Melting, Solidification and Sintering/Coalescence of Nanoparticles

DISSERTATION

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Abstract

The research goal of this work is to develop an understanding of the mechanism of nanoparticle melting, solidification and sintering resulting from a laser-triggered nanoscale spark-plasma heat source. The study is motivated by the fact that physical properties of nanoparticles exhibit a strong size effect due to significant increase of surface area to volume ratio thus affects nanoparticle consolidation and related material processes. Molecular dynamics (MD) is a promising simulation method for understanding of material behaviors at nanometer scales and is selected as a major computational tool for this study.

A reversible nonhomogeneous surface premelting model of Au nanoparticles is demonstrated by our simulations. With temperature increase liquid-like atoms first appear at some vertices and edges of surface facets, then small liquid regions grow and at temperatures close to the particle melting temperature, most of the remaining solid-like surface atoms reside on \{111\} planes which are most stable against surface premelting. The appearance of a contiguous liquid layer (complete surface premelting) is size dependent and is not observed in very small nanoparticles.

An integrated molecular dynamics and two-temperature computational model has been developed to study ultrafast laser irradiation of Au nanoparticles at low intensity where surface premelting and solid-liquid phase transition are major interests. Conditions for temporary superheating and stable overcooling were examined carefully.
Nonhomogeneous surface premelting mechanism like that in the equilibrium melting was also observed. The appearance of a contiguous liquid layer (complete surface premelting) is size dependent and is not related to surface premelting history. As shown by simulations when temperature of Au nanoparticles is stabilized they are in the thermodynamically equilibrated state and their lattice temperature and fraction of remaining solid atoms are function of only absorbed laser energy and independent on laser pulse duration.

Microcanonical critical droplet theory (MCD) was applied to interpret the stabilized state of our ultrafast melting simulations. Two forms of melting instability observed in our MD simulations, namely globally stable to metastable state and metastable to catastrophic solid inner core collapse, are also revealed by the MCD theory.

Systematic study of two Au nanoparticles sintering was conducted. Due to the high surface-to-volume ratio, nanoparticles can be significantly heated by surface energy release during sintering. During sintering in the liquid phase, the initial neck growth can be well described by the viscous flow model. For two particles with initial temperature just below the single particle melting temperature, the initial neck growth is initially controlled by viscous flow and then later by grain boundary diffusion. At initial temperatures well below melting, the sintering process occurs very rapidly and ends with a non-spherical oval particle shape. This is attributed to formation of liquid-like atoms in the neck region.
Dedication

This document is dedicated to my family.
Acknowledgments

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# Nomenclature

## Latin Symbols

- $a$: Lattice parameter
- $A$: Surface area or Surface area to volume ratio
- $A_{sph}$: Surface area of the final sphere
- $b$: Width of the grain boundary
- BOP: Bond-Orientational Order Parameters
- $c$: Dimensionless parameter scaling the attractive term
- $C$: Aspect ratio
- $C_p$: Constant-pressure heat capacity
- $C_v$: Constant-volume capacity
- $C_g$: Heat capacity of gas molecules
- $D$: Surface or Grain boundary diffusion coefficient
- $E$: Internal energy
- $E_a$: Activation energy
- $E^{coh}$: Bulk cohesive energy per atom
- $g(r)$: Radial distribution function (RDF)
- $G$: Gibbs free energy
- $H$: Enthalpy
$I_x$  Moment of inertia in the collision direction

$I_{sph}$  Moment of inertia of the final sphere

$k_B$  Boltzmann constant

$K$  Field enhancement factor

$l$  Thickness of the thin film

$L$  Latent heat of fusion

$L_f$  The heat of solidification

$L_{cc}$  Center-to-center distance

$M$  The number of configurations used in the calculation

$N$  Number of atoms in the system

$N_b$  The number of bonds

$P$  Pressure

$\text{PE}$  Potential energy

$Q_{cm}(r)$  Local bond-orientational order parameter

$\bar{Q}_{cm}(r)$  Average local bond-orientational order parameter

$Q_i$  Second-order invariants in the bond-orientational order parameter

$r$  Radius or displacement

$r$  The displacement vector

$R$  Universal gas constant or Radius

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\( R_0 \)  
Initial radius of two sintering particles

\( R_{Au} \)  
Au atomic distance

\( R_g \)  
Gyration radius

\( \mathbf{R}_{cm} \)  
Displacement vector of mass center

\( R_g(\alpha = x, y, z) \)  
Gyration radius at different directions

RDF  
Radial Distribution Function

RMS  
Root-mean-square

RMSD  
Root-mean-square thermal displacement

\( s \)  
Specific entropy

\( S \)  
Entropy

\( t \)  
Thickness of the liquid shell or Time

\( T \)  
Temperature or Time

\( T_{avg} \)  
Average temperature

\( T_0 \)  
Bulk melting temperature

\( T_f \)  
Freezing temperature

\( T_{ins} \)  
Instantaneous temperature

\( T_m \)  
Melting temperature

\( v = \delta^3 \)  
Atomic volume

\( V \)  
Volume of the system
\( \bar{V} \)  
Molar volume

\( V(r) \)  
Two-body potential

\( W_l \)  
Third-order invariants in the bond-orientational order parameter

\( \hat{W}_l \)  
Reduced third-order invariants

\( x_n \)  
Neck radius

\( Y_{lm}(\theta, \phi) \)  
Spherical harmonics

\( Z \)  
Collision rate with gas molecules or Valance of atoms

**Greek Symbols**

\( \alpha \)  
Thermal expansion coefficient

\( \gamma \)  
Surface or Interfacial energy

\( \delta = v^{\frac{1}{3}} \)  
The atomic size

\( \varepsilon \)  
Dimensionless parameter scaling the overall energy or Emissivity

\( \eta \)  
The particle viscosity

\( \theta \)  
The polar angle in a spherical coordinate

\( \mu \)  
Chemical potential

\( \zeta \)  
Correlation length within the liquid phase

\( \rho \)  
Density or Local electron density
\( \rho_N \)  
System number density

\( \tau_c \)  
The characteristic collision time

\( \tau_{cool} \)  
Characteristic cooling time by heat transfer

\( \tau_f \)  
Characteristic coalescence time

\( \sigma_{SB} \)  
Stefan-Boltzmann constant

\( \phi \)  
The azimuthal angle in a spherical coordinate

**Subscript**

0  
Value at the bulk melting temperature

\( b \)  
Bulk

\( c \)  
The critical value

\( \text{ext} \)  
External

\( f \)  
Freezing

\( g \)  
Grain boundary

\( l \)  
Liquid phase

\( m \)  
Melting

\( M \)  
Matrix

\( p \)  
Nanoparticles

\( s \)  
Solid phase or Surface
\( v \)  
Vapor phase

**Superscript**

\( b \)  
Bulk

coh  
Cohesion

hom  
Homogeneous

\( p \)  
Nanoparticles
Chapter 1. Introduction

Nanoparticles or nanoclusters are defined as nanometric size aggregates of atoms or molecules with a number of atoms from 10 to $10^6$ [1][2]. Nanoparticles containing a few hundred atoms with a radius of 1-2nm have strongly size-dependent material properties (for example, elastic modulus, melting point, latent heat of fusion). At this size, some peculiar physical phenomena are also observed, such as noncrystalline structures, quantum confinement in semiconductor particles or surface plasmon resonance in some metal particles. For larger particles with tens of thousands of atoms and radii in the range of 5nm and more, the size phenomena are not pronounced with properties approaching the bulk limit with size increase. This size effect is explained by the high surface area to volume ratio in nanoparticles. The percentage of atoms on the surface of a material becomes significant in nanoscale materials. For example, for a Au nanoparticle with a radius around 1nm, more than half of the total atoms actually sit on the surface. Surface energy then becomes comparable to cohesive energy. While for particles larger than 1nm, the percentage of atoms on the surface is minuscule.

Nanoparticles have been manufactured and found to possess wide applications. It is well known that the high surface area to volume ratio of nanoparticles can be applied to produce the effective catalyst. Hollow Pt nanoparticles are used successfully as the recyclable heterogeneous catalyst for suzuki coupling reactions [3]. Although bulk Au is chemically inert and has often been regarded to be poorly active as a catalyst, Au
nanoparticles turn out to be surprisingly active for many reactions, such as CO oxidation and propylene epoxidation [4]. Nanoparticles are also useful in the biomedical industry. Semiconductor nanocrystals are prepared for use as fluorescent probes in biological staining and diagnostics, producing a better emission spectrum [5]. The localized surface plasmon resonance (LSPR) biosensor is based on the optical properties of Ag nanoparticles and used in the study of antibody [6]. Nanoclusters are also the building blocks for the growth of larger nanostructures on the substrate [7].

This dissertation is part of the project “Nanoscale Solid Freeform Fabrication Process with a Photo-Assisted Spark Plasma Thermal Source” funded by the National Science Foundation (DMI-0500454). In this project, metal nanoparticles are first deposited onto the substrate using the spin coating technique. Spark plasmas produced by the simultaneous concentration of pulsed femtosecond laser energy and electrical energy (from a current-controlled power source) at nanoprobe tips are then used for melting, sintering and subsequent solidification of those nanoparticles to produce three-dimensional nanoscale structures. Since physical and chemical properties of metal nanoparticles exhibit a strong size effect due to significant increase of surface area to volume ratio, a fundamental understanding of melting, solidification, sintering/coalescence and other related material processes in nanoscale materials is necessary. It has been established that Molecular Dynamics (MD) simulation is a promising tool for the understanding of material behaviors at nanometer spatial and femtosecond time scales.

In this dissertation, we will focus on thermodynamic and kinetic phenomena of Au nanoparticles during melting, solidification, and sintering/coalescence under the
condition with and without ultrafast laser irradiation. In Chapter 2, the objectives of
current study are formulated. Chapter 3 reviews continuum theories of
melting/solidification process and typical phenomena in metal nanoparticles’ phase
transition. Several analytical models of melting and solidification are introduced. Past
experimental studies and molecular dynamics simulations regarding to Au nanoparticles
are also discussed. Chapter 4 presents simulation results on equilibrium melting and
solidification of bulk Au and Au nanoparticles. Chapter 5 presents simulation results on
the melting of Au nanoparticles under ultrafast laser irradiation. Chapter 6 applies
microcanonical critical droplet theory (MCD) to interpret the thermodynamic equilibrium
state of nanoparticles in ultrafast melting simulations of last chapter. In Chapter 7,
continuum theories of two sintering particles and past MD simulation results are
reviewed first. Constant energy and constant temperature MD simulations are performed
to understand the applicability of continuum mass transport mechanisms in the sintering
of Au nanoparticles. Sintering of Au nanoparticles under ultrafast laser irradiation is also
discussed briefly in this chapter. At last, Chapter 8 summarizes obtained results.
Throughout this dissertation, various techniques, such as the caloric plot, radial
distribution function (RDF) plot, or bond-orientational order parameters (BOP) analysis
are utilized to analyze the results.
Chapter 2. Objectives

By performing simulations to single Au nanoparticle melting and solidification processes (with and without ultrafast laser irradiation) and two free Au nanoparticles sintering/coalescence, we hope to reach the following goals:

1) To understand the surface premelting mechanism of nanoparticles and its effect on the sintering/coalescence.

2) To understand the ultrafast laser melting mechanism of nanoparticles, and effects of various process parameters like input pulse energy and pulse length.

3) To develop an analytical kinetic model based on MD simulations which describes thermal evolution of nanoparticles under ultrafast laser irradiation.

4) To understand the mass transport mechanism in the sintering of Au nanoparticles and investigate whether existing continuum sintering theory is valid for nanoparticles or new theory needs to be developed.

The long range objective is to develop a multiscale model accounting for consolidation of a nanoparticle array on the substrate under femtosecond laser and nanoscale spark-plasma heat sources.

To accomplish above objectives, a large amount of scientific developments are needed in MD simulations, in particular
1) To determine a reliable metal potential and MD simulation procedures in the calculations of Au nanoparticles.

2) To generate a set of size-dependent material properties applicable to Au nanoparticles.

3) To integrate ultrafast laser heat sources into MD simulations.
Chapter 3. Equilibrium Melting and Solidification of Nanoparticles: Overview of Theory and Experiment

3.1 Phase Transition in Metals and Metal Nanoparticles

Both melting and solidification deal with the process that occurs between two distinct solid and liquid phases. According to thermodynamics [8], the essential driving force behind this phase transition is a decrease in the Gibbs free energy $G$, which could be defined as

$$ G = E + PV - TS + \sum_i \mu_i N_i $$

(3.1)

where $E$ is the internal energy, $P$ is the pressure, $V$ is the volume of the system, $T$ is the temperature, $S$ is the entropy, $N_i$ is the number of particles in the $i$th phase and $\mu_i$ is the specific chemical potential associated with that phase. Then the general equilibrium condition applied to a closed system that may undergo a change in the chemical composition becomes

$$ dG = -SdT + VdP + \sum_i \mu_i dN_i = 0 $$

(3.2)

For the system containing two phases of a pure substance at equilibrium, this is equivalent to require that the chemical potential in each phase is identical. Most of the phenomenological phase transition models are then derived from equality of Gibbs free energy or chemical potential between two phases at equilibrium.
3.1.1 Classical nucleation theory of metals

The kinetic solidification process of metals is better described by two separate steps: the formation of stable crystalline nuclei from thermal fluctuations in the metastable liquids and the subsequent growth of these nuclei into larger crystals [9].

In an ambient liquid phase, there always exist atomic-level stochastic fluctuations in the local density and concentration. Small so-called embryos (atomic aggregates with a structure similar to the new phase) can be created from this thermal fluctuation and may grow through the attachment of individual atoms in the liquids [10]. However, the initial growth of these embryos is always unstable because it is accompanied by an increase in the Gibbs free energy until a critical $\Delta G_c$ and a critical size of the nucleus $r_c$ have been reached. Following nucleus growth then becomes thermodynamically favorable and the Gibbs free energy decreases with time [9].

According to different site distributions of the critical nuclei, the nucleation is classified into two categories. In the homogeneous nucleation, solid nuclei spontaneously appear in all parts of the liquid system, for example, like that in a pure metal. The critical Gibbs free energy increase $\Delta G_{c}^{\text{hom}}$ in the nucleation (also referred as the activation energy barrier against the nucleation), and the critical nucleus size $r_{c}^{\text{hom}}$ are represented as [10]

$$\Delta G_{c}^{\text{hom}} = \frac{16\pi \gamma_{sl}^3 v_s^2}{3(\Delta \mu)^2}, \quad r_{c}^{\text{hom}} = \frac{2\gamma_{sl} v_s}{\Delta \mu}$$  \hspace{1cm} (3.3)

where $\gamma_{sl}$ is the interfacial energy between the solid and the liquid phase, $v_s$ is the atomic volume in the solid phase, and $\Delta \mu = \mu_l - \mu_s$ stands for the chemical potential difference between the liquids and the solids. $\Delta G_{c}^{\text{hom}}$ and $r_{c}^{\text{hom}}$ could be significantly reduced by
cooling the fluids to the freezing temperature $T_f$ below the equilibrium melting temperature $T_m$. The difference $\Delta T = T_m - T_f$ is called the supercooling of the system. It is related to the chemical potential difference $\Delta \mu$ in Eq. (3.3) as [10]

\[ \mu_l - \mu_s = L \frac{\Delta T}{T_m} \tag{3.4} \]

where $L$ is the latent heat of fusion. It is noteworthy that $\Delta G^\text{hom}$ and $r^\text{hom}$ becomes infinity at the melting temperature. The liquids have to be supercooled before starting the stable nucleation and the solidification process.

