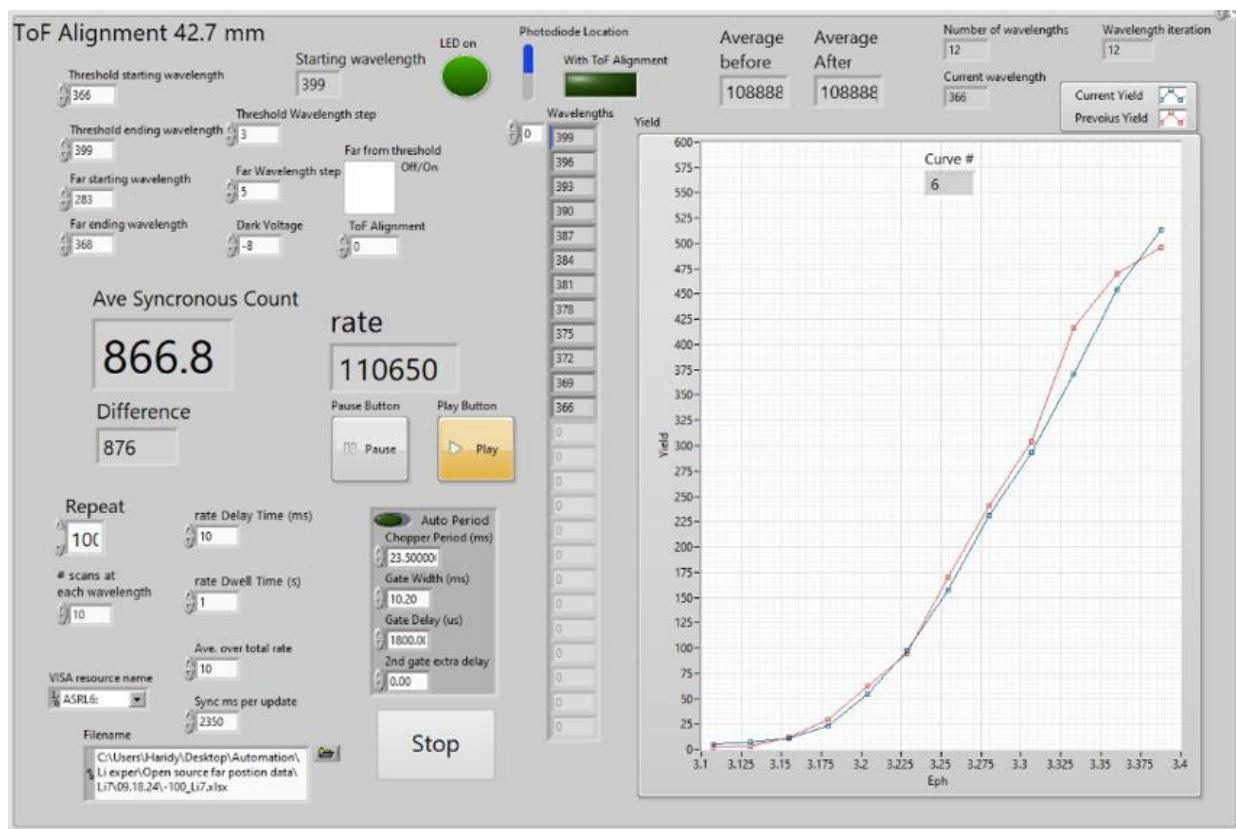


Figure C.3. Front panel of Automation (fast) code.

The “automation fast” code utilizes a sequence structure where the different components of the photoionization experiment are done one after another. Notice that each sequence is made of different sequences; this is to ensure that all motors have arrived at the proper locations before starting a measurement and simplifies the code. After the last pulse from the Arduino is sent to the motors, there is a slight delay (300 ms) then it sends completed to LabVIEW. After which the sequence is complete and moves on to the next sequence which are measurement subVIs. This allowed us to troubleshoot each subVI separately before combining the whole code. This also makes the code robust; in principal changes can be made to the subVIs (for example using a different synchronization scheme) without having to change the logic of the code. Below you will find screenshots of the block diagram for each step.

1. Measuring photon flux for all wavelengths.

Here, the analog voltage from the lock-in amplifier is measured. The lock-in amplifier is triggered to the frequency of the optical chopper (42 Hz), voltage that the lock-in outputs is proportional to the photocurrent of the photodiode. The photodiode response curve is fitted to an eleventh order polynomial. Hence, the measured photocurrent divided by the response gives a number proportional to the number of photons.