The second mechanism is associated with solid nuclei in the liquids which commonly appear on suspended impurity particles or on the walls of the solid container. This kind of nucleation is termed as heterogeneous nucleation and the corresponding activation energy barrier is much less than that in the homogeneous nucleation mechanism. Thus, the heterogeneous nucleation is more common in the real liquids [9][10].

### 3.1.2 Surface melting of metals

Although the liquids can be significantly supercooled before the solidification proceeds, the solids are hardly superheated above their melting temperatures. Surface melting plays a key role in explaining the origin of this asymmetry [9]. Excessive specific surface free energy in the system is define as $\Delta \gamma = \gamma_s - \gamma_l - \gamma_{sl}$, where the subscript $s$ and $l$ stands for the solid and the liquid phase respectively [11]. For most metallic liquids in contact with solids of the same composition, $\Delta \gamma$ is a negative value. Thus, the surface layer will favor for the melting by lowering its free energy. At the elevated temperature,
this melted surface layer will then serve as a nucleation site for the continuous melting of the whole solid core, thereby preventing the superheating of bulk materials. On the contrary, the formation of a solid layer covering a liquid core at the temperature above the melting point is not energetically favorable, making the surface freezing usually impossible. Surface melting mechanism was observed experimentally on flat metal surfaces by Frenken and van der Veen [12] and since then has been confirmed in numerous studies which have been summarized in [13][14]. It was also found that the existence of surface melting on flat surfaces of bulk solids is orientation-dependent due to the anisotropy of the surface energy excess $\Delta\gamma$. For metals, complete surface melting occurs on crystal faces with open atom packing such as the (110) faces of an FCC crystal. Densely packed crystal faces such as FCC (111) are generally nonmelting. Metallic surfaces with intermediate atom packing densities such as the (100) faces of FCC crystals tend to exhibit incomplete melting [11].

3.1.3 Metal nanoparticles’ phase transition

Phase transitions of nanoparticles are quite different from their bulk counterparts due to their large surface area to volume ratio. A recent paper gave an excellent review on this subject [1]. The key points can be summarized as follows:

1) The melting temperature decreases with a reduction of the particle size.

2) The latent heat of fusion is reduced too and may finally disappear below a certain particle size.

3) Surface premelting may occur in which the surface begins to melt at a temperature much below the melting point of the whole nanoparticle. The thickness of this liquid layer, which greatly depends on the local curvature, increases continuously
with temperature until a uniform curvature of the solid core is formed. The remaining solid core then melts suddenly.

4) In very small nanoparticles, dynamic coexistent (DC) states of liquid and solid phases are observed from molecular dynamics simulations in the vicinity of melting. In contrast with the coexistence of macroscopic phases in which two distinct phases are present in equilibrium in the same system, individual nanoparticles may fluctuate in time between entirely solid-like states and entirely liquid-like states, like isomers.

3.2 Phenomenological Models of the Size-Dependent Melting Temperature

As mentioned in Section 3.1, most phenomenological models dealing with the phase transition starts from changes of Gibbs free energy or chemical potential between two phases in equilibrium. In this section, we will discuss two classical thermodynamic models, followed by one recently developed model based on the size-dependent cohesive energy and the Lindemann’s criterion. It will be shown that the latest model has advantages of not only describing the melting point reduction in free nanoparticles but also the degree of superheating in embedded nanoparticles.

3.2.1 The classical Pawlow’s model and its modifications

In 1909, Pawlow made the first attempt to derive the size-dependent melting temperature reduction in small particles [15]. This model was then extended and modified by other authors. In this section, we first describe the classical Pawlow’s model
following the treatment of Buffat and Borel [16] and then discuss several modifications taken into account of the second order term or the temperature effect.

Consider a spherical particle with its melting temperature \( T_m \) at a given pressure \( P \), as compared with the bulk melting temperature \( T_0 \) at a given pressure \( P_0 \). The basic assumption is that the melting occurs throughout the whole particle simultaneously. In analogy with the bulk melting, we can equate the chemical potential \( \mu_l \) and \( \mu_s \) of the solid and the liquid particle at \( T_m \) as:

\[
\mu_l(P, T_m) = \mu_l(P, T_m)
\]

The chemical potential can be expanded in the vicinity of the triple point \((T_0, P_0)\) up to the first order as

\[
\mu(P, T) = \mu(P_0, T_0) + \frac{\partial \mu}{\partial T} \bigg|_{T_0} (T - T_0) + \frac{\partial \mu}{\partial P} \bigg|_{T_0} (P - P_0)
\]

(3.6)

The well-known Gibbs-Duhem equation indicates that

\[
\left. \frac{\partial \mu}{\partial T} \right|_{P_0} = -s_0, \quad \left. \frac{\partial \mu}{\partial P} \right|_{T_0} = \frac{1}{\rho_0}
\]

(3.7)

where \( s_0 \) is the specific entropy and \( \rho_0 \) is the density at \((T_0, P_0)\). Thus from Eq. (3.6), (3.7) and the equality \( \mu_l(P_0, T_0) = \mu_l(P_0, T_0) \), we obtain

\[
-s_0(T - T_0) + \frac{1}{\rho_0}(P_l - P_0) = -s_0(T - T_0) + \frac{1}{\rho_s}(P_s - P_0)
\]

(3.8)

Since \( P_l \) and \( P_s \) are the Laplace pressure in small particles, they are much larger than the external pressure \( P_{\text{ext}} \) or \( P_0 \) and are related to surface energy as

\[
P_l = P_{\text{ext}} + \frac{2\gamma_l}{r_l} \approx \frac{2\gamma_l}{r_l}, \quad P_s = P_{\text{ext}} + \frac{2\gamma_s}{r_s} \approx \frac{2\gamma_s}{r_s}
\]

(3.9)

where \( r_l \) and \( r_s \) stand for the particle radius. Substituting Eq. (3.9) into (3.8) we have
\[-s_{i0}(T - T_0) + \frac{2\gamma_i}{\rho_{i0}r_i} = -s_{s0}(T - T_0) + \frac{2\gamma_s}{\rho_{s0}r_s}\]  \hspace{1cm} (3.10)

If in Eq. (3.10) the particle radius and the surface tension are independent of temperature, i.e. \(\gamma_i = \gamma_{i0}; \gamma_s = \gamma_{s0}; r_i = r_{i0}; r_s = r_{s0}\); and from the particle mass conservation,

\[
\frac{r_{i0}}{r_{s0}} = \left(\frac{\rho_{i0}}{\rho_{s0}}\right)^{1/3} \hspace{1cm} (3.11)
\]

Then using the expression \(L_0 = T_0(s_{i0} - s_{s0})\) and substituting Eq. (3.11) into (3.10), we finally obtain

\[
1 - \frac{T_m}{T_0} = \frac{2}{\rho_{s0}r_{s0}L_0} \left[\gamma_{s0} - \gamma_{i0} \left(\frac{\rho_{s0}}{\rho_{i0}}\right)^{2/3}\right] \hspace{1cm} (3.12)
\]

Clearly in this model the reduction of the particle melting temperature is inversely proportional to the particle radius.

Castro et al. [17] argued that the temperature dependence of thermodynamic variables must be taken into account. They expanded Laplace pressure as

\[P = \frac{2\gamma}{r} + P_{\text{ext}} \approx \frac{2\gamma_0}{r_0} (1 - (\eta_0 + \alpha_0)(T_m - T_0)) \hspace{1cm} (3.13)\]

where \(\alpha_0\) and \(\eta_0\) are defined as

\[
\alpha_0 = -\left.\frac{1}{r \frac{\partial r}{\partial T}}\right|_{T_0}; \quad \eta_0 = -\left.\frac{1}{\gamma \frac{\partial \gamma}{\partial T}}\right|_{T_0} \hspace{1cm} (3.14)
\]

Then the particle melting temperature becomes

\[
1 - \frac{T_m}{T_0} = \frac{2}{L_0\rho_{s0}r_{s0}} \left[\gamma_{s0} \left[1 + (\eta_{s0} + \alpha_{s0})(T_0 - T_m)\right] - \gamma_{i0} \left(\frac{\rho_{s0}}{\rho_{i0}}\right)^{2/3} \left[1 + (\eta_{i0} + \alpha_{i0})(T_0 - T_m)\right]\right] \hspace{1cm} (3.15)
\]
Buffat and Borel [16] expanded the chemical potential in the vicinity of the triple point \((T_0, P_0)\) up to the second order and gave a more accurate prediction of the size-dependent melting temperature in comparisons with their experimental data.

### 3.2.2 The liquid-shell model

In this model, a liquid layer with fixed thickness \(\delta\) is assumed to form on top of the solid core like surface melting. This approach was originated by Reiss and Wilson [18] in 1948, where the restriction of uncompressible particles was applied. Several authors modified this model to account for the particle compressibility. Here we follow the treatment given by Chushak and Bartell [19], who made the clear distinction among several meanings of the particle radius.

![Figure 3.1: Stages of melting in the liquid shell model and various meanings of the particle radius (shaded area is the solid)](image)

A sketch of three melting stages in the liquid-shell model is given in Figure 3.1, where various radii are defined. \(r_{ls} \) is the particle radius when the solid core is covered by the liquid shell. \(r_{ls} \) is in general not equal to \(r_l\) although most of previous derivations
mistakenly took this assumption. \( \delta \) is the liquid shell thickness. The Laplace pressure exerted upon the solid core is then

\[
P_s \approx \frac{2\gamma_s}{r_{lm}} + \frac{2\gamma_{sl}}{r_{lm} - \delta}
\]  

(3.16)

Substituting Eq. (3.16) into (3.8), we have

\[
1 - \frac{T_m}{T_0} = \frac{2}{\rho_s L_0} \left[ \frac{\gamma_{sl0}}{r_{lm} - \delta} + \frac{\gamma_{f0}}{r_{lm}} \left( 1 - \frac{r_{lm}}{r_{l0}} \frac{\rho_{s0}}{\rho_{l0}} \right) \right]
\]  

(3.17)

The ratio \( r_{lm} / r_{l0} \) in Eq. (3.17) is

\[
\frac{r_{lm}}{r_{l0}} \approx \left( \frac{\rho_{l0}}{\rho_{s0}} \right)^{1/3} + \frac{\delta}{r_{l0}} \left( 1 - \frac{\rho_{s0}}{\rho_{l0}} \right)
\]  

(3.18)

Therefore for small \( \delta \), Eq. (3.18) becomes

\[
1 - \frac{T_m}{T_0} = \frac{2}{\rho_s L_0} \left\{ \frac{\gamma_{sl0}}{r_{lm} - \delta} + \frac{\gamma_{f0}}{r_{lm}} \left[ 1 - \left( \frac{\rho_{s0}}{\rho_{l0}} \right)^{2/3} \right] \right\}
\]  

(3.19)

It is clear that Pawlow’s model is a special case of the liquid-shell model when an infinitesimal thick liquid layer \( \delta=0 \) is applied.

Kofman et al. [20] derived a similar equation by including the short-range interaction term in estimating the solid-liquid interfacial energy and considering uncompressible spherical particles only, the final expression of the melting temperature was written as

\[
1 - \frac{T_m}{T_0} = \frac{2\gamma_{sl0}}{\rho_s L_0 (r_{lm} - \delta)} \left( 1 - e^{-\xi} \right) + \frac{S r_{lm}^2}{\rho_s L_0 \xi (r_{lm} - \delta)^2} e^{-\xi} 
\]  

(3.20)

where \( \xi \) is the correlation length within the liquid phase and
\[ S' = \gamma_{s0} = \left[ \gamma_{10} + \gamma_{s10} \left( \frac{r_{lm} - I}{r_{lm}} \right)^2 \right] \tag{3.21} \]

### 3.2.3 The liquid-drop model

The previous two models are both derived based on classical thermodynamics. Recently Nanda et al. [21] developed a new model via the size-dependent cohesive energy and the Lindemann’s criterion of melting. It turns out that this new model can be extended to understand other phenomena such as the melting temperature for low-dimensional systems or the superheating of nanoparticles embedded in a matrix.

According to this model, the cohesive energy per atom for nanoparticles is expressed as

\[ E_{p}^{coh} = E_{coh} = \frac{3\nu y_s}{r} \tag{3.22} \]

where \( E_{coh} \) represents the bulk cohesive energy per atom and \( \nu \) is the atomic volume. Tateno [22] related the melting temperature of bulk materials to the bulk cohesive energy based on the Lindemann’s criterion of melting as

\[ T_0 = nE_{coh} f^2 / 3k_BZ \tag{3.23} \]

where \( n \) is the exponent of the repulsive part of the interaction potential between constituent atoms, \( Z \) is the valance of the atoms, \( f \) is the characteristic fraction which is the ratio of the atomic displacement at \( T_0 \) to the interatomic separation at equilibrium, and \( k_B \) is the Boltzmann constant. It was shown in [21] that for most elements the following empirical relationship holds

\[ E_{coh} = 0.0005736T_0 + c \tag{3.24} \]

The unit of \( E_{coh} \) and \( T_0 \) is eV and K respectively, and \( c \) is the intercept of the fitting line.
Suppose Eq. (3.24) holds for nanoparticles too if $E_{coh}$ is replaced by $E_{p}^{coh}$ and $T_0$ is replaced by $T_m$, then

$$1 - \frac{T_m}{T_0} = \frac{3v}{0.0005736r} \left( \frac{\gamma_s}{T_0} \right) = \frac{\beta A}{6}$$

(3.25)

where $\beta = \frac{6v}{0.0005736 \left( \frac{\gamma_s}{T_0} \right)}$ is a material constant and $A$ is the surface area to volume ratio. For nanoparticles, $A = 3/r$; for nanowires, $A = 2/r$ and for thin films, $A = 2/l$ ($l$ is the thickness of the thin film).

For nanoparticles embedded in a matrix, if surface atoms are completely saturated with the atoms of the surrounding matrix, solid surface energy will be replaced by the interfacial energy, leading to a modified Eq. (3.22) as

$$E_{p}^{coh} = E_{coh} - \frac{3v(\gamma_s - \alpha \gamma_{sM})}{r}$$

(3.26)

where $\gamma_{sM}$ is solid surface energy of the surrounding matrix and $\alpha$ represents the level of interaction between atoms of nanoparticles and those of the surrounding matrix; $\alpha = 0$ for free nanoparticles and $\alpha = 1$ if there is epitaxy between nanoparticles and the matrix. If $\alpha \gamma_{sM} > \gamma_{sM}$, nanoparticles could be superheated above the bulk melting temperature $T_0$.