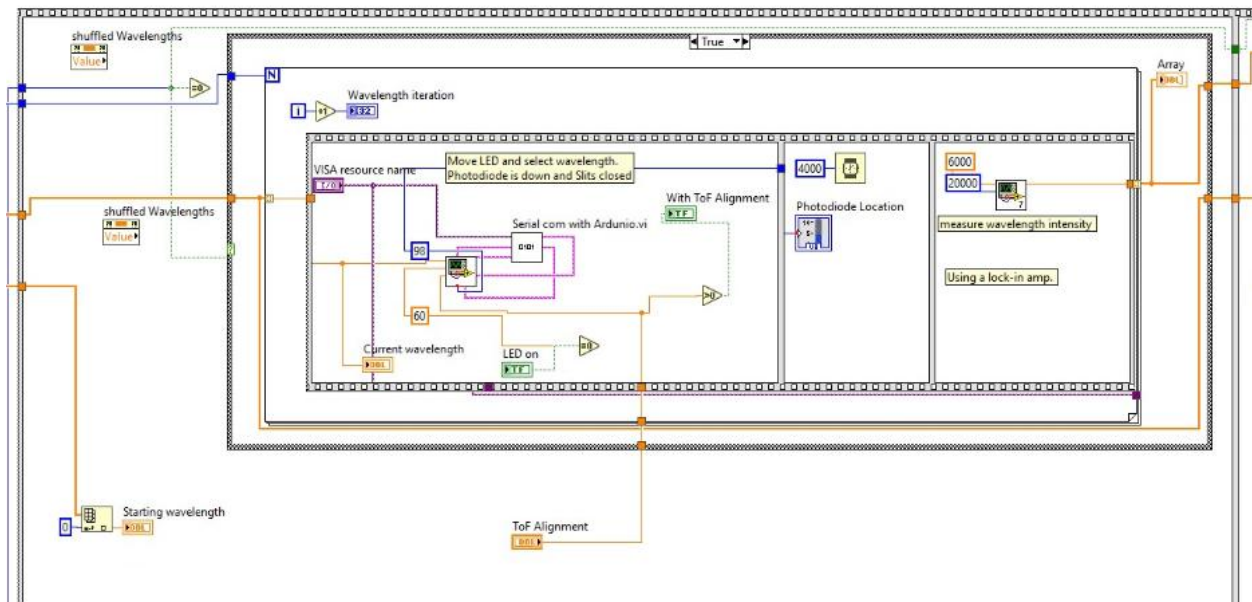


Figure C.4. First sequence of the automation, block diagram of measuring the wavelength intensities.

2. Move motors and measure background signal using the LED.

This is to normalize the yield curve by the total counts.

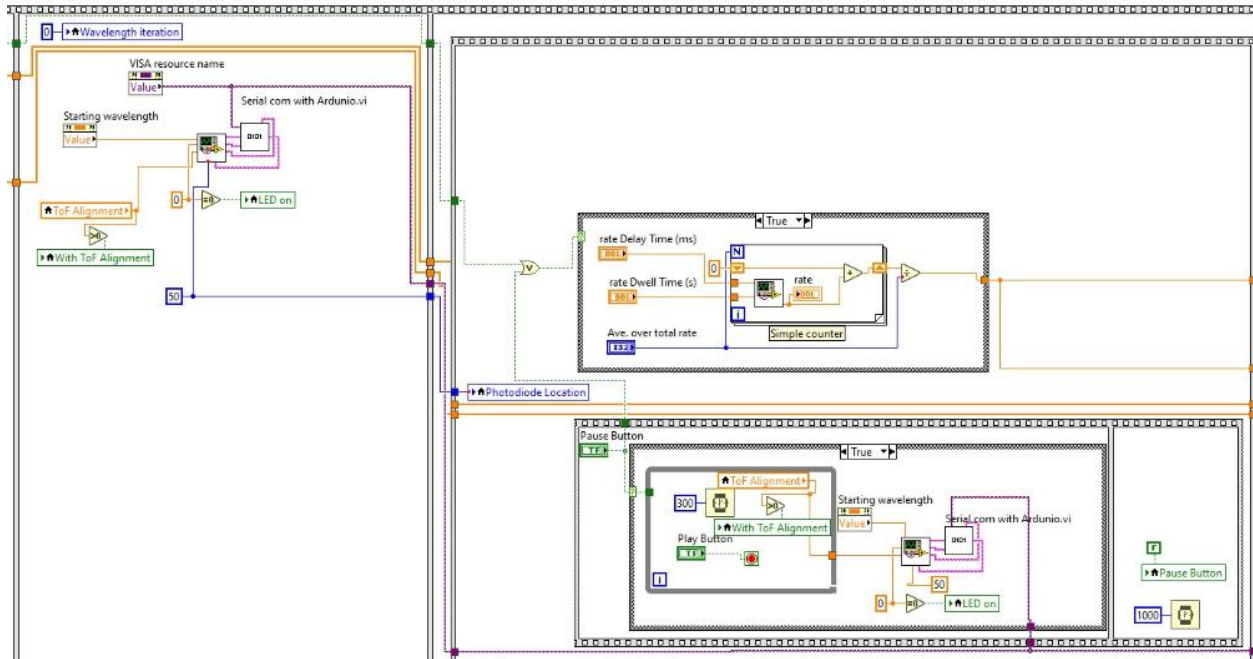


Figure C.5. Second sequence of the automation, block diagram for measuring the cluster beam background intensity. For stable curves, we found a value of around 100 Kcps (counts per second) to produce good yield curves.

3. Then move motors and measure synchronized counts.

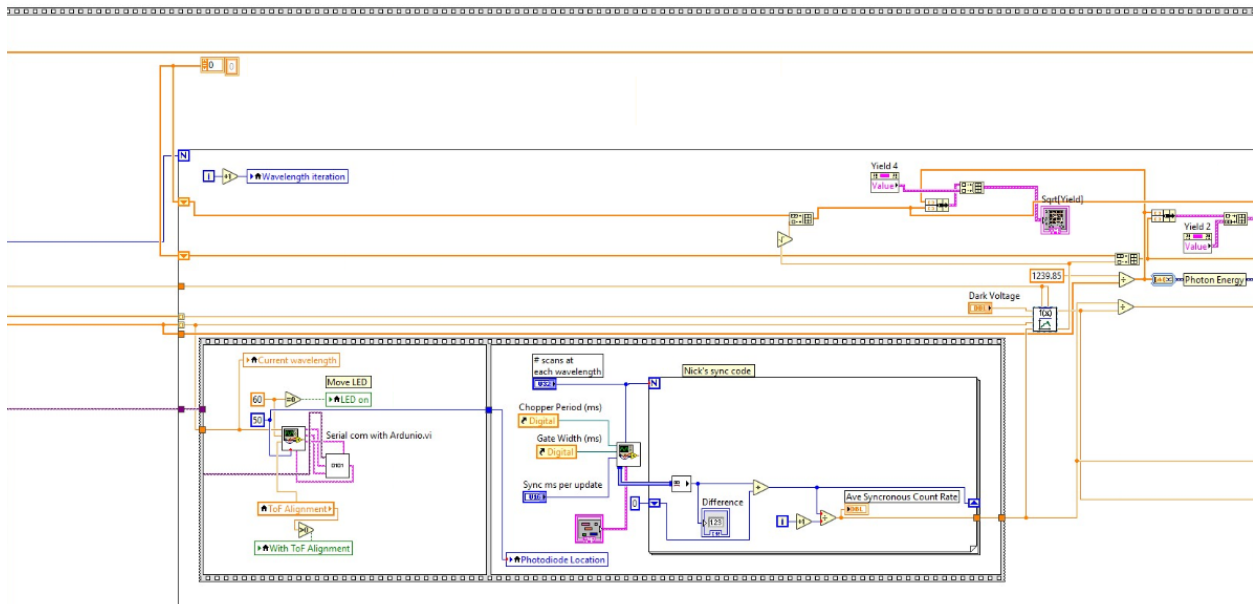


Figure C.6. Block diagram of the synchronization code.

The synchronized counts code uses Dr. Nicholas Guggemos code explained in detail in his thesis [81]. His code is initially used to determine the gate width and delay. Then a subVI of it is

used in the automation code that extracts the synchronized counts.

4. Finally, move motors and measure background signal again.

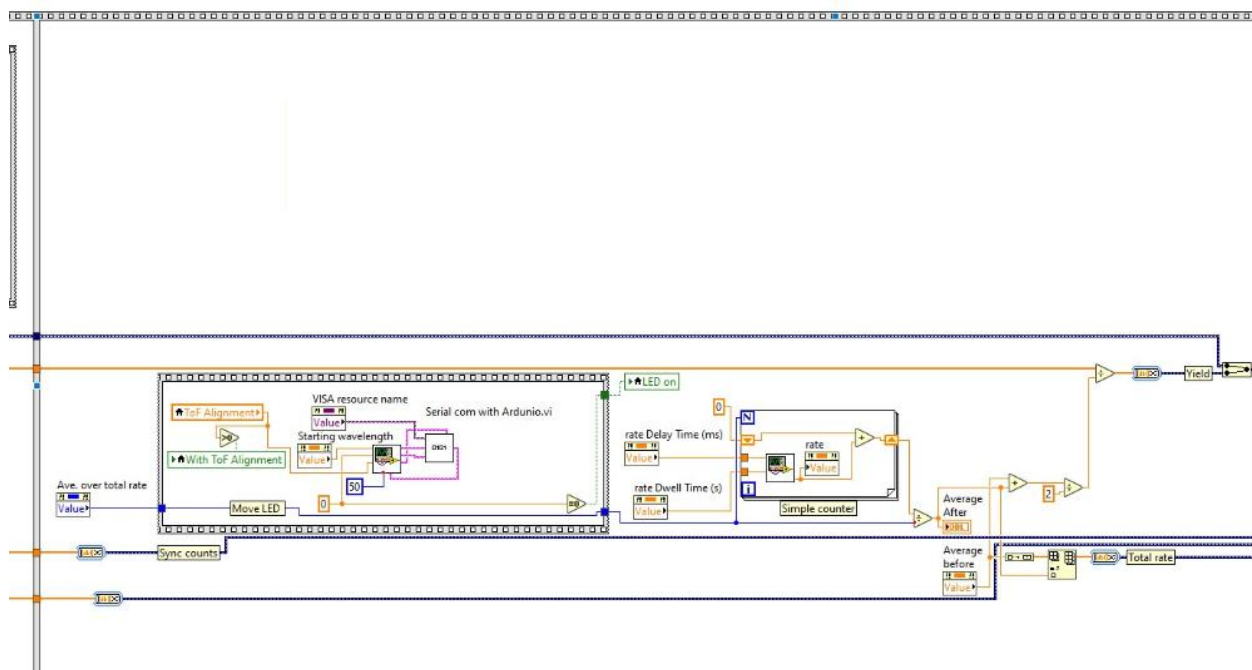


Figure C.7. Final sequence which is a repeat of step 3.

The code outputs all the data collected (photon current, relative power, total count, synchronized counts, wavelengths, and photon energy). This is important for troubleshooting systematic errors such as the one in Figure A.4. Additionally, this code could be easily modified to include size selected measurements by adding a subVI of output voltages for the Extrel QC150 quadrupole power supply.

In summary, the sequence of this code is as follows. After calibration of the monochromator, the automation fast code sends a serial command to move the photodiode to 99 mm of the linear feedthrough to measure the photon flux of the UV lamp. After the photon flux measurement, another serial command is sent to move the photodiode out of the way. The code was paused by pressing the pause button in the Front panel. TOF measurement was done use the MCS32 in a different windows 7 computer. After the MCS profile is a acquired (usually takes 5

mins), the play button is pressed to continue the code. A 3D printed mount holding a stepper motor to the top flange where an L bracket is connected to the shaft of the motor. The other end of the bracket is connected to a tube where the LED is clamped. For stability of the LED, a heatsink was mounted to the LED (the LED was kept at a constant current of 0.33 A). The total counts of the signal took 10 seconds.

Then it is the yield curve collection. Serial commands are sent to move the motor to the proper wavelength. The counts were acquired for 10 seconds at every wavelength. After collecting the yield curve, the total rate is measured again to measure the signal did not change by more than 10%. Then another TOF scan was taken after the data of the fast automation code is automatically saved.

Appendix D: Mathematica codes

All mathematica notebooks can be accessed on GitHub.

<https://github.com/sheekhooatef15/Near-threshold-photoionization-experiment-analysis>

D.1 Time-of-flight and work function code:

The time-of-flight (TOF) spectra were converted into cluster-size distributions using the extraction voltages and instrument geometry. The electric fields in the source and drift regions were calculated as

$$E_s = \frac{U_f - U_m}{s},$$

$$E_d = \frac{U_m}{d},$$

where U_f and U_m are the front and middle extraction voltages, respectively, while s and d denote the corresponding electrode separations.

The dimensionless acceleration parameter is given by

$$k_0 = \frac{s_0 E_s + d E_d}{s_0 E_s},$$

and the total acceleration energy is

$$U_t = e(s_0 E_s + d E_d),$$

where e is the elementary charge.

The cluster size corresponding to a measured flight time t was then determined from

$$N(t) = 2 \left[\frac{t \times 10^{-3}}{1.02 \left(2\sqrt{k_0} s_0 + \frac{2\sqrt{k_0}}{\sqrt{k_0} + 1} d + D_0 \right)} \right]^2 \frac{U_t}{m},$$

where m is the mass of a single atom and D_0 is the flight distance.