### 3.3 Experimental Observation of Melting of Au Nanoparticles

Experimental measurement of nanoparticles’ melting can be divided into two major categories [1][23]:

1) Study of changes of some physical properties across the melting point (for example, changes in diffraction patterns or the rate of evaporation)
2) Measurement of the caloric curve $E=E(T)$ (i.e. total internal energy versus temperature)

Takagi [24] made the first observation of the melting temperature reduction in 1954. Transmission electron microscopy was used to monitor changes in the diffraction pattern associated with the disappearance of the state of order in the study of Pb, Sn and Bi. Electron and x-ray diffraction nanocalorimetry techniques have been used later [16] but all of these methods are applicable to deposited nanoparticles only. Martin et al. [25] were the first to publish a size dependence of the melting temperature of free particles by relating the disappearance of the ordered structure on mass spectra to the melting point. Calorimetry of free nanoparticles has been applied successfully by Haberland’s group [26] to Na clusters and by Bachels et al. [27] to Sn clusters.

To the author’s knowledge, only three references are available on melting experiments of Au nanoparticles deposited upon amorphous substrates. We will review these results in the following sections.

3.3.1 Sambles (1971) experiment

Sambles [28] conducted the first experiment on the melting of Au nanoparticles rested on heated carbon substrates in a vacuum environment. From observations of the evolution of small gold particles by electron microscopy at a constant temperature, he reported that the rate of evaporation underwent a sharp increase at a temperature which was below the melting temperature of bulk materials. He attributed this to the different evaporation coefficient between solid and liquid Au and assigned that temperature as the melting temperature of small particles which were brought to be melted by evaporation.
A plot of the melting temperature against the particle radius within the range of 10nm to 40nm was given in the paper. This method is not applicable to ultra fine particles since precise measurements of the size variation are required during the evaporation process [16]. The liquid-shell model gave a better fitting towards the plot with two adjustable parameters as $\sigma_{sl}=0.27\pm 0.01\text{N/m}$ and $\delta=2.2\pm 0.5\text{nm}$, although experimental results also agreed satisfactorily with the prediction of the classical Pawlow’s model.

3.3.2 Buffat and Borel (1976) experiment

Another classical experiment was conducted by Buffat and Borel [16] in 1976. Au nanoparticles were formed by the condensation of gold vapor on a thin amorphous carbon film mounted on a gold mesh of the type used for electron microscopy. By monitoring diffraction patterns produced by electron microscopy, they found that patterns of rings obtained from crystalline powders were relatively narrower than those obtained from liquids. Thus, by using a heated stage in an electron microscope, it was possible to determine the temperature at which morphological changes of the rings occur and, thereby, to determine the melting temperature of the very small particles. This method is well suited for particles whose radius is greater than 1nm. However, because of the dispersion of particle sizes in a specimen, this method only permits the determination of a range of melting temperatures for an ensemble of particle sizes.

A plot of the melting temperature against the particle radius within the range of 1nm to 12nm was given in this paper. The measurements did not permit a conclusive choice among any models but it agreed more closely with the prediction of the 2nd order Pawlow’s model. For the liquid-shell model, it gave a thickness of the liquid layer around
0.62nm, much less than that determined from Sambles’ experiments. The existence of the size-dependent liquid layer may help to solve this discrepancy.

3.3.3 Castro et al. (1990) experiment

The latest experiment was performed by Castro et al. [17] in 1990. The field-emission current from an individual nanoparticle was used to study a size-dependent change in shape of the nanoparticle as a function of temperature. The field enhancement factor $K$, which depends solely on the particle geometry relative to the substrate, can lead to high sensitivity of the field-emission current to overall particle geometry. During the solid-liquid transition, the particle is able to spread out and wet the surface. Changes in particles’ geometry result in a change in the overall field-emission pattern from the particle, which is used to signify the phase transition.

The melting temperature obtained from this study was systematically less than the results in [16]. The variable Debye-Waller factor instead of a constant value used in [16] may account for this deviation. The much stronger interaction energy between Au nanoparticles and W substrate in this study than that between Au and C substrate in [16] is another possible reason.
4.1 Introduction

As discussed in Section 3.1.2, the term “surface premelting” defines a phenomenon during the melting of a substance where a liquid layer is first formed on the solid surface and continues to thicken with temperature increase until the solid core melts. The energetic requirement for surface premelting is that the solid surface energy $\gamma_s$ exceeds the sum of the liquid surface energy $\gamma_l$ and the solid-liquid interfacial energy $\gamma_{sl}$ [9]. This melting mechanism was observed experimentally on flat metal surfaces by Frenken and van der Veen [12] and since then has been confirmed in numerous studies which have been summarized in [13][14]. It was also found that the existence of surface premelting on flat surfaces of bulk solids is orientation-dependent due to the anisotropy of the surface energy excess $\Delta\gamma = \gamma_s - \gamma_l - \gamma_{sl}$ [11]. For example, MD simulations of bulk Au showed that {110} surfaces were completely premelted [29] whereas {111} surfaces remained stable up to the bulk melting temperature, indicating complete lack of surface premelting [30]. A liquid layer was also generated on {100} surfaces, but its thickness did not increase with temperature [31].

Surface premelting has been observed experimentally in nanoparticles like Pb/SiO; Pb/Al₂O₃ [20], Pb [32][33], Sn [27] and Cu nanorods [34]. This mechanism was used to
explain shape transformations of Au nanorods [35] and nanoparticles [36] at temperatures lower than the particle melting temperature and the anomalous low temperature evaporation behaviors [37]. Recently, Ruan et al. [38] have experimentally observed the reversible surface premelting of Au nanoparticles (2-20nm) under femtosecond laser irradiation using ultrafast electron nanocrystallography. Experimental observations of surface premelting in 61.5nm Au nanoparticles were reported by Plech et al. [39]. Several authors have also studied the existence of surface premelting in Au nanoparticles with molecular dynamics (MD) simulations. Most of these studies use constant temperature simulations (the canonical ensemble) to represent the melting of loosely supported nanoparticles with the substrate acting as a thermostat. Ercolessi et al. [40] and Lewis et al. [41] have interpreted enhanced surface and sublayer diffusivity and atomic displacements at elevated temperatures as indicators of surface premelting. Kuo and Clancy [42] have studied Au nanoparticles containing 300 to 3,000 atoms. During heating of these clusters they found solid-state structural transformation from the initial FCC structure to icosahedra followed by a transition to the “quasimolten” state in which nanoparticles fluctuated between several solid structural motifs frequently. Wang et al. [43] showed that facets on the surface of icosahedral Au nanoparticles “softened” but remained ordered and did not premelt below the particle melting temperature. In some studies, constant energy simulations (the microcanonical ensemble) were performed to address the melting of nanoparticles having poor thermal exchange with their surroundings, such as clusters in inert gas atmospheres. Cleveland et al. [44][45] studied Au clusters up to 459 atoms. They detected the same structural transformation as Kuo and Clancy [42] did; however they did not observe the transition to the “quasimolten”
state. Instead, in the largest 459-atom cluster, a phase coexistence state, in which the upper part of the cluster is solid and the lower part is liquid, was found before the complete particle melting. The stability of this phase coexistence state was explained based on the microcanonical critical droplet (MCD) theory by Hendy et al. [46]-[48]. Some interesting phenomena, like an S-bend in the microcanonical caloric curve [44],[45] or negative heat capacities [49], were also reported in constant energy simulations of other metal clusters.

Thus, no direct evidence of a continuous growth of a liquid-like surface layer prior to the melting of a whole Au nanoparticle was found in MD simulations, which seems in contradiction to the experimental findings. Better understanding of this phenomenon is essential not only from the theoretical point of view but also for quantitative analysis of nanoparticle coalescence, assembling and sintering. In this chapter, we used the bond-orientational order parameter (BOP) analysis [50] to characterize the melting of Au nanoparticles with the aim of investigating the existence of surface premelting or structural disordering prior to the melting of a whole nanoparticle. Based on our simulations, we have identified a new mechanism of nonhomogeneous surface premelting of Au nanoparticles. It starts on the vertices and edges of surface facets and is characterized by a monotonic increase with temperature of the fraction of “liquid-like” atoms on the nanoparticle surface which forms a completely premelted surface only in larger nanoparticles. At temperature close to the particle melting point, most of the solid-like surface atoms are found belonging to \{111\} planes which are the most stable against surface premelting on flat surfaces. With temperature increase a continuously thickening and size-dependent equivalent liquid-like layer is
defined. It is also found that this surface premelting process is reversible as has also been observed experimentally for Pb nanoparticles.

This chapter is organized as follows: In Section 4.2, simulation procedures and key elements of the BOP analysis are outlined. In Section 4.3, results for melting temperature and latent heat of fusion of bulk Au are presented. In Section 4.4, results of Au nanoparticles of various sizes are presented and compared with analytical models. Section 4.5 is devoted to a detailed BOP analysis of Au nanoparticle melting using both global and local BOPs. Surface premelting is identified using local BOPs. Temperature increase rates of fractions of liquid-like surface atoms in various sized nanoparticles are fitted by the same exponent using size-independent parameters, yielding for activation energy of liquid-like surface atoms formation 1kJ/mol. Section 4.6 presents a complete picture of our nonhomogeneous model of surface premelting for Au nanoparticles. Section 4.7 summarizes our findings.

4.2 Computational Methods

4.2.1 Simulation procedures

MD simulations were performed at the Ohio Supercomputing Center (OSC) with the publicly available source code DL_POLY_2 [51]. The Quantum Sutton-Chen (Q-SC) many-body potential is used in our simulations. It has the same functional form as the Sutton-Chen potential [52] but was re-parameterized by Ikeda et al. [53] to include quantum corrections and additional experimental data. Constant temperature is maintained by the Nosé-Hoover thermostat [54][55] while constant zero pressure is
maintained by the Melchionna modification of the Hoover barostat [55][56]. The time
step is set to 4fs. The Visual Molecular Dynamics (VMD) package [57][58] and the
Maximal Speed Molecular Surface (MSMS) program [59] are used to display and
animate atomic configurations throughout this work.

In our simulations, eleven spherical nanoparticles with different numbers of atoms
(N=456-2,360) were studied. Beside the crystalline FCC structure, Au nanoparticles can
possess different noncrystalline nanostructures such as Marks decahedron and Mackay
icosahedron. It is generally accepted [1][47][60] that the icosahedron is favored at small
sizes while FCC is expected for larger sizes. The Marks decahedron may be favored in
the intermediate range. The size range of structural transitions is strongly material and
temperature dependent. FCC was found to be preferable at low temperatures in our
particle size range in two studies with different potentials: the embedded atom method
(EAM) potential by Cleveland et al. [44][45] or the Rosato-Guillopé-Legrand (RGL)
potential by Baletto et al. [61]. For this reason no special investigation of energetically
preferred structures for the Q-SC potential was performed in this study and the spherical
nanoparticles were all prepared from the perfect FCC structure. In our simulations the
nanoparticles were subjected to a heating process consisting of a series of constant
temperature simulations starting from 50K with 50K temperature increments (near the
particle melting temperature it was decreased to 10K). Since the melting of free Au
nanoparticles was simulated, no periodic boundary conditions have been applied. The
integration time step was set to 4fs. At each temperature, the nanoparticles were
equilibrated for 100ps and another 100ps were used to accumulate the statistical data.
After the equilibration the atomic configurations were considered uncorrelated if they
were selected with at least 20 time steps. A longer equilibration time was used for large nanoparticles to keep a reasonable temperature fluctuation $\delta T$ in the canonical ensemble [62]:

$$< (\delta T)^2 > \approx \frac{2}{d} \frac{< T^2 >}{N}$$

(4.1)

where $< ... >$ is the time average and $\delta T = T - < T >$. Calculations of the bulk Au melting temperature were performed in a similar way, using 3D periodic boundary conditions (PBC) with 12x12x12 FCC unit cells (6,912 atoms) at constant zero pressure.

4.2.2 Bond-orientational order parameter (BOP) analysis

The bond-orientational order parameter (BOP) analysis proposed by Steinhardt et al. [50] is applied to characterize the melting of Au nanoparticles. In this method, the bond is defined as a vector joining the central atom $i$ with its neighboring atoms $j$ that is within a given cutoff radius. For Au, we choose the cutoff radius as 3.4Å, which is 1.2 times the atomic distance in FCC Au (2.885Å at 300K). This distance, as demonstrated in Section 4.5.1, insures that all the atoms in the first coordination shell are counted as nearest neighbors.

The local BOP $\bar{q}_{lm}(i)$ for each atom $i$ is calculated as

$$\bar{q}_{lm}(i) \equiv \frac{1}{N_b(i)} \sum_{i=1}^{N_b(i)} Y_{lm}(\theta(r),\phi(r))$$

(4.2)

where $Y_{lm}(\theta(r),\phi(r))$ are spherical harmonics associated with the bond $r$; $N_b(i)$ is the number of bonds an atom has with its neighbors; $l$ and $m$ are integers that satisfy $-l \leq m \leq l$. To hold $\bar{q}_{lm}(i)$ invariant under coordinate transformations, two sets of parameters $q_i$ and $\hat{w}_i$ are constructed:
\[ q_l \equiv \left( \frac{4\pi}{2l+1} \sum_{m=-l}^{m=l} |\vec{q}_{lm}|^2 \right)^{1/2} \quad (4.3) \]

\[ \hat{W}_j \equiv \sum_{m_i,m_2,m_3} \binom{l}{m_1} \binom{l}{m_2} \binom{l}{m_3} \times \vec{q}_{lm_1} \vec{q}_{lm_2} \vec{q}_{lm_3} \left( \sum |\vec{q}_{lm}|^2 \right)^{1/2} \quad (4.4) \]

Note that the term in parentheses in Eq. (4.4) is a Wigner 3j symbol.