Because the transformation from flight-time space to cluster-size space is nonlinear, the measured intensity was corrected using the Jacobian transformation,

$$I(N) = \frac{I(t)}{\frac{dN}{dt}},$$

where $I(t)$ is the measured time-of-flight intensity.

The resulting cluster-size distribution was fitted with a log-normal function,

$$f(N) = \frac{c}{N\sigma\sqrt{2\pi}} \exp \left[-\frac{(\ln N - \mu)^2}{2\sigma^2} \right],$$

where c is a scaling factor and μ and σ are fitting parameters obtained by nonlinear least-squares fitting.

The most probable cluster size corresponds to the maximum of the fitted distribution and is given by

$$N_{\text{peak}} = \exp(\mu - \sigma^2).$$

The width of the cluster-size distribution was characterized by the full width at half

maximum (FWHM). The half-maximum points N_1 and N_2 were obtained from

$$f(N) = \frac{1}{2} f(N_{\text{peak}}),$$

and the FWHM was calculated as

$$\text{FWHM} = |N_2 - N_1|.$$

To account for finite-size effects, the size-dependent work-function correction was calculated using

$$\Delta W(N) = \frac{27.21}{r_s N^{1/3}},$$

where r_s is the Wigner-Seitz radius.

The average correction associated with the fitted cluster-size distribution was obtained from

$$\langle \Delta W \rangle_{\text{fit}} = \frac{\sum_i \Delta W(N_i) f(N_i)}{\sum_i f(N_i)},$$

where $f(N_i)$ is the fitted log-normal distribution evaluated at the cluster sizes present in the experimental dataset.

A second estimate of the average work-function correction was calculated directly from the measured cluster-size distribution. After Gaussian smoothing of the experimental intensities, the correction was determined from

$$\langle \Delta W \rangle_{\text{exp}} = \frac{\sum_i \Delta W(N_i) I_s(N_i)}{\sum_i I_s(N_i)},$$

where $I_s(N_i)$ denotes the smoothed experimental cluster-size distribution.

The analysis yields the fitted log-normal parameters μ , σ , and c , the most probable cluster size N_{peak} , the FWHM of the distribution, and both fitted and experimentally weighted work-function corrections.

D.2 Ionization energy fit and Fowler plot algorithm:

Determination of the fitting range

One of the most important parts of the code is `BestPosition[]` and `BestLastPosition[]`.

These routines automatically determine:

- the threshold region where Fowler theory is valid,
- the optimal lower fitting limit,
- the optimal upper fitting limit.

The algorithm repeatedly performs nonlinear Fowler fits while progressively removing data points. The fitting region that maximizes the goodness of fit while maintaining physically meaningful parameters is selected. This reduces user bias in choosing the fitting interval.

Extraction of ionization potentials

The function `YieldIPFit[]` analyzes multiple yield curves measured at the same temperature.

The procedure is:

- group repeated measurements,
- average the yield curves,
- randomly resample the data,
- perform many nonlinear Fowler fits,
- average the fitted parameters.

This Monte-Carlo style approach improves robustness against noise and provides stable estimates of: $IP(T)$ and B where IP is the ionization energy and B is the Fowler fitting constant.

Appendix E: Cluster beam velocity measurement

To characterize the nanoparticle beam velocity, a mechanical chopper was installed in the electron-gun chamber 1.45 m upstream of the detector. The rotating chopper periodically interrupted the nanoparticle beam, producing a sequence of discrete nanoparticle packets, as illustrated in Figure 17(a). The arrival times of these packets were recorded using a multichannel scaler (MCS). Because the MCS trigger was synchronized to a particular chopper position, the

arrival time of the reference packet depended only on the flight time of the nanoparticles between the chopper and the detection region, as shown schematically in Figure E.1(a). The nanoparticle velocity can therefore be estimated directly from the measured time delay according to $v = L/t$, where L is the distance between the chopper and the detection region and t is the measured flight time. Typical measured velocities are shown in Table E-1.

Table E-1 velocity of Li cluster beam at 245 sccm He flow, oven temperature 480 to 500 C, at varies thermalization tube temperature.

Temperature (K)	v (m/s)
173	175
273	190
373	196

For water cooled condensation source and smaller clusters (~ 1000 Li atoms) the cluster speed was measured to be higher than the typical cluster sizes used for the experiments in Chapter 4 and 5. For a typical flight distance of approximately 1.5 m and a measured arrival time of approximately 3 ms (as shown in Figure E.1 (b)), the nanoparticle velocity was found to be

$$v \approx \frac{1.5 \text{ m}}{3 \times 10^{-3} \text{ s}} \approx 500 \text{ m/s.}$$

To eliminate possible systematic errors arising from misalignment between the optical encoder and the chopper blades, measurements were performed with the chopper rotating in both clockwise and counterclockwise directions.

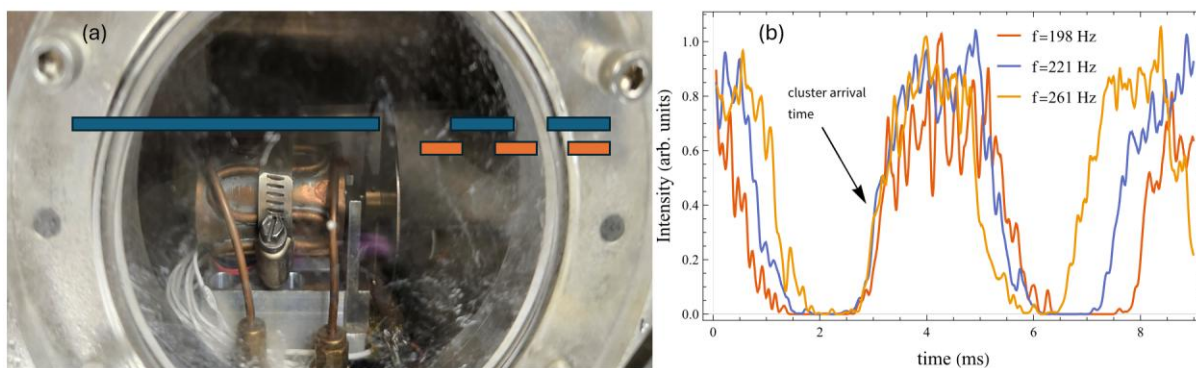


Figure E.1. (a) Mechanical chopper wheel used for nanoparticle beam velocity measurements. The blue line is a schematic of the cluster beam (~ 3 mm diameter), the beam is going from left to right and as it passes the chopper, the beam becomes segmented. Two different frequencies are shown for the chopped beam (b) MCS spectra obtained at different chopper rotation frequencies. While the positions of the periodically generated beam packets vary with chopper frequency, the arrival time of the reference packet remains unchanged. The corresponding flight time (cluster arrival time) provides a direct measurement of the nanoparticle beam velocity.

Appendix F: Effects of contamination on the yield curve

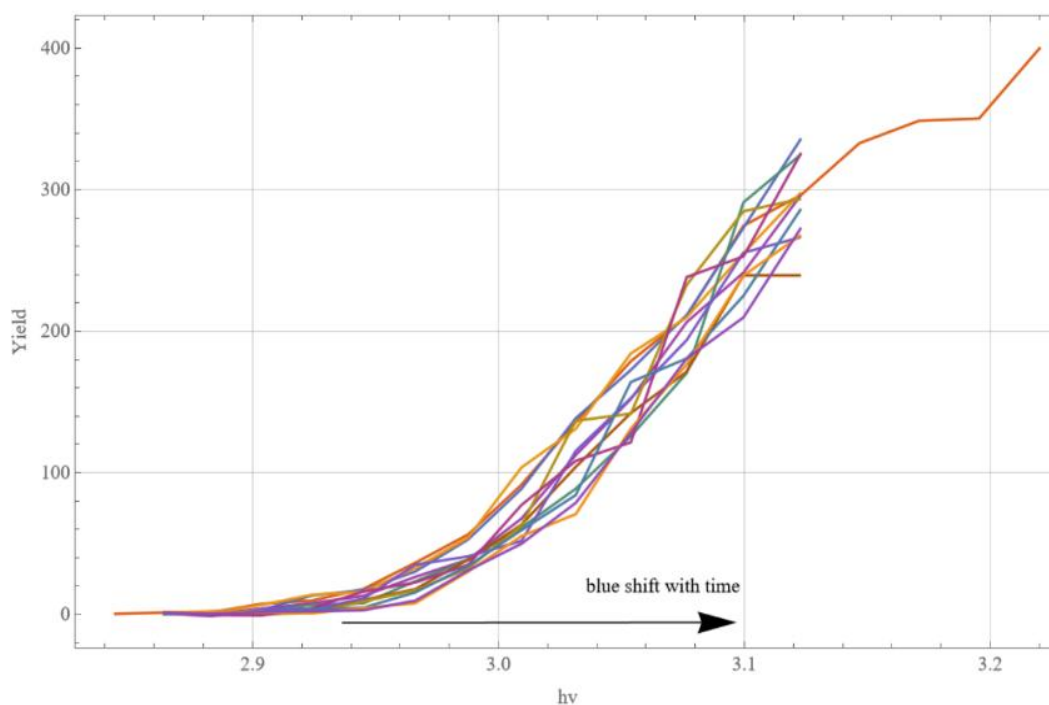


Figure F.1 Yield curve of contaminated Na clusters. The duration of the experiment was 2 hours. Each curve is about 15 minutes apart. The yield curve and hence the ionization energies of the nanoparticles are increasing as the increase. Once a sample was contaminated from a leak in the source chamber it took hours to stabilize again. Similar effect was observed for Li. We observed no significant change in the nanoparticle size distribution.

The impact of oxidation on the work function varies significantly across metal classes.

While oxidation typically raises the work function of transition metals, alkali metals exhibit the opposite behavior, showing a distinct decrease in work function upon oxidation (see Figure F.1).

This divergence likely stems from differences in atomic packing density and surface structure. In alkali metals, the open lattice allows oxygen atoms to penetrate beneath the top atomic layer [82] rather than remaining adsorbed on the outer surface. This subsurface incorporation produces an electric dipole layer that reduces the potential barrier making it easier for electrons to escape into vacuum.

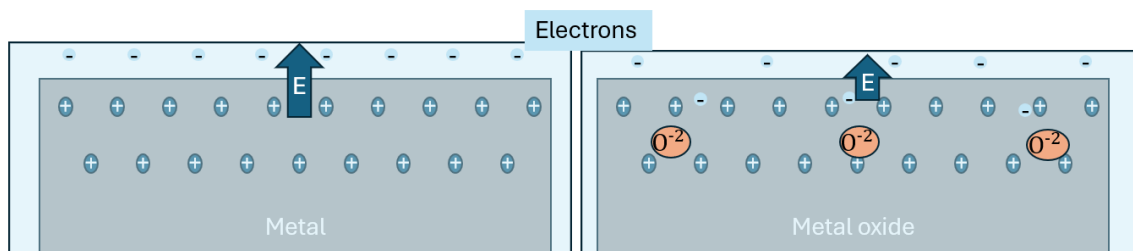


Figure F.2. Schematic of clean alkali metal (left) and alkali metal oxide (right). For the left, the spill out electrons and the ion core creates an electric field that pulls electrons down. On the right the electrons are pulled to the oxygen which creates a weaker or could even flip the direction of the electric field, so electrons are easier to remove.