The global BOP \((Q_i, \hat{W}_f)\) for a group of \(N\) atoms is calculated by replacing the variable \(\vec{q}_{lm}(i)\) in Eq. (4.3) and (4.4) with \(\vec{Q}_{lm} \equiv \sum_{i=1}^{N} \sum_{j} N_b(i) \vec{q}_{lm}(i) / \sum_{i=1}^{N} N_b(i)\). Four global BOPs \((Q_4, Q_6, \hat{W}_4, \hat{W}_6)\) are usually sufficient to identify different crystalline structures of the selected system [42]. In the liquids, \(Q_i\) and \(\hat{W}_f\) all approach zero.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>(Q_4)</th>
<th>(Q_6)</th>
<th>(\hat{W}_4)</th>
<th>(\hat{W}_6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCC</td>
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<td>0.57452</td>
<td>-0.15932</td>
<td>-0.01316</td>
</tr>
<tr>
<td>HCP</td>
<td>0.09722</td>
<td>0.48476</td>
<td>0.13410</td>
<td>-0.01244</td>
</tr>
<tr>
<td>BCC</td>
<td>0.03637</td>
<td>0.51069</td>
<td>0.15932</td>
<td>0.01316</td>
</tr>
<tr>
<td>SC</td>
<td>0.76376</td>
<td>0.35355</td>
<td>0.15932</td>
<td>0.01316</td>
</tr>
<tr>
<td>Icosahedra</td>
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<td>0.66332</td>
<td>0</td>
<td>-0.16975</td>
</tr>
<tr>
<td>liquid</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 4.1: The global BOPs for common crystal structures [42]

Wolde et al. [63][64] developed a method using the local BOP parameters to distinguish between liquid-like and solid-like states for every single atom in their studies.
of crystal nucleation. Although the local BOP $q_6$ for each atom is large not only in solids but also in liquids, the global BOP $Q_6$ for a group of atoms is around 0.5 in common crystal structures whereas in liquids it is zero. The basic idea of Wolde et al. is to check the add-up coherence of the local BOP $q_6$. To every atom $i$, a normalized complex vector $\vec{q}_6(i)$ is defined, with its $13 (=2\times6+1)$ components as

$$\vec{q}_6(i) = \frac{1}{\sqrt{\sum_{m=-6}^{6} |\vec{q}_{bm}(i)|^2}}\sum_{m=-6}^{6} \vec{q}_{bm}(i)$$

(4.5)

The bond between atoms $i$ and $j$ is counted as “crystal-like” if the inner product of their corresponding vectors $\vec{q}_6(i) \cdot \vec{q}_6(j)$ exceeds 0.5. Furthermore, Wolde et al. used the criterion of “seven or more crystal-like bonds” to define solid-like states for inner atoms; otherwise it is considered as liquid-like. Since surface atoms have fewer neighboring bonds than inner atoms do, for surface atoms we have modified this criterion. We define a surface atom to be “solid-like” if it has six or more “crystal-like” bonds; if it has less than six “crystal-like” bonds it is defined as “liquid-like”. Unlike the atomic diffusivity which is usually obtained from a group of simulated atomic configurations over tens of picoseconds, this method allows the determination of atoms’ phase states with a single atomic configuration.

4.3 Bulk Melting Temperature and Latent Heat of Fusion

In this section, bulk Au MD simulations are performed and several important thermodynamic properties are extracted from calculations. They will be compared with
experimental values, and will later serve as the inputs for theoretical models applied for comparisons with our MD simulations in Section 4.4.

4.3.1 Melting and solidification temperature

The caloric plot (potential energy versus temperature) is shown in Figure 4.1. The clear, sharp jump in the plot indicates that bulk Au will melt at 1385K, 48K higher than the experimental bulk melting temperature 1337.33K [65]. It is quite normal for MD bulk simulations to predict a higher melting temperature. The heating rate is usually as high as 10^{10}K/s in the simulation, comparable to that in the planar shock-wave loading or intense laser irradiation. A liquid seed from where the liquid could nucleate and grow is not easy to form due to the absence of surfaces by using periodic boundary conditions. Hence, superheating in the crystals is not evitable [66].

Some authors have used other metal potentials to predict the melting temperature of bulk Au. We summarize their results in Table 4.2, together with our calculation and the experimental value. It is clear that the Q-SC potential gives a better prediction than any others except the “glue” potential, which takes into account the melting temperature during the parameterization process.
Figure 4.1: The caloric curve of bulk Au

<table>
<thead>
<tr>
<th>Potential</th>
<th>$T_m$</th>
<th>Potential</th>
<th>$T_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;Glue&quot;</td>
<td>1357K [67]</td>
<td>SC</td>
<td>1065K (this work)</td>
</tr>
<tr>
<td>EAM</td>
<td>1090K [44]</td>
<td>Q-SC</td>
<td>1385K (this work)</td>
</tr>
<tr>
<td>MEAM</td>
<td>1500K [42]</td>
<td>Experiment</td>
<td>1337.33 [65]</td>
</tr>
</tbody>
</table>

Table 4.2: The melting temperature $T_m$ of bulk Au predicted by MD simulations

Different heating rates can also affect the simulated caloric curve and bulk melting temperature. In Figure 4.1, the heating rate is $5 \times 10^{11}$ K/s, but it decreases to $10^{11}$ K/s in the vicinity of melting temperature from 1300K to 1500K. If constant $(5 \times 10^{11}$ K/s) or higher $(10^{12}$ K/s) heating rate is used, as shown in Figure 4.2, the caloric
curve during the phase transition becomes broader and the simulated melting temperature is increased.

![Graph showing the caloric curve of bulk Au in the vicinity of melting temperature (1300K to 1500K) using different heating rates](image)

Figure 4.2: The caloric curve of bulk Au in the vicinity of melting temperature (1300K to 1500K) using different heating rates

From Figure 4.1, the solidification temperature of bulk Au is found to be 765K. The hysteresis loop is clear in the caloric plot, indicating a roughly 620K supercooling. Notice that at the same temperature, the system after the melting-solidification cycle has a higher potential energy. This suggests that not all of the crystalline orders have been restored during the fast solidification process in MD simulations. In this figure, the heat of solidification $L_f$ is found to be less than the latent heat of fusion $L_0$. Assuming the same entropy change $\Delta S$ during phase transitions, $L_f$ is approximated as
4.3.2 Surface energy

The potential energy (PE) of bulk materials $PE_b$ and nanoparticles $PE_p$ in MD simulations can be expressed as

\[
PE_b = NE^{coh}
\]
\[
PE_p = NE^{coh} + \gamma A
\]

where $A$ is the surface area of nanoparticles and $E^{coh}$ is the bulk cohesive energy per atom calculated from the potential energy divided by the number of atoms in the periodic cell. The surface area is negligible for bulk materials due to the use of periodic boundary conditions. By performing simulations on nanoparticles (detailed results are presented in the Section 4.4), we can then determine the Au surface energy from the potential energy difference using Eq. (4.7).

Figure 4.3 shows the calculated surface energy varied with the size of nanoparticles at 300K (solid phase) and 1500K (liquid phase). It is safe to say the surface energy is weakly dependent on the particle size and average surface energy at 300K is determined as $0.85\pm0.01$N/m, while at 1500K, $0.61\pm0.02$N/m. These data are consistent with the simulation results by Kimura et al. [68] using the same potential at the absolute zero, which gave the value from 0.691 N/m to 0.872N/m dependent on the specific crystal plane. Using the EAM potential, Lewis et al. [41] also found the solid surface energy as 0.90 N/m and liquid one as 0.74 N/m, pretty close to our results. However, experiments tend to give much larger surface energy no matter in the solids or liquids. Tyson and Miller [69] obtained the surface energy at the absolute zero from surface
tension measurements as 1.506N/m. At the melting temperature 1337.33K, Miedema [70] gave the value of 1.40N/m for the solids while Egry et al. [71] recently reported the value of 1.15N/m for the liquids.

![Surface energy versus Radius of Au nanoparticles at 300K and 1500K](image)

Figure 4.3: Surface energy versus Radius of Au nanoparticles at 300K and 1500K

4.3.3 Other thermodynamical properties

The density can be calculated from varying sizes of the periodic cell. In Figure 4.4, we compare the simulated bulk Au density with experimental values which are derived from a thermal expansion experiment [72] and are extrapolated down to 50K and up to 1337K (the experimental bulk Au melting temperature). The simulated densities coincide
well with the experimental values at low temperatures but deviate for about 5% at 1337K. This is because parameters of the Q-SC potential are optimized specially at the absolute zero. Densities from this calculation right before and after the melting temperature (1395K here) are $17.32 \times 10^3 \text{kg/m}^3$ and $15.98 \times 10^3 \text{kg/m}^3$ correspondingly.

Figure 4.4: Comparison of bulk Au density between experimental values [72] and MD simulation results

The constant-pressure heat capacity in MD simulations is evaluated through the expression

$$C_p(T) = \frac{d(PE)}{dT} + \frac{3R}{2}, \quad (4.8)$$
where $R$ is the universal gas constant. At 298K, this gives a value of 25.94J/(mol·K), slightly larger than the experimental result 25.42J/(mol·K) [73].

The latent heat of fusion at the bulk melting temperature $L_0 (= H_{l0} - H_{s0})$ is determined from the enthalpy versus temperature plot. The simulated value 12.35kJ/mol is again similar as the experimental value 12.55kJ/mol [74]. This suggests that the Q-SC potential is also useful to give material properties at the high temperature.

4.4 Nanoparticle Melting Temperature and Latent Heat of Fusion

4.4.1 The particle melting temperature and latent heat of fusion

The number of atoms and the particle radius at 300K, immediately before and after the particle melting and at the bulk melting temperature for each nanoparticle are listed in Table 4.3. The radius of a spherical particle $R$ is obtained from the equation

$$R = \sqrt[3]{\frac{5}{3}} R_g = \sqrt[3]{\frac{5}{3}} \frac{1}{N} \sum_{i=1}^{N} |R_i - R_{cm}|^2$$

(4.9)

and averaged over 200 configurations, where $R_g$ is the gyration radius, $R_i$ is the position of a single atom and $R_{cm}$ is the position of the particle’s mass center. This definition of radius is used throughout this dissertation and is also used to calculate volume and surface area of nanoparticles. However, some authors [75][76] add an additional term (half of the atomic distance $1/2R_{Au}$) in defining the radius.

Caloric curves (potential energy versus temperature) simulated for melting processes of nanoparticles of different sizes, together with the bulk Au, are shown in Figure 4.5. Melting temperatures correspond to the sharp jumps in those plots, which are characteristic of first-order phase transitions. The melting temperature $T_m$ of Au
nanoparticles is significantly depressed when compared with the bulk Au and size dependent. For example, a 456-atom nanoparticle (i.e. 1.22nm in radius at 300K) will melt at only 835K whereas a 22,360-atom nanoparticle (i.e. 4.49nm in radius at 300K) will melt at 1075K. However, the bulk Au melting temperature $T_0$ is as high as 1385K. Nanoparticles generally have a higher molar potential energy due to the large surface area to volume ratio, but will decrease to the bulk value for very large $N$. Large fluctuations near the particle melting temperature are due to the decreased temperature increment.

<table>
<thead>
<tr>
<th>Number of atoms $N$</th>
<th>Particle radius (Å)</th>
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<th>before melting</th>
<th>after melting</th>
<th>1385K</th>
</tr>
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<td>31.5986</td>
<td>32.2082</td>
<td>32.8319</td>
<td></td>
</tr>
<tr>
<td>22360</td>
<td>********</td>
<td>********</td>
<td>********</td>
<td>********</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.3: Sizes and radii of nanoparticles at various temperatures
To get the latent heat of fusion, we fit the enthalpy linearly as a function of temperature in solid and liquid regions respectively and calculate their differences at the particle melting temperature. The results are tabulated with the particle melting temperature in Table 4.4.
<table>
<thead>
<tr>
<th>Number of atoms $N$</th>
<th>Melting temperature $T_m$ (K)</th>
<th>Latent heat of fusion $L$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>276</td>
<td>805</td>
<td>7.796</td>
</tr>
<tr>
<td>456</td>
<td>835</td>
<td>5.218</td>
</tr>
<tr>
<td>736</td>
<td>915</td>
<td>6.307</td>
</tr>
<tr>
<td>1088</td>
<td>945</td>
<td>6.962</td>
</tr>
<tr>
<td>1556</td>
<td>965</td>
<td>7.974</td>
</tr>
<tr>
<td>2112</td>
<td>985</td>
<td>8.164</td>
</tr>
<tr>
<td>2808</td>
<td>1005</td>
<td>8.266</td>
</tr>
<tr>
<td>3604</td>
<td>1015</td>
<td>8.808</td>
</tr>
<tr>
<td>4664</td>
<td>1025</td>
<td>9.420</td>
</tr>
<tr>
<td>5768</td>
<td>1035</td>
<td>9.595</td>
</tr>
<tr>
<td>7164</td>
<td>1045</td>
<td>9.801</td>
</tr>
<tr>
<td>22360</td>
<td>1075</td>
<td>9.959</td>
</tr>
</tbody>
</table>

Table 4.4: The melting temperature and latent heat of fusion of Au nanoparticles

4.4.2 Comparison on the particle melting temperatures with experimental results and theoretical predictions

As discussed before, only three papers have been found to describe melting temperatures of small Au nanoparticles. Sambles [28] gave the data for relatively large nanoparticles, with the radius in the range of 6nm to 40nm. Buffat and Borel [16] studied Au nanoparticles between 1nm to 10nm in radius, similar as the ones used in our simulation. Castro et al. [17] tested even smaller Au nanoparticles down to a radius of 0.6nm. These experimental results are compared with the calculated particle melting temperatures in Figure 4.6. The agreement for particles less than 2nm in radius is satisfactory. For large radius, MD simulations give somewhat lower melting temperatures.
Figure 4.6: Comparison on the particle melting temperature with experiments

Figure 4.7 compares the calculated particle melting temperatures with values predicted by two theoretical models discussed in Section 3.2. The data from two models (Eq. (3.12) and Eq. (3.19)) are shown by points for the same nanoparticle radius. To make consistent comparisons, most material properties were calculated from our MD simulations rather than taken from available experimental data: $r_{s0}$ and $r_{\text{lim}}$ is listed in Table 4.1 at the temperature just before the particle melts; $\rho_{s0}=17.32\times10^3\text{kg/m}^3$, $\rho_{s0}=15.98\times10^3\text{kg/m}^3$ and $L_0=12.35\text{kJ/mol}$ at the calculated bulk melting temperature 1385K (see Section 4.3.3); $\gamma_{s0}=0.85\text{N/m}$ at 300K and $\gamma_{l0}=0.61\text{N/m}$ at 1500K (see Section 4.3.2); the estimation of size-dependent liquid layer thickness $\delta$ is discussed in Section 4.6.2. As the only adjustable parameter in both models, $T_0$ is used to fit $T_m$ data and
indicates the extrapolated bulk melting temperature. Although the Pawlow model gives a better prediction (lower standard deviation $\sigma=14.4$K), the liquid-shell model also agrees satisfactorily with the simulated results. By taking into account the inaccuracy in material properties, especially that surface energy should be anisotropic and temperature-dependent, the distinction between the two models is not significant enough to permit a conclusive choice of the melting mechanism (surface premelting or not). Notice that the extrapolated $T_0$ in both models are much lower than the calculated bulk melting temperature $1385$K with periodic cells. This is associated with overheating in the bulk case as will be discussed further in Section 4.5.3. A discrepancy between the extrapolated and the calculated bulk melting temperature was also found by Qi et al. [75] who simulated caloric curves for Ni nanoparticles.