Appendix G: Heater and Heat shield assembly

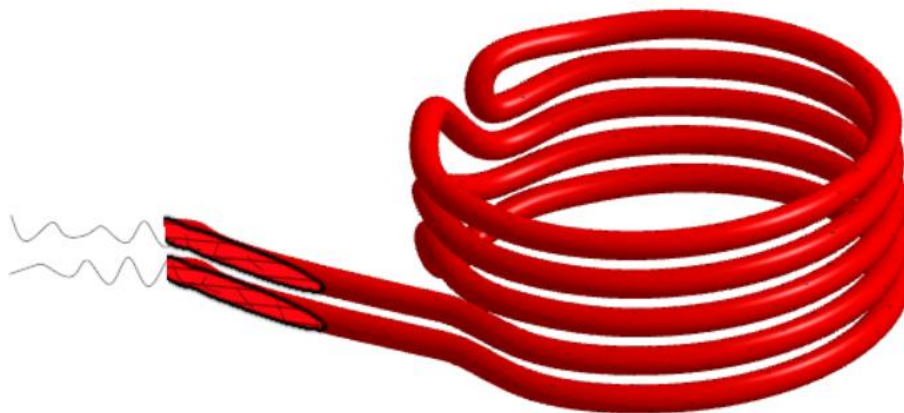


Figure G.1. Heater wound around a ceramic crucible. The bifilar coil configuration allows both leads to exit at the same location while providing a non-inductive winding path through axial magnetic field cancellation. To concentrate power density at the crucible, the lead wires are straightened and doubled back on themselves to minimize electrical resistance and prevent lead heating.

The heat shield is built around a commercially available high-purity ceramic Alumina from McMaster-Carr (part 7545N26, 1" Diameter; 3/4" Height). The heating element is constructed using either 28-gauge or 30-gauge Kanthal wire coiled around a 20-gauge mandrel and threaded through a 1/8" diameter ceramic sleeve (the resistance of the kanthal should be ~30-45 Ω). This coiled element is wound (wounding pattern in Figure G.1) around the alumina core and secured in place by wrapping a single turn of 0.005" thick copper foil around it. Once assembled, the heater is baked out for one hour at 50 watts using the Kanthal element itself. This thermal treatment forms a thin passivating alumina oxide layer on the Kanthal wire to provide additional electrical protection while simultaneously annealing the copper foil, making it sufficiently malleable to conform tightly around the heater and ceramic core for optimal heat transfer.

With the copper wrapper installed, the complete heater assembly measures approximately 1.5 inches in diameter, establishing the inner diameter needed for the surrounding multi-layer heat shield system. The heat shield layers are fabricated from 0.005" thick stainless-steel (SS) sheets separated by 4 mm SS threaded inserts acting as standoff spacers. To accommodate the increasing circumference of each concentric layer, three mounting holes are drilled into each flat sheet using a 3/32" drill bit, spaced 4.00 cm apart for the first sheet, 4.84 cm for the second, and 5.68 cm for the third, though these holes can also be cut into slots for easier assembly alignment. Each sheet is then rolled into a cylinder and spot-welded while keeping the hole spacing constant or folded over itself to drill an overlapping alignment hole. The base of the heat shield consists of two parallel SS plates cut with integrated tabs that spot-weld directly to the walls, spaced apart using two 4 mm threaded inserts.

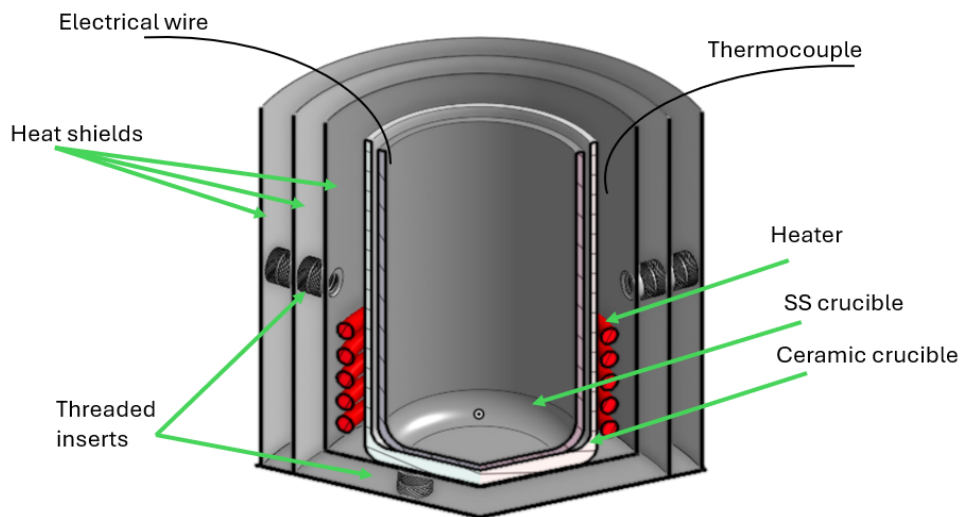


Figure G.2. CAD cross section view of the complete heat shield source assembly.

An intermediate ceramic crucible serves as an insulating barrier between the inner SS crucible and the heater core, allowing high voltages to be applied during electric discharge experiments without shorting to or damaging the heating element. Precaution must be taken during operation to ensure the SS crucible is always either explicitly grounded or tied to a defined voltage supply. Leaving the crucible floating leads to static charge accumulation over time, causing erratic micro-discharges and severe signal instability. Prior to experimental loading, the entire assembly undergoes a vacuum bakeout until the source pressure drops below 30 mtorr. Following sample loading, the system is run overnight at approximately 200 °C, or slightly above the melting point of the target metal.

A notable limitation of this heat shield design is its thermal lag. Upon adjusting the heater power, the temperature requires approximately three minutes to reach equilibrium. Consequently, monitoring and familiarizing oneself with this thermal response during initial bakeout is recommended. Under typical operating conditions, the ceramic reaches approximately 400 °C at a power input of 40 to 50 W. For operational power levels exceeding 100 W, 28-gauge or 24-gauge kanthal wire should be used to safely handle the higher current demands. Note that

the resistance of kanthal wire is nearly constant across a wide temperature range.

When working with alkali metals such as sodium (Na), the cleaning and sample-loading procedure is straightforward. First, ensure the SS crucible is clean by scrubbing it with a wire brush mounted on a drill or rotary tool. Next, sonicate the entire assembly for 10 minutes in a 50/50 mixture of distilled water and isopropanol, air-dry it for 30 minutes, and perform a vacuum bakeout at 500 °C. While the system bakes, prepare a clean workspace. Once the source chamber pressure drops to 30 mtorr, turn off the heater and allow the assembly to cool down. Active liquid nitrogen or water cooling for the source chamber jacket is unnecessary during this phase, as thermal isolation between the oven and heat-sensitive components (such as vacuum gaskets) is highly effective.

After cooling for approximately two hours, vent the system and extract the source assembly. Fill an SS bowl halfway with mineral oil and completely submerge the Na metal. Keeping the metal fully immersed to prevent oxidation, scrape off the weathered outer oxide layer on all sides using a thin SS spatula. The cleaned Na chunk should be sized to fill roughly half of the SS crucible. Once cleaned, transfer the Na into a hexane bath to wash off the residual mineral oil. The Na must remain completely submerged in the hexane; while oxidation occurs much slower in hexane than in air, the metal will still accumulate a visible oxide layer if left submerged for longer than one minute.

Because the system was pre-baked, verify that the heaters and thermocouples are fully operational before handling the metal. Transport the beaker containing the submerged Na to the source, place the Na directly into the SS crucible, and align the source with the vacuum chamber. Insert two screws through the flange mounting holes for alignment and turn on the roughing pump before tightening the flange hardware; the vacuum draw provides sufficient initial sealing

force to hold the flange in place. Once under vacuum, double-check that the heaters and thermocouples are still functioning properly. If all diagnostics are normal, fully tighten the flange hardware and engage the backing and diffusion pumps.

Speed is critical during this transfer: the entire sequence—from removing the Na from the mineral oil to sealing the chamber under roughing vacuum—should take under 10 seconds to prevent oxidation. If a hardware or electrical fault is detected after transferring the Na, immediately remove the metal from the SS crucible and submerge it back into the mineral oil bath. Once the issue is resolved, repeat the hexane rinse and loading sequence.

Following an experiment, a very thin film of Na metal typically covers a large surface area of the source. First pull out the SS crucible and plug it with a rubber plug. The thin film on the assembly can be safely cleaned by immersing it directly into water. If there are large or thick Na chunks on the shield, carefully remove them first before placing the heat shield assembly in water. Place the chunks into the SS crucible, and seal it with a rubber plug before cleaning the remaining thin film in water. If the SS crucible itself contains significant residual metal, scrape it out under mineral oil first; once most of the bulk metal is removed, the SS crucible can be submerged in water. Small residual Na chunks can be safely neutralized by wrapping them in approximately three paper towels, clamping them shut with vice grips, and submerging them in water to control the reaction. For the interior of the source chamber, leaving the chamber open to the atmosphere overnight will react away most of the Na via ambient air moisture. Any remaining thin layer can then be safely cleaned with water.

The cleaning and loading procedure is essentially identical for Li and K, with a few critical material-specific modifications. Because Li has an exceptionally low density and floats in most organic solvents, it must be held submerged using tweezers during the scraping and rinsing

steps to prevent exposure to air. Unlike Na and K, the inside of the source after a Li experiment can be cleaned immediately with water. K requires extreme caution due to its significantly higher chemical reactivity, as it can spontaneously ignite in air under sufficiently humid ambient conditions. Consequently, water must never be used for cleaning or quenching residual K; isopropanol must be used exclusively as a safer neutralizing agent for all K-contaminated components. Generally, leaving the source slightly open and vented overnight allows ambient moisture to gently react away most of the metal residual before adding it in water to react the remaining small amount of K. It is ok to clean with water only after the K looks foamy (no traces of metal chunks) and was washed with isopropanol.

Crucially, never vent the system while the source jacket is still cold from LN cooling. Wait at least two to three hours after LN flow has ceased before venting. If vented prematurely, atmospheric water vapor will condense inside the cold source chamber, causing a vigorous reaction with the residual metal when the assembly is removed.

A new similar heat shield design is optimized to be 3D printed. This would be almost fully assembled and requires very little labor. The design has not yet been tested or manufactured.

Appendix H: Metal 3D printed heat shield design

The designs were made in Onshape for easy accessibility: [Source assembly](#).

The accessibility and precision of metal additive manufacturing—specifically direct metal laser sintering (DMLS) of stainless steel (e.g., 316L SS)—motivate a fully integrated 3D-printed heat shield architecture. This approach allows complex thermal shielding models to be iteratively designed, simulated, and fabricated with high dimensional fidelity. Figure H.1 and Figure H.2 demonstrate intricate geometries featuring internal channels and patterned lattice

structures that are impractical or impossible to fabricate via conventional machining. Beyond reducing overall weight and footprint, the 3D-printed channels and thin-walled struts significantly restrict conductive heat transfer by minimizing solid cross-sectional contact areas between concentric shield layers. Furthermore, printing the assembly as a single monolithic component eliminates the physical interfaces, threaded fasteners, and spot-welds required in multi-piece fabrications, thereby simplifying assembly and enhancing structural rigidity.