Figure 4.7: Au nanoparticle melting temperature versus inverse of radius compared with the Pawlow’s model [15] and the liquid-shell model [18][19]
4.4.3 Comparison on the particle latent heat of fusion with analytic models

The particle latent heat of fusion is found to be less than the bulk latent heat of fusion $L_0$. Bachels et al. [77] tried to explain this phenomenon based on the surface premelting theory. They argued that a liquid layer, with the thickness independent on the size of nanoparticles, is formed before the particle melting temperature. Latent heat of fusion is then used to melt the remaining solid core. When the particle size decreases, the size of the remaining solid core decreases too, leading to a smaller latent heat of fusion. The particle latent heat of fusion will disappear when a critical particle size is reached and after that may be significantly enhanced because the surface premelting theory no longer holds.

Kofman et al. [78] found that, without assuming the surface premelting mechanism, by taking into account of size-dependent surface free energy of spherical particles, the similar trend can also be predicted. Considering that the particle is composed of surface and core regions, and assuming that the core region has the same latent heat of fusion as the bulk materials, the enthalpy for a particle containing $N$ atoms can be written as [75]

$$H_{s,N}^p = H_{s,N}^b + \gamma s0 A; \quad H_{l,N}^p = H_{l,N}^b + \gamma l0 A$$

(4.10)

and the nanoparticle latent heat of fusion $L_N^p$ is

$$L_N^p = H_{s,N}^p - H_{l,N}^p = H_{l,N}^b - H_{l,N}^b + (\gamma s0 - \gamma l0) A = L_{0,N} + (\gamma s0 - \gamma l0) A$$

(4.11)

Finally by converting Eq. (4.11) to the molar quantity, we get

$$L_p = L_0 - \frac{3(\gamma s0 - \gamma l0)}{r s0} \overline{V}$$

(4.12)
where $\bar{V}$ is the molar volume.

In Figure 4.8, we compare the calculated particle latent heat of fusion with predictions made by Eq. (4.12). $\bar{V}$ is taken to be $1.195 \times 10^{-5}$ m$^3$/mol, corresponding to the average value of the liquid and solid density at the bulk melting temperature. Note that MD simulations agree very well with Eq. (4.12), with the largest deviation less than 10%. However, this good agreement does not preclude the existence of surface premelting which is not accounted for in the model. Indeed, as illustrated in Figure 4.5 for the largest 22,360-atom nanoparticle, $L_p$ obtained from MD simulated caloric curves is not measured from the potential energy difference at temperatures just before and after particle melting ($T=T_m$). Instead it is obtained by asymptotically extrapolating from high and low temperatures and thus accounting for caloric changes before the melting temperature is reached. If surface premelting does occur, it will not affect $L_p$ obtained from MD simulations because the amount of energy to create a liquid layer has already been included into this value.
4.5 BOP Study of Surface Premelting

4.5.1 Selection of cutoff radius

The construction of BOPs requires that only the nearest neighboring atoms of a central atom $i$ are included in the evaluation of the local BOP $q_{lm}(i)$. This requirement is fulfilled by carefully choosing an appropriate cutoff radius. Figure 4.9 shows the radial distribution function (RDF) plots at several temperatures in bulk Au melting simulations. The RDF indicates the probability of finding two atoms separated by a certain distance $r \pm \Delta r$ and can be obtained experimentally using neutron-scattering techniques [79]. The first peak in these plots corresponds to the position of the first coordination shell surrounding a central atom. Figure 4.10 shows the global BOP $Q_6$ versus the cutoff radius at several temperatures. BOPs should be independent of cutoff radius; however they decay as it becomes too large (especially at high temperatures). Thus we select a largest
possible cutoff radius from the constant range of parameter $Q_6$. Our analysis reveals that the cutoff radius 3.4Å satisfies such requirements. As indicated by a vertical line in Figure 4.9, this cutoff radius includes almost all the atoms within the first peak in the evaluations of BOPs.

![Radial Distribution Function plots at different temperatures from 6,912-atom periodic cell bulk Au simulations](image)

Figure 4.9: Radial distribution function (RDF) plots at different temperatures from 6,912-atom periodic cell bulk Au simulations
Figure 4.10: Global BOPs versus cutoff radius at different temperatures from 6,912-atom periodic cell bulk Au simulations

4.5.2 Analysis of surface premelting by global BOPs

To better understand the melting of bulk Au and Au nanoparticles, the global BOPs for inner and surface atoms are calculated separately and then averaged over 100 configurations at each temperature. For nanoparticles, surface atoms are those resting on the surface, whereas for bulk materials, they are atoms located on the boundaries of the periodic cell. The cone algorithm [43] is used to choose surface atoms from atomic configurations. Other atoms beneath the surface layer are counted as inner atoms.

Figure 4.11 and Figure 4.12 show dependences of the global BOPs on temperature during the melting of bulk Au, 456-atom and 7,164-atom free Au nanoparticles. The global BOPs for inner atoms are shown by solid symbols and denoted by “IQi” or “IWi”. Those for surface atoms are shown by open symbols and denoted by
“SQ_i” or “SW_i”. The heating process is started from an ideal FCC structure at absolute zero. At low temperatures, the four parameters for both inner and surface atoms are very close to the predicted values for the FCC structure. As temperature increases, these parameters gradually change. However, the dominant structure is still thought to be FCC since the absence of any sharp transitions below the melting temperature indicates that no solid-state structural transformations occur. At the melting temperature, all four parameters abruptly jump to zero, indicating a clear phase transition to liquid states. Notice that the liquid values are not identically zero due to thermal fluctuations. The global BOPs of surface atoms behave quite differently for bulk solids and nanoparticles. In the bulk Au simulations, surface atoms on the boundaries of the periodic cell have BOPs identical to inner atoms. This is because with the use of periodic boundary conditions, no real surface exists in the periodic cell, and those boundary atoms behave the same as inner atoms. By contrast, in the free Au nanoparticle simulations, the global BOPs of surface atoms begin to deviate from those of inner atoms significantly below the particle melting temperature, suggesting that the surface is “softer” than the inner region of the nanoparticle.
Figure 4.11: Global BOPs versus temperature from the 6,912-atom periodic cell bulk Au simulation. BOPs are for "surface" (S) (i.e., boundary) and "inner" (I) regions of the cell; \( T_0 = 1385\) K.
Figure 4.12: Global BOPs versus temperature for free Au nanoparticles of two sizes. BOPs are for "surface" (S) and "inner" (I) regions of the nanoparticle. 

a) 456-atom Au nanoparticle ($T_m=835$K)

b) 7164-atom Au nanoparticle ($T_m=1045$K)
4.5.3 Analysis of surface premelting by local BOPs

Although the global BOP analysis shows different average behaviors of inner and surface atoms in free nanoparticles, it does not identify the underlying phenomenon responsible for this difference. In addition to surface premelting, surface solid-state structural transformations may also lead to reduced global BOPs. In this section, the local BOP $q_6$ of every atom is calculated and its add-up coherence is evaluated to identify solid-like or liquid-like states. All the results presented below are averaged over 100 stored configurations.

Figure 4.13 shows the evolution of the fraction of liquid-like to the total number of atoms versus temperature for surface and inner regions of free Au nanoparticles during heating (solid symbols). At low temperatures, most atoms are solid-like (a small fraction of surface atoms in the 456-atom Au nanoparticle are determined to be liquid-like, indicating some deficiency of the current algorithm). In contrast to the inner regions, which are melted mainly at the particle melting temperature, a large fraction of surface atoms are liquid-like well below the melting temperature. For example, at 950K (100K below the melting temperature of the 7,164-atom Au nanoparticle), only 1.16% of the inner atoms are identified as “liquid-like”, compared with 34.13% of the surface atoms. The fraction of liquid-like surface atoms increases gradually with temperature, suggesting a gradually increasing degree of surface premelting. However, the surface layer is not completely melted below the particle melting temperature and therefore the global BOPs still have a finite value (Figure 4.12). In the large 7164-atom Au nanoparticle, 88.12% of surface atoms are liquid-like at a temperature 5K below the particle melting temperature. This fraction is much higher than that in the small 456-atom Au nanoparticle, for which
only 51.21% of surface atoms are liquid-like. Figure 4.14 shows together the global BOP $Q_6$ and fraction of liquid-like atoms. It is clear that for the surface region (S) the reduction of the global BOP $SQ_6$ is associated with an increase of the fraction of liquid-like atoms, especially at temperatures above 500K. For the inner region (I), the decrease of inner BOP $IQ_6$ comes mainly from structural “softening” at high temperatures.

Simulations show that there are no observable abrupt changes in caloric curves for the increasing fraction of liquid-like surface atoms during melting. This indicates a significant difference between surface premelting, which is a second-order phase transition, and whole particle melting, which is a first-order transition. To investigate the reversibility of surface premelting, the nanoparticles were cooled from 5K below the particle melting temperature (this is done following the same procedure as for heating). Typical results are presented in Figure 4.13a and b by open symbols. No hysteresis is observed in the fraction of liquid-like atoms for surface premelting. These simulations support experimental findings [20][32][38][39] which also demonstrated that surface premelting is completely reversible. However, when the cooling starts from 1500K (well above the melting temperature of the entire nanoparticle), a clear hysteresis (Figure 4.13c) is observed for both surface and inner atoms.

Surface premelting also helps to understand the discrepancy discussed in Section 4.4.2 between the extrapolated $T_0$ and the calculated, using the periodic cell, bulk melting temperature (1,385 K) (Figure 4.7). At elevated temperatures, the liquid-like free surface serves as a nucleation site for continuous melting of the whole solid core, thereby preventing the nanoparticles from superheating. When the periodic cell is used in bulk Au simulations, the material can be superheated due to the absence of free surfaces and thus
the existence of large quantities of liquid-like atoms. Recently, an alternative simulation method that doesn’t employ a periodic cell was used by Luo et al. [80] to calculate the bulk Au melting temperature. They constructed a coexisting solid-liquid (two-phase) system with a clear planar solid-liquid interface. The melting temperature was determined as that at which there was no movement of the planar solid-liquid interface. Using the same Q-SC potential, they determined an equilibrium bulk melting temperature of 1075K for Au, which was thought to be the temperature without any superheating. This calculation implied that the degree of superheating in bulk materials predicted using periodic boundary conditions can be significant.
Figure 4.13: Fraction of liquid-like atoms versus temperature for free Au nanoparticles of two sizes: a) and c) 456-atom Au nanoparticle ($T_m=835K$) b) 7164-atom Au nanoparticle ($T_m=1045K$). “S” stands for “surface” and “I” stands for “inner” regions of the nanoparticle. In a) and b), Cooling starts just below melting temperature of the entire nanoparticle, while in c) Cooling starts from 1500K. Several snapshots of atomic configurations in the orthographic projection are also shown with liquid-like atoms colored black.
Figure 4.14: Comparisons between the global BOP $Q_6$ and fraction of liquid-like atoms versus temperature during the melting for free 7,164-atom Au nanoparticle ($T_m=1045K$). “S” stands for “surface” and “I” stands for “inner” regions of the nanoparticle.
4.5.4 Activation energy for liquid-like surface atoms formation

To better understand the temperature growth rate of the fraction of liquid-like surface atoms, kinetic curves, similar to those shown in Figure 4.13 for 456-atom and 7,164-atom Au nanoparticles, have been obtained for nanoparticles of other sizes. These curves are fitted from 500K to the temperature just before whole particle melting according to the equation:

\[ F - F(T=50K) = F_0 \exp\left(\frac{k_B T}{E_a}\right) \]  

(4.13)

where \( F \) is the fraction of liquid-like surface atoms, \( T \) is temperature, \( k_B \) is Boltzmann constant and \( E_a \) is activation energy of liquid-like surface atoms formation. The term \( F(T=50K) \) is needed since phase states of atoms at vertices or edges cannot be determined correctly by the current algorithm if they do not have five nearest neighbors. A number of surface atoms (between 0 and 24) are erroneously determined to be liquid-like even at the lowest temperature 50K.

Figure 4.15a presents temperature growth rates of fractions of liquid-like surface atoms for six larger samples of Au nanoparticles (\( N=2,808-22,360 \)). These curves can be fitted exceptionally well by Eq. (4.13) in the logarithmic scale through \( \ln(F_0)=-8.86318 \) and \( k_B/E_a=0.0082K^{-1} \), yielding a statistical measure of degree of correlation \( R^2 \) as high as 0.99. In Figure 4.15b, the same parameters are used to fit the growth rates for five smaller Au nanoparticles (\( N=456-2,112 \)). Higher scatter of data is observed in this case (\( R^2 \) of 0.84), while larger particles in this region tend to be closer to the fitted line. Thus, we have reached a very important conclusion: the formation of liquid-like surface atoms in Au nanoparticles, independent of their particular sizes, follows similar exponential temperature growth rates described by Eq. (4.13).
From $k_B/E_a=0.0082K^{-1}$, the activation energy $E_a$ for the formation of liquid-like surface atoms is 0.99kJ/mol. This is a fairly small value compared with the bulk or particle latent heat of fusion (Figure 4.8). As discussed in Section 4.4.3, successful application of Kofman et al.’s model implies that inner atoms in nanoparticles have the same latent heat of fusion as those in bulk materials (i.e. 12.35kJ/mol). Considering that in FCC every inner atom has 12 nearest neighboring bonds, the energy required to change the phase state of a single bond is just 1.03kJ/mol, almost identical to $E_a$. This fact is expected because in the current algorithm, a surface (inner) atom is defined as solid-like if having more than five (six) “crystal-like” neighboring bonds; otherwise it is defined as liquid-like. Thus to form a liquid-like atom, it is sufficient to break a single “crystal-like” bond. Surface premelting then seems more akin to a second-order rather than a first-order phase transition.
Figure 4.15: Growth rates of fractions of liquid-like surface atoms versus temperature a) for six larger samples of nanoparticles (N=2,808-22,360); the straight line is fitted using Eq. (4.13); b) for five smaller samples of nanoparticles (N=456-2,112); the straight line is the same line as used in a)

\[ \ln(F - F(50K)) = \ln(F_0) + k_B T / E_a \]

Correlation: \( R^2 = 0.9906 \)

\[ \ln(F_0) = -8.86318 \pm 0.09214 \]

\[ k_B / E_a = 0.0082 \pm 0.00011 \]
4.6 Nonhomogeneous Surface Premelting Model

4.6.1 Evolution of surface solid/liquid-like regions and its relationship with local surface orientations

As stated in Section 4.1, the existence of surface premelting on flat surfaces of bulk solids is found to be orientation-dependent due to the anisotropy of the surface energy excess \( \Delta \gamma = \gamma_s - \gamma_l - \gamma_{sl} \) [11]. For example, using the “glue” potential, MD simulations of bulk Au showed that \{110\} surfaces were completely premelted [29] whereas \{111\} surfaces remained stable up to the bulk melting temperature, indicating complete lack of surface premelting [30]. A liquid layer was also generated on \{100\} surfaces, but its thickness did not increase with temperature [31]. Our own melting simulations, using the Q-SC potential, of flat Au surface premelting indicate that the melting temperatures of \{111\} surfaces are higher than that of \{110\} or \{100\} surfaces. Although continuous growth of the surface liquid layer was found on all surface planes prior to melting, the \{111\} surfaces have the smallest liquid layer thickness at the same temperature below the flat surface melting temperature, with the \{110\} surfaces having the largest. It is important to understand if the above findings also hold for nanoparticles; if so, this will help to understand why surface premelting in Au nanoparticles is a nonhomogeneous, gradually occurring process.