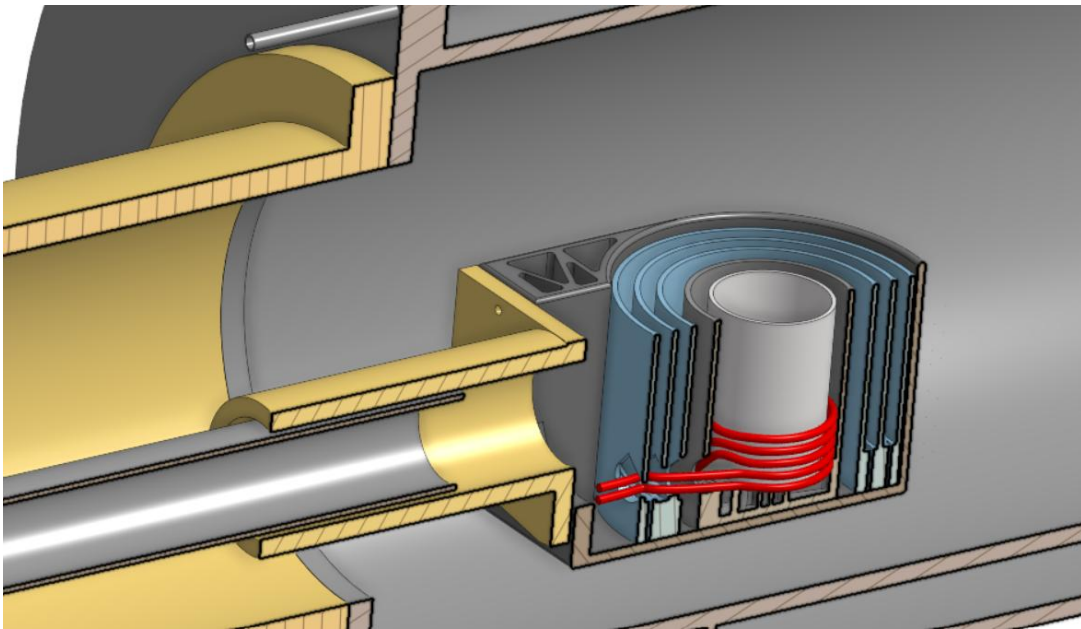


Figure H.1. Cross-sectional view of a 3D-printable heat shield assembly attached to existing hardware. The red coil represents the heater (heating wire and ceramic fiber) wound around a white alumina ceramic core. The heater passes through teardrop-shaped holes optimized for 3D-printing compatibility. The primary layer (grey) connects to subsequent layers (blue) via long, thin studs, each featuring offset teardrop geometries to eliminate direct line-of-sight thermal radiation paths. The heat shield slide into a 3D printed holder and is mounted to the brass coupler (existing part) which connects the shaft to the assembly.

Figure H.3 is the thermal simulation results using Fusion 360, the results are promising indicating that the 3D-printed design provides an ideal configuration. The colder the outer wall can be maintained, the colder the thermalization tube becomes due to a reduced overall heat load. When using the water-cooled box without heat shielding (see Figure 2.1), the outlet water temperature reaches as high as 80 °C, while the minimum temperature remains at the 16 °C inlet

temperature. Therefore, implementing heat shields is the optimal approach; they lower the overall thermal radiation from the oven assembly, thereby reducing the temperature of both the source chamber and the thermalization tube.

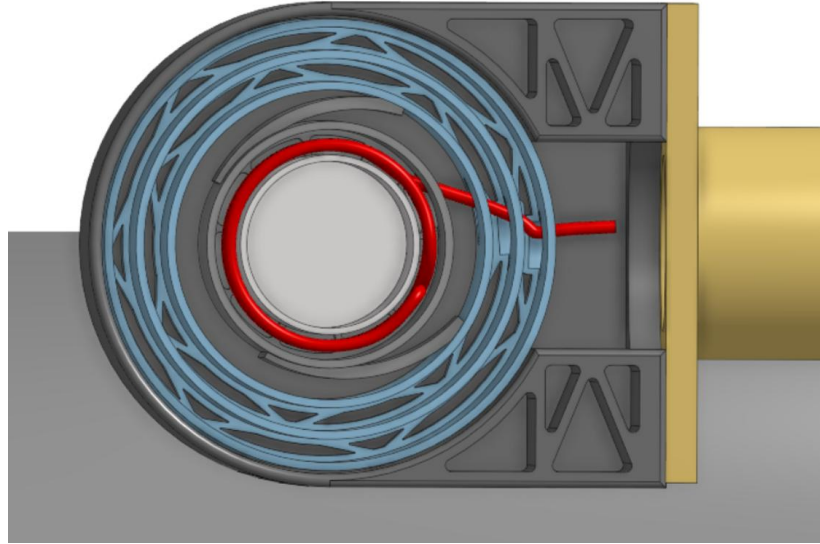


Figure H.2. Top view of the heat shield. The channels are made for both reducing heat transfer and weight.

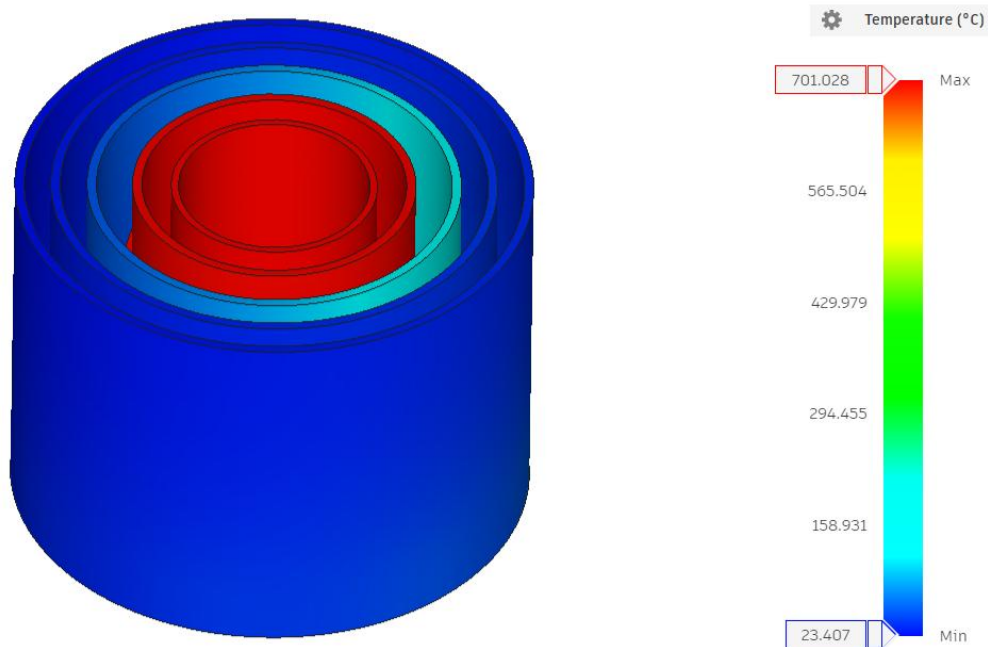


Figure H.3. Results of thermal simulations using Fusion 360. The thermal simulation parameters were defined as follows: An applied temperature of 700 °C was set on the wall of the ceramic crucible and the first layer of the heat shield. All surfaces were set to radiate with an emissivity of 0.3. The ambient temperature was defined as -150 °C, and the convection coefficient across all surfaces was set to 0.01 W/(m²·°C)