The local surface orientation was calculated for each solid-like atom based on its nine closest neighbors [81]-[83]. If the angle between the obtained normal vector and any of the three crystallographic planes \{111\}, \{100\} or \{110\} is less than 15\(^\circ\), that atom is considered as belonging to that plane. As examples, the corresponding snapshots of single atomic configuration are shown as inserts in Figure 4.16a&b for the 456 and
7,164-atom Au nanoparticles. They are also shown in a larger scale in Figure 4.16c&d.

At 50K, the surface is clearly faceted. The surface premelting occurs in three stages: 1) at 600K, liquid-like atoms (red) begin to appear at some vertices or edges of surface facets. Since the orientation algorithm is not sufficiently accurate at sharp edges of the faceted surface, the orientation was not determined for some solid-like atoms (white). This “edge premelting” phenomenon is well known in the melting of 2D solids [84]. Wang et al. [43] also found that the increasing mobility of vertex and edge atoms greatly contributes to the initial structural “softening” in their icosahedral gold clusters. 2) from 600K to 800K (1000K) in the 456-atom (7,164-atom) Au nanoparticle, the edges get rounder and broader and contain mostly liquid-like atoms; those liquid-like regions are created by the joining of neighboring liquid-like atoms and the solid-like facets shrink in size with only atoms belonging to {111} or {100} planes left. 3) Finally, at 5K below the particle melting temperature, a large portion of the surface becomes liquid-like. The largest solid-like region is found on the {111} plane, which is most stable against surface premelting on flat surfaces. Note that not every {111} plane is solid-like. This agrees with the formation of premelted surface layers on flat unbounded Au {111} surfaces that were observed in our MD simulations.

Since each image in Figure 4.16c&d represents only one configuration at a given temperature, to obtain a statistically representative result associating surface atoms with different crystallographic planes, we have generated 1,000 configurations for the 7,164-atom Au nanoparticle at several different temperatures. Next for every surface atom the number of configurations was counted in which the surface atom is solid-like (approximately 1,350 surface atoms exist before the particle melting). Only atoms which
are solid-like in more than 500 configurations are considered stable. They are usually in the central parts of solid-like surface “islands” whose boundaries may vary from configuration to configuration even at the same temperature. For these stable solid-like atoms, we have determined the corresponding local crystallographic planes in each configuration. Figure 4.17 shows the probability for such an atom to be on a specified crystallographic plane at several temperatures near the particle melting temperature. Most of the stable solid-like surface atoms reside on the \{111\} plane. The probability increases with temperature indicating the relative stability of this plane in Au nanoparticles. This observation is consistent with the stability of \{111\} planes in bulk Au up to the bulk melting temperature [30].
Figure 4.16: a)&b) Fraction of liquid-like atoms versus temperature for free Au nanoparticles of two sizes: N=456 (T_m=835K) and N=7164 (T_m=1045K). “S” stands for “surface” and “I” stands for “inner” regions. Heating, denoted by solid symbols, starts at 50K; Cooling, denoted by open symbols, starts 5K below the particle melting temperature to show the reversible surface premelting. c)&d) Snapshots of atomic configurations in the orthographic projection for above two nanoparticles at different temperatures. Blue: solid-like atoms on {111} planes; Green: solid-like atoms on {100} plane; Black: solid-like atoms on {110} plane; White: other solid-like atoms; Red: liquid-like atoms.
Figure 4.17: Probability of the stable solid-like atom to be on a specified crystallographic plane at different temperatures for the 7,164-atom Au nanoparticle. Only atoms which are solid-like in more than half of 1000 configurations are considered as stable. These atoms mainly reside on \{111\} planes which are the most stable against surface premelting.

4.6.2 Growth of liquid regions and equivalent liquid-like layer thickness

We have seen liquid-like regions form on the Au nanoparticle surface prior to melting; this we attribute to orientation-dependent surface premelting: different local surface planes on nanoparticles have different surface premelting potentialities. With temperature increase these liquid-like surface regions not only increase in area but deepen into the inner regions of the nanoparticle even prior to formation of a contiguous liquid layer on the surface. This is illustrated in Figure 4.18a by snapshots of atomic configurations indicating solid-like regions and liquid-like regions at the temperature 5K below the nanoparticle melting temperature. Compared with the rather round liquid-like regions, the solid-like core is faceted. The liquid-like region in the 7,164-atom
nanoparticle forms a contiguous “connected” liquid surface layer (complete premelting) whereas in the 456-atom nanoparticle, no such layer spanning the entire nanoparticle is observed (partial premelting). A quantitative study of the connectivity of these liquid-like regions on the nanoparticle surface using percolation theory will be given later to help determine the state of surface partial premelting or complete premelting. The liquid-like or solid-like states of nanoparticle atoms for each atomic layer have been determined by using the “cone” algorithm [43]. In Figure 4.18b, results in the first four layers are presented for the 7,164-atom nanoparticle. With temperature increase, the fraction of liquid-like atoms in every layer increases almost monotonically, behaving like the liquid-like layer thickening. The equivalent liquid-like layer thickness $\delta$ is defined as the summation of fractions of liquid-like atoms in all the atomic layers times the average atomic layer thickness $\bar{h}$ ($\bar{h} = R/n_L$, where $R$ is radius of Au nanoparticle and $n_L$ is number of atomic layers). This parameter, as a function of temperature, is plotted by a dotted line to illustrate the evolution of surface premelting in Figure 4.18b. Before the whole particle melts, this value remains relatively small (less than 0.56nm), whereas after that it is close to the particle radius.

The thickness $\delta$ at the temperature 5K below the particle melting temperature is shown in Figure 4.18c for all the eleven sizes of Au nanoparticles we have considered. Clearly, $\delta$ doesn’t increase monotonically with particle size; instead, from analysis of the results (like those shown in Figure 4.18b) for all nanoparticle sizes, they are grouped based on the number of activated layers (those containing liquid-like atoms). When $456 \leq N \leq 1,556$, the first two layers are activated before the particle melting. When $1,556 \leq N \leq 7,164$, the first three layers are activated. Finally for nanoparticles $N > 7,164$, at
least the first four layers are activated. It is noticeable that in each group, $\delta$ differs little; but between groups, the change is significant especially for the largest-size nanoparticles group. One can attribute the large change in $\delta$ for this last group to formation of a contiguous liquid layer, i.e., complete surface premelting (see below). Buffat and Borel [16] considered Au nanoparticle size similar to ours and obtained liquid layer thickness 0.62nm. Au nanoparticles studied by Sambles [28] are much larger and have a radius between 5nm and 30nm. This leads to a liquid layer thickness as high as 2.2nm. These authors estimated the liquid layer thickness through the fitting of experimental or MD simulated size-dependent melting temperature using the liquid-shell model using a single parameter $\delta$ for nanoparticles of all sizes.
Figure 4.18: a) Snapshots of atomic configurations for free Au nanoparticles of two sizes: N=456 at 830K (T_m=835K) and N=7,164 at 1040K (T_m=1045K). Liquid-like atoms are red and solid-like atoms are white. The liquid surface layer is clearly nonhomogeneous b) Fraction of liquid-like atoms in first four layers and equivalent liquid-like layer thickness δ (dotted line in log scale) versus temperature for the 7,164-atom Au nanoparticle c) δ at a temperature 5K below the particle melting temperature versus radius of Au nanoparticles: three groups based on the number of layers containing liquid-like atoms are identified.

4.6.3 Partial and complete surface premelting: percolation study

As have been discussed above, the nonconnected continuous regions (“lakes”) formed by liquid-like atoms appear with temperature increase. For the larger 7,164-atom Au nanoparticle, these separate regions finally coalesce into one largest region containing almost all the surface liquid-like atoms just before the particle melting. Since the fraction of liquid-like surface atoms usually does not reach 100% before particle melting, the
question can be raised, when can one say that a contiguous liquid layer is formed on the surface (in other words, the surface is completely premelted)?

In our work, a percolation theory [85]-[87] has been applied to study quantitatively the occurrence of the transition (percolation) from disconnected liquid regions to a contiguous liquid layer. A percolation problem has been considered on surfaces of nanoparticles at different temperatures. The element occupation probability $p$ is just the fraction of liquid-like surface atoms. A liquid-like continuous region is defined as a group of liquid-like atoms with spacing less than the predefined cutoff radius 3.4Å. The percolation threshold $p_c$ is reached when with increase of temperature a contiguous liquid-like region first spans the whole surface; this state is defined as complete surface premelting. Our objective is to test at any given temperature, whether the fraction of liquid-like surface atoms $p$ is above $p_c$ or not. The algorithm is as follows: first, the largest liquid-like surface region in every configuration at the same temperature is found; next, for any two atoms $i$ and $j$ in this largest region, the inequality $||r_i + r_j|| \leq \varepsilon$ is checked, where $r_i$ and $r_j$ are position vectors originating at the center of the particle, and $\varepsilon$ equals 0.5Å or 1.0Å. Although $\varepsilon$ is zero if the nanoparticle is spherical, values 0.5Å or 1.0Å are chosen based on the fact that $||r_i + r_j||_{\text{min}}$ in the fully melted nanoparticle varies between 0.40Å and 0.675Å depending on the particle size. If this inequality is satisfied, atoms $i$ and $j$ are on two “opposite” sides of the surface. This implies that the largest liquid region has spanned the whole surface and the percolation point $p_c$ is reached in this configuration. 100 different configurations have been considered for each temperature and each size and the fraction of configurations in which at least one pair of “opposite” atoms can be found is calculated. Table 4.5 presents the results for the 456-atom and the
7,164-atom Au nanoparticle. The fraction of configurations in which the percolation threshold is reached decays very quickly with temperature decrease. For the larger 7,164-atom Au nanoparticle at 1040K, the percolation threshold is reached in every configuration, i.e., a contiguous liquid-like layer spanning the whole surface is always found. However, at a temperature 30K lower (1010K), this contiguous spanning liquid-like layer doesn’t appear in any configuration. For the smaller 456-atom Au nanoparticle, even at 830K (5K below the particle melting temperature) only 32% of the configurations contain a contiguous spanning liquid-like layer. Thus, we found that the status of surface premelting largely depends on the particle size. In small nanoparticles, the surface is usually partially premelted, but in large enough nanoparticles, the surface is always completely premelted.

To determine the temperature dependence of the liquid-like region growth, we define a parameter, called the normalized largest region size, $S_{\text{max}}$ as the number of atoms included in the largest region divided by the total number of surface liquid-like atoms. This parameter, as a function of temperature, is plotted in Figure 4.19 for Au nanoparticles of two different sizes; these curves are terminated by the particle melting temperature. It again indicates that all the surface liquid-like atoms in larger nanoparticles are connected to each other before the whole particle melts but fall into several “unconnected” competing regions in small nanoparticles.
<table>
<thead>
<tr>
<th>Temperature</th>
<th>N=456</th>
<th>N=7,164</th>
</tr>
</thead>
<tbody>
<tr>
<td>ε=0.5 Å</td>
<td>0.09</td>
<td>0</td>
</tr>
<tr>
<td>ε=1.0 Å</td>
<td>0.32</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table 4.5: Fraction of configurations versus temperature in nanoparticles of two sizes in which the percolation threshold $p_c$ is reached: surface is completely premelted in the larger 7,164-atom Au nanoparticle; in the smaller 456-atom Au nanoparticle, surface is only partially premelted in most of the configurations.

Figure 4.19: Normalized largest liquid-like region size $S_{max}$ versus temperature for free Au nanoparticles of two sizes: N=456, $T_m$=835K and N=7,164, $T_m$=1045K.
4.7 Summary and Conclusions

In this chapter, nonhomogeneous melting mechanism of various sized Au nanoparticles (N=456 to 22,360) was studied systematically by molecular dynamics simulations. By adapting a method of atomic structural characterization developed by Wolde et al. [63][64] we have identified liquid-like atoms by computing the add-up coherence of the local BOP $q_6$. This provides the first direct evidence of surface premelting or structural disordering prior to the melting of the whole nanoparticle. We have concluded that the melting is initiated on the surface of a nanoparticle. Liquid-like atoms start to appear in vertices or edges of surface facets. These liquid-like edges get rounder and broader with temperature increase but solid-like facets shrink in size. At temperature close to the particle melting point, most of solid-like surface atoms are found belonging to {111} planes which are stable against surface premelting on flat surfaces of bulk solids. For larger Au nanoparticles like $N \geq 7,164$, the surface is completely premelted whereas for smaller nanoparticles like $N = 456$, it is only partially premelted. The ratio of the number of liquid-like surface atoms to the total number of surface atoms increases with temperature and follows the same exponential growth rate for different sized Au nanoparticles. The activation energy of liquid-like surface atoms formation (1kJ/mol) is much smaller than the bulk Au or particle latent heat of fusion and corresponds to the energy required to change the phase state of any single bond between atoms. Due to this small activation energy, surface premelting is demonstrated as a reversible process, in correspondence with two experimental reports [20][32]. Surface premelting can proceed into the inner region of Au nanoparticles without a completely premelted surface. The equivalent liquid-like layer thickness $\delta$ is shown to be size-
dependent and thickening continuously with temperature increase. Its value at 5K below the particle melting temperature depends strongly on the number of activated layers and falls between 0.15\text{nm} and 0.60\text{nm} in sizes we considered, which is comparable to other studies [16][28].

Surface premelting reduces superheating of nanoparticles during melting. This explains a discrepancy between the melting temperature extrapolated from simulation results for nanoparticles of increasing size and the melting temperature predicted by bulk Au simulations. As shown in the global BOP plots, in bulk Au simulation, melting is not initiated on periodic cell boundaries but occurs in the whole cell at the same temperature. The superheating is then inevitable in this condition.
Chapter 5. Melting under Ultrafast Laser Irradiation: MD Simulations

5.1 Introduction

Ultrafast laser processing of metal nanoparticles has been an intensive research area in the past decade. A fundamental understanding of ultrafast and nonequilibrium processes induced in nanoparticles is beneficial. Generally speaking [88], when solids are irradiated by ultrafast laser pulses, the resulting nonequilibrium thermal phenomena include instantaneous heat absorption in electrons, gradual heat exchange between hot electrons and cold atoms, and limited heat conduction from solids to the surrounding medium. If the laser intensity is high enough, melting, evaporation or ablation could occur. The physical and chemical properties of nanoparticles exhibit strong size effects due to their high surface area to volume ratios. This further complicates the subject. For example, melting temperatures are significantly reduced at nanoparticle sizes below 5nm. Besides this, melting in nanoparticles could start on selective surface crystalline planes at a temperature lower than the temperature when the whole nanoparticle melts. This “surface premelting” at low temperatures may facilitate sintering of nanoparticles and formation of nanoscale features.

Numerous experimental efforts have been undertaken to expand application areas of ultrafast laser processing of metal nanoparticles. Optical spectroscopy [89]-[91] with very low laser intensity has been widely used to probe ultrafast electron/lattice dynamics
in metal nanoparticles. The particle temperature is obtained indirectly by relating the transmission/reflection coefficient to temperature-dependent dielectric constants or average particle sizes. Morphological changes of spheroidal nanoparticles or nanorods into nanospheres [92]-[97] have been induced by ultrafast laser at low temperatures and were attributed to surface premelting. Increasing laser intensity causes fragmentation, size reduction or enlargement of nanoparticles to the uniform distribution [98]-[102], or the coalescence of Au nanoparticles supported on a quartz substrate [103]. At high laser intensity, irradiated metal nanoparticles also act as localized heat sources. They may undergo explosive vaporization to create nanoholes in the silicon substrate [104] or provide photothermal therapy on cancer cells [105]-[106].

Numerical models have been proposed recently to obtain a deeper understanding of microscopic mechanisms of ultrafast laser interaction with metal nanoparticles. Hydrodynamic computational models [107][108] were applied for understanding irradiation of Au nanoparticles in aqueous media. Equilibrium equations of state of bulk materials were assumed there, which may not be accurate for nanoparticles with strong size dependent physical properties and under ultrafast nonequilibrium conditions. Direct molecular dynamic (MD) simulations use carefully specified interatomic interactions, and make no assumptions about thermal processes. To the authors’ knowledge, only few such MD efforts are available: a study of explosive phase transitions and fragmentation of nanoparticles [109] and simulations of vibration modes and elastic properties of Au nanoparticles [110].

This chapter focuses on the microscopic mechanism of heating and phase evolution resulted from ultrafast laser irradiation of Au nanoparticles. Since heat
conduction to the surrounding medium is omitted in our analysis, it best represents cases for free-standing nanoparticles in the inertia gas or nanoparticles on the amorphous substrate with rather slow heat conduction so that the total energy conservation will not be violated. It is shown, among our major new results, that at some laser energies the nanoparticle is superheated at some stage of the melting evolution followed by a thermodynamically stable supercooling stage. At somewhat smaller laser energies a surface premelting occurs with a thermodynamically stable liquid-solid coexistence state.

The chapter is structured as following. An integrated MD and two-temperature (TTM) computational model is detailed in Section 5.2. Structural characterization method of solid/liquid atoms and percolation analysis of surface premelting are outlined in Section 5.3.1 and 5.3.2 respectively. In Section 5.4.1, the evolution of electron temperature $T_e$, lattice temperature $T_l$ and fraction of solid atoms $\eta$ are outlined in general. Different aspects of the kinetic curves are studied in great detail in the following sections. Namely, Section 5.4.2 discusses nonhomogeneous surface premelting under ultrafast laser irradiation. Section 5.4.3 discusses results of percolation studies when disconnected surface liquid regions turn into a contiguous surface liquid layer. Section 5.4.4 evaluates conditions for temporary lattice superheating. Section 5.4.5 discusses the melting front velocity and catastrophic solid inner core melting. Section 5.4.6 discusses the equilibrated $T_l$ and $\eta$ at different laser pulse durations and related constant energy simulations. Section 5.5 summarizes our findings.
5.2 Computational Model for Nanoparticle State Evolution under Ultrafast Laser Irradiation

5.2.1 Integration of TT and MD models for metals

For metals and metallic materials, computational modeling of ultrafast laser irradiation is commonly based on the two-temperature model (TTM) [88][111], which was named after its separate treatment of electron temperature $T_e$ and lattice temperature $T_l$. Here “lattice temperature” doesn’t necessarily imply that materials retain the crystalline order. It simply represents a measure of temperature through atomic vibrations, and is different from “electron temperature” which measures electronic vibrations. TTM describes thermal phenomena like instantaneous heating of electrons by laser irradiation, energy exchange between hot electrons and cold lattice, and corresponding lattice heating by two coupled nonlinear differential equations:

$$
C_e(T_e) \frac{dT_e}{dt} = \nabla \cdot \left[ K_e(T_e, T_l) \nabla T_e \right] - G(T_e - T_l) + S
$$

$$
C_l(T_l) \frac{dT_l}{dt} = \nabla \cdot \left[ K_l(T_l) \nabla T_l \right] + G(T_e - T_l) + \dot{E}_{\text{out}}
$$

Here the quantities with subscripts $e$ and $l$ are associated with electrons and lattice, respectively. $C$ and $K$ are constant pressure heat capacity and thermal conductivity, $G$ is the electron-lattice coupling factor by which the rate of energy exchange between electrons and the lattice is determined, $S$ is the energy source of laser heating, and $\dot{E}_{\text{out}}$ is the rate of energy dissipation into surrounding media.

Despite wide applications of the analytical TTM, it bears some inherent limitations as stated in [112]: it does not accommodate accurate material phase evolution during thermal processes. In our case, the physics of surface premelting and solid-liquid
phase transitions occurring under highly nonequilibrium conditions induced in metal nanoparticles by ultrafast laser irradiation is not yet well understood and therefore could not be described reliably by analytical kinetic equations and thus not be included in the analytical TTM. On the contrary, MD simulations provide results based on carefully specified interatomic interactions, and make no assumptions about physical processes of surface premelting and solid-liquid phase transitions. It is advantageous to integrate MD simulations with the analytical TTM model for providing a more realistic description of induced thermal phenomena.

An integration scheme of these two methods, originally proposed by Ivanov and Zhigilei [112] and applied to metal thin films, is adapted in this work to free metal nanoparticles. This integration scheme mimics physical fact that energy exchange between electrons and the lattice is achieved through collisions. The first equation of (5.1) is solved by forward finite difference at the beginning of each time step to update the electron temperature $T_e$. MD simulations are then applied in replacing the second equation of (5.1) to calculate atomic motions. Since atomic velocity distribution in our simulated nanoparticles is always found to satisfy Maxwell-Boltzmann distribution, the lattice temperature $T_l$ could be defined from kinetic energy $E_k$ as $2E_k = NkT_l$, where $N=3n-6$ is degree of freedom and $k$ is the Boltzmann constant. The energy coupling term $G(T_e-T_l)$, as shown in Eq. (5.2), is evaluated at the end of each time step and is expressed as an external force adding to the Newton equations in MD simulations of the next time step:

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i + \xi m_i \mathbf{v}_i$$

where $\xi = G(T_e - T_l) / \sum m_i (\mathbf{v}_i)^2$
Here \( m_i, \mathbf{r}_i \) and \( \mathbf{v}_i \) are the mass, position, and velocities of an atom \( i \), and \( \mathbf{F}_i \) is the interatomic force acting on atom \( i \).

5.2.2 The model assumptions

Several simplifications have been introduced when adapting the integrated TTM-MD scheme in [112] from metal thin films to free Au nanoparticles.

First, energy diffusion term \( \nabla \cdot [K \nabla T] \) in both electrons and the lattice is omitted. In [112], the 50nm thick free-standing thin film is discretized spatially into small cells (typically \( \sim 1 \)nm thick with a cross section area 4nm\( \times \)4nm). Electrons and the lattice within the same cell are in the state of local equilibrium and exchange energy locally. In our simulations, we considered the whole nanoparticle as a single cell in local equilibrium. Electrons and the lattice are assumed to be heated homogeneously and possess the same \( T_e \) or \( T_l \) everywhere. Since the effective laser energy deposition depth in Au is estimated to be larger than 100nm [113] and our simulated nanoparticle sizes are less than 3.3nm, above assumption is reasonable. Due to this assumption, atomic velocity distribution in our simulated nanoparticles is always found to satisfy Maxwell-Boltzmann distribution so that the lattice temperature \( T_l \) could be defined from kinetic energy \( E_k \).

Second, energy dissipation term \( E_{\text{out}} \) is also not considered. Therefore our simulations best represent cases for free-standing Au nanoparticles in the inertia gas or Au nanoparticles on the amorphous substrate with rather slow heat conduction so that total energy is conserved after the laser pulse terminates. We estimated that the characteristic cooling time \( \tau_c \) for Au nanoparticles in air is on the order of several tens of nanoseconds [114]; whereas for Au nanoparticles in aqueous solutions, \( \tau_c \) as long as
several hundreds of picoseconds was reported [115]. Both time scales are well beyond the duration of ultrafast laser pulses (150fs~100ps) or solid-liquid phase transitions in our simulations.

Third, the energy source of laser heating $S$ has a temporal Gaussian distribution, but its spatial profile on the plane normal to laser beam propagation is taken as uniform because the laser spot size (>0.1μm) is much larger than our simulated nanoparticle sizes (<3.3nm).

$$S = \sqrt{\frac{\beta}{\pi}} \frac{E_0}{\sigma_L} \exp\left[-\beta \left(\frac{t-2\sigma_L}{\sigma_L^2}\right)^2\right]$$  \hspace{1cm} (5.3)

where $\beta$=4ln2, $\sigma_L$ is laser pulse duration and $E_0$ is molar absorbed laser energy by nanoparticles (unit: kJ/mol). In this chapter, $E_0$ is the only parameter to characterize input laser intensity, which greatly facilitates comparisons of results from different nanoparticle sizes and laser pulse durations. For nanoparticles in aqueous solutions, the Beer-Lambert law relates $E_0$ with measurable laser fluence $F_0$:

$$E_0 = F_0 \left(1 - 10^{-\alpha l} \right) / C l$$  \hspace{1cm} (5.4)

where $l$ is the depth of a region from the incident surface of the laser beam, $\alpha$ is molar absorption coefficient at current laser wavelength, and $C$ is the concentration of nanoparticles. For the phenomenon occurring in the vicinity of the irradiated surface ($l\rightarrow0$), $E_0$ becomes independent of $C$ and $l$, and Eq. (5.4) is simplified to $E_0=2.3\alpha F_0$. For pulses following a temporal Gaussian distribution, laser fluence $F_0$ (J/cm$^2$) is further related to laser intensity $I_0$ (W/cm$^2$) as $F_0=1.0645\sigma_L I_0$.

Fourth, surface plasmon resonance is neglected in our simulations. The typical resonance wavelength for spherical Au nanoparticles is lower than 600nm [90][91]. We
considered in this chapter only ultrafast laser pulses with a wavelength above 775nm (the suitable working range for many ultrafast laser systems).

5.2.3 Selections of thermophysical properties

Thermophysical properties have to be carefully chosen in numerical evaluations of the integrated TTM+MD model. When electron temperature $T_e$ is lower than 10% of the Fermi temperature $T_F$, electron heat capacity $C_e(T_e)$ is usually taken to be linearly proportional to $T_e$ as $C_e(T_e) = \gamma T_e$ and the electron-lattice coupling factor $G$ is constant [112][116]. Based on first-principle electronic structure calculations, Lin et al. [117] tabulated the dependence of electron heat capacity $C_e$ and electron-lattice coupling factor $G$ on electron temperature $T_e$ up to $2 \times 10^4$K for eight metals including Au. Compared with conventional approximations, the new material property set indicates much higher $C_e$ and $G$ at strong laser excitations when $T_e > 3000$K. Figure 5.1 compared simulation results with different material property sets: the solid line was simulated with thermophysical properties in [117], whereas the dashed line was simulated with constant $G (=3.06 \times 10^{11} \text{Wmol}^{-1}\text{K}^{-1})$ and $\gamma (=6.42 \times 10^{-4}\text{Jmol}^{-1}\text{K}^{-2})$. At $E_0=40\text{kJ/mol}$, the newly developed material property set clearly predicts lower maximum electron temperature, faster lattice temperature increase and earlier decrease of fraction of solid atoms, consistent with its larger $C_e$ and $G$ at strong laser excitations. However, equilibrated states have little dependence on different selections of thermophysical properties. Throughout this chapter, only $C_e$ and $G$ in [117] are used.
Figure 5.1: Electron-lattice temperature equilibration process and evolution of fraction of solid atoms simulated using conventional approximations of thermophysical properties ($C_e=\gamma T_e$ and $G=\text{const}$, dashed line) and newly tabulated electron temperature dependent thermophysical properties ($C_e=\gamma(T_e)T_e$ and $G(T_e)$, from Lin et al. [117], solid line). a) Electron temperature $T_e$; b) Lattice temperature $T_l$; its oscillation is due to elastic vibrations of nanoparticles; c) Fraction of solid atoms $\eta$ of the 7,164-atom Au nanoparticle under ultrafast laser irradiation (pulse duration $\sigma_L=150\text{fs}$, absorbed energy $E_0=40\text{kJ/mol}$).
Figure 5.1 continued

5.2.4 MD simulation procedures

Simulations were performed at the Ohio Supercomputing Center (OSC) with the publicly available MD source code DL_POLY_2 [51]. For our ultrafast melting simulations, the MD code was modified to incorporate the analytical TTM model as detailed in Section 5.2. Constant temperature is maintained by the Nosé-Hoover thermostat [54][55]. Constant pressure is maintained by the Melchionna modification of the Hoover barostat [55][56]. The integration time step for both analytical TTM model and MD simulations was set to 4fs. It ensures that the total energy in the integrated model is conserved with the maximum energy drift of less than 0.01% during any of the simulations discussed in this chapter. The Visual Molecular Dynamics (VMD) package [57][58] and the Maximal Speed Molecular Surface (MSMS) program [59] were used to display and animate atomic configurations.
DL_POLY_2 provides the Quantum Sutton-Chen (Q-SC) many-body potential [53] for metals. For bulk Au modeled by 3D periodic boundary conditions (PBC) with 12×12×12 FCC unit cells (6,912 atoms) at constant zero pressure, as shown in Section 4.3, our simulations predict the melting temperature is 1385K and latent heat of fusion is 12.35kJ/mol, pretty close to the experimental value 1337K and 12.55kJ/mol respectively.

Several sizes of Au nanoparticles (N=456-7,164) prepared from a perfect FCC crystal were considered in this chapter. Their radii at room temperature and size-dependent melting temperatures are listed in Table 5.1. Before ultrafast melting simulations, nanoparticles were equilibrated in 300K for 200ps within constant temperature ensemble maintained by the Nosé-Hoover thermostat. A wide range of absorbed laser energy $E_0$ (5~40kJ/mol) and laser pulse duration $\sigma_L$ (150fs~100ps) were then applied. Au nanoparticles evolve freely for the first 150ps to 600ps (depending on the length of $\sigma_L$) to undergo melting and phase transitions. Additional 50ps was added in the end to generate equilibrated electron temperature $T_e$, lattice temperature $T_l$ and fraction of solid atoms $\eta$. All the presented results, unless otherwise specified, are averaged over ten independent runs with different initial Au nanoparticle configurations dumped at 300K.

In addition to ultrafast melting simulations, we have also performed constant energy equilibrium melting simulations for the purpose of comparison. Starting from initial temperature 300K, Au nanoparticles were subjected to a heating process consisting of a series of increasing energy levels from 1kJ/mol to 40kJ/mol. At the first time step of each energy level, atomic velocities of Au nanoparticles were scaled proportionately to
mimic energy increase. Au nanoparticles were then allowed to evolve freely for 150ps and additional 50ps was simulated to generate the equilibrated data.

<table>
<thead>
<tr>
<th>$N$</th>
<th>$R$ (nm) at 300K</th>
<th>$T_m$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>456</td>
<td>1.22</td>
<td>835</td>
</tr>
<tr>
<td>736</td>
<td>1.43</td>
<td>915</td>
</tr>
<tr>
<td>1,556</td>
<td>1.84</td>
<td>965</td>
</tr>
<tr>
<td>3,604</td>
<td>2.44</td>
<td>1015</td>
</tr>
<tr>
<td>7,164</td>
<td>3.07</td>
<td>1045</td>
</tr>
</tbody>
</table>

Table 5.1: Spherical Au nanoparticles studied in this chapter: the number of atoms, radius at room temperature and their size-dependent melting temperatures.

5.3 Analysis Methods

5.3.1 Structural characterization of solid-like and liquid-like atoms

In our previous study of nanoparticle equilibrium melting simulations (Chapter 3), we have applied a local bond-orientational order parameter (BOP) method, developed by Wolde et al. [63][64], to identify solid-like and liquid-like atoms. This method has been detailed in Section 4.2.2. The cone algorithm [43] was used to select surface atoms from atomic configurations. The side length of the cone ($a$) is 5.0Å and its angle ($\theta$) is $\pi/3$. Any atoms beneath the surface layer are counted as inner atoms.

In equilibrium melting simulations, atomic positions averaged over a number of configurations are usually used to perform local BOP analysis in order to reduce the effect of thermal oscillations of atoms and reflect the physical meaning of order parameters as a statistically averaged quantity. In highly nonequilibrium ultrafast laser
irradiation melting simulations, one question arises immediately that how many configurations should be averaged to obtain atomic positions without damaging the time evolution study of melting. Figure 5.2 shows our experiments on this issue. Clearly under $\sigma_L=150\text{fs}$ and $E_0=40\text{kJ/mol}$, i.e., the most violent irradiation considered in our simulation cases, time evolution of fraction of surface and inner solid-like atoms determined from the instantaneous configuration, and from the configuration averaged over 25 or 50 consecutive time steps (a time span of 0.1 or 0.2ps), look almost identical. In our following analysis, only the instantaneous configuration, dumped at an interval of 25 time steps, will be used in determining solid-like and liquid-like atoms. This choice is based simply on favoring a much smaller saved trajectory file size. However, as justified by Figure 5.2, it will not lose the physical meaning of order parameters as a statistically averaged quantity.
Figure 5.2: Fraction of solid atoms on the surface and in inner regions determined by local bond-orientational order parameter (BOP) method. Time variation curves calculated from the instantaneous atomic configuration and from the atomic configuration averaged over 25 or 50 consecutive time steps (a time span of 0.1 or 0.2ps) are almost identical. Note that calculations use the 7,164-atom Au nanoparticle under laser pulse duration $\sigma_L=150$fs and absorbed laser energy 40kJ/mol, i.e. the most violent irradiation considered in our simulation cases.

5.3.2 Percolation study of surface premelting

The percolation theory is applied on surfaces of nanoparticles to study quantitatively the transition (percolation) from disconnected liquid regions to a contiguous liquid layer. This theory discusses the effects of varying the connectivity of elements (particles, sites, or bonds) in a system on its physical properties, such as conductivity or permeability [85]-[87]. We define a connected group of elements as an island. The connectivity in the system is a function of the element occupation probability $p$ and is usually measured by average or largest island size. At the percolation threshold
$p=p_c$, these measures of connectivity undergo a sharp transition. The largest island is found to span the whole system or become infinite in size. The system becomes conductive or permeable. The percolation transition is analogous to second-order phase transition.

In our percolation study, we have defined the element occupation probability $p$ as the fraction of liquid surface atoms. A liquid island (connected liquid surface region) is defined as a group of liquid surface atoms with spacing less than the predefined cutoff radius $3.4\text{Å}$. The percolation threshold $p_c$ is reached when a contiguous liquid island first spans the whole surface of nanoparticles. We define this state as complete surface premelting. The algorithm is as follows: first, the largest liquid island is identified in each configuration; second, minimum of $\|\mathbf{r}_i + \mathbf{r}_j\|$ is determined for any two atoms $i$ and $j$ in this island, where $\mathbf{r}_i$ and $\mathbf{r}_j$ are position vectors originating from the center of the nanoparticle; third, if in one configuration and its successive configurations, the inequality $\|\mathbf{r}_i + \mathbf{r}_j\|_{\text{min}} \leq \varepsilon$ is satisfied, we claimed that the percolation threshold is reached. Here $\varepsilon$ equals $0.5\text{Å}$ for the 7,164-atom Au nanoparticle. This value is selected based on the fact that $\|\mathbf{r}_i + \mathbf{r}_j\|_{\text{min}}$ in the fully melted nanoparticle is around $0.40\text{Å}$. The satisfaction of this inequality indicates that atoms $i$ and $j$ are on two “opposite” sides of the surface, and thus the largest island has spanned the whole surface.
5.4 Simulation Results and Discussions

5.4.1 Time variations of electron temperature $T_e$, lattice temperature $T_l$ and fraction of solid atoms $\eta$

Figure 5.1 (solid lines) presents typical time variations of three important properties (electron temperature $T_e$, lattice temperature $T_l$ and fraction of solid atoms $\eta$) of the 7,164-atom Au nanoparticle after ultrafast laser irradiation. Here, laser pulse duration $\sigma_L$ is 150fs and absorbed laser energy $E_0$ is 40kJ/mol. As assumed in Section 5.2.2, laser energy is absorbed instantaneously through photon-electron interactions and increases electron temperature $T_e$ (Figure 5.1a) up to $8 \times 10^3$K by the end of the pulse duration. In the meanwhile, lattice temperature $T_l$ (Figure 5.1b) increases only by 100K, and will continue to increase by electron-lattice collisions between hot electrons and the cold lattice. The energy exchange rate $G(T_e-T_l)$ is determined by the coupling factor $G$ and temperature difference between $T_e$ and $T_l$. In the current simulation, it takes 30ps to bring electrons and the lattice into equilibrium. The equilibrated temperature is much lower than the maximum electron temperature $8 \times 10^3$K because of greater lattice heat capacity, but still higher than the 7,164-atom Au nanoparticle melting temperature 1,045K, indicating that the nanoparticle has been completely melted. As evidenced by Figure 5.1c, fraction of solid atoms $\eta$ decreases smoothly to zero and the nanoparticle is gradually melted.

Lattice temperature $T_l$ in Figure 5.1a oscillates several cycles at a period of approximately 2ps before increasing to the equilibrated value. These oscillations are associated with the breathing vibration mode of nanoparticles [91]. A free sphere
vibrating in its fundamental mode expands and contracts in the radial direction. Its period $T$ is

$$T = \frac{2\pi R}{\eta C_l}, \text{ where } \tan \eta = \frac{4\eta}{4 - \eta^2 \frac{C_s^2}{C_l^2}}$$

Here $C_l$ and $C_s$ are longitudinal and shear velocity. For the 7,164-atom Au nanoparticle, $C_l=3376\text{m/s}, C_s=1183\text{m/s}$ and $R=3.07\text{nm}$. This gives a vibrating period of 1.92ps, very close to what we have estimated (2ps) from Figure 5.1a. The breathing vibration mode has a strong effect on optical transmission coefficients of nanoparticles and has been widely used to probe ultrafast dynamics of nanoparticles after laser excitations. Hartland [91] presented an excellent review on this topic recently.

Time variations of $T_l$ and $\eta$ are not always like those shown in Figure 5.1. Comparisons of kinetic curves ($T_l$ and $\eta$ versus time) at different $E_0$ are shown in Figure 5.3 for the same laser pulse duration $\sigma_l=150\text{fs}$. In Figure 5.3a, $T_l$ increases monotonically (except oscillations) with time only at $E_0$ below 20kJ/mol or above 40kJ/mol. At intermediate $E_0$ between 25 and 32kJ/mol, temporary superheating of lattice temperature $T_l$ above the particle melting temperature $T_m$ (=1045K) was found. Also, equilibrated particle temperature does not simply increase with $E_0$ either when superheating occurs. For example, at $E_0=25\text{kJ/mol}$ the equilibrated lattice temperature is 1040K, whereas at $E_0=30\text{kJ/mol}$ it drops to 1000K. At $E_0=32\text{kJ/mol}$, it increases back to 1055K, slightly above $T_m$ (=1045K).

Figure 5.3b presents comparisons on fraction of solid atoms $\eta$. Au nanoparticles melt deeper and faster at higher $E_0$. At $E_0=20\text{kJ/mol}$, the equilibrated $\eta$ is 0.92 and most of the liquid-like atoms are on the surface, i.e. surface premelting. When $E_0$ increases to
25kJ/mol, only 68% of total atoms remain solid-like, indicating that a significant amount of inner atoms are also melted. At $E_0=30$kJ/mol, all atoms become liquid-like after 100ps. However, nanoparticles are in an supercooled state with their equilibrated $T_l$ 45K lower than $T_m$. Finally, a slight increase of $E_0$ by 2kJ/mol will bring supercooled nanoparticles into normal liquid ones. Similar findings have also been observed at longer laser pulse durations or in a smaller 456-atom Au nanoparticle. As shown in Figure 5.4, the only difference is that smaller nanoparticle become pure liquid at a lower absorbed laser energy $E_0=20$kJ/mol due to its lower melting temperature 835K.

In the following sections, different aspects of kinetic curves shown in Figure 5.3 and Figure 5.4 are discussed in detail. We focus on features of heating and melting processes with time. Section 5.4.2 discusses nonhomogeneous surface premelting under ultrafast laser irradiation. Section 5.4.3 discusses results of percolation studies when disconnected surface liquid regions turn to a contiguous surface liquid layer. Section 5.4.4 discusses conditions for temporary lattice superheating. Section 5.4.5 discusses the melting front velocity and catastrophic solid inner core melting. Section 5.4.6 discusses the equilibrated $T_l$ and $\eta$ at different laser pulse durations and related constant energy simulations.
Figure 5.3: (Color online) Lattice temperature $T_l$ and fraction of solid atoms $\eta$ versus time of the 7,164-atom Au nanoparticle at different absorbed laser energy $E_0$ (from 20 to 40kJ/mol) at the same laser pulse duration $\sigma_L=150\text{fs}$. a) $T_l$ ($E_0$ decreases from top to bottom curves) and b) $\eta$ ($E_0$ increases from top to bottom curves). The dashed horizontal line in a) is the particle melting temperature $T_m=1045\text{K}$. The inserts show long time behaviors for intermediate energy range $E_0=25\sim32\text{kJ/mol}$. Solid points and solid squares indicate the time when surface premelting starts and when complete surface premelting is reached respectively.
Figure 5.4: (Color online) Same as in Figure 5.3 but for the 456-atom Au nanoparticle. Absorbed laser energy $E_0$ varies from 16 to 25kJ/mol. a) Lattice temperature $T_l$ ($E_0$ decreases from top to bottom curves) and b) fraction of solid atoms $\eta$ ($E_0$ increases from top to bottom curves). The dashed horizontal line in a) is the particle melting temperature $T_m=835$K. The inserts show long time behaviors for intermediate energy range $E_0=18$–20kJ/mol. As in Figure 5.3, solid points and solid squares indicate the time when surface premelting starts and when complete surface premelting is reached respectively.
5.4.2 Nonhomogeneous surface premelting under ultrafast laser irradiation

In Section 4.6, we proposed the nonhomogeneous surface premelting mechanism for the constant temperature equilibrium melting of Au nanoparticles. It was found that with temperature increase, liquid-like atoms appear first in local surface crystallographic planes \{110\} or \{100\}; and surface liquid-like regions can grow deeper into inner regions before the formation of a contiguous premelted surface layer. In Section 5.2.2, we assumed electrons and the lattice in our simulations are heated homogeneously and possess the same $T_e$ or $T_l$ everywhere, i.e., the nanoparticle itself is in local equilibrium. This assumption allows us to extend the concept of surface premelting defined in thermodynamic equilibrium conditions to cases of ultrafast laser melting of nanoparticles. As we will show below, a similar observation has been found.

Figure 5.5 presents fractions of liquid atoms in the top four atomic layers of the 7,164-atom Au nanoparticle at various absorbed laser energies $E_0$ from 20kJ/mol to 40kJ/mol. In all four cases, melting initiates on the surface. For example, at the lowest $E_0=20$kJ/mol, 40% of the surface atoms are liquid-like but the inner region remains solid with less than 10% of liquid atoms in the layer next to the surface. The equilibrated lattice temperature 963K in this case is much lower than the particle melting temperature 1045K. Following surface premelting, the inner region begins to melt at higher $E_0$ as shown from Figure 5.5b to Figure 5.5d. A significant fraction of inner atoms becomes liquid-like prior to the complete melting of the surface layer. In other words, liquid regions not only expand on the surface but also deepen into the inner regions. Figure 5.5b and Figure 5.5c also suggest that the lattice temperature drop, after temporary superheating, is connected with melting of the inner volume of nanoparticles.
Figure 5.5: Fractions of liquid atoms in the top four atomic layers of the 7,164-atom Au nanoparticle at various $E_0$: a) 20kJ/mol b) 25kJ/mol c) 30kJ/mol d) 40kJ/mol. The lattice temperature $T_l$ is also shown by thick black lines.
To determine crystalline planes where surface premelting starts, the local surface orientation was calculated for each solid atom in every configuration based on its nine closest neighbors. The following algorithm [81]-[83] was used. If, in the solid-like atom
position, the angle difference between the local surface normal and any of three
crystallographic planes \{111\}, \{100\} or \{110\} is less than 15°, that atom is considered as
being on that crystallographic plane. Some surface atoms may locate on vertices or
surface edges and do not fall on any crystallographic planes. As an example, snapshots of
atomic configurations during ultrafast laser melting (σ_L=150fs, E_0=25kJ/mol) were shown
in Figure 5.6a for the 7,164-atom Au nanoparticle, where solid atoms are colored
differently based on their local crystallographic planes. The initial surface is clearly
faceted. After 5ps, liquid atoms (red) start to appear at some vertices or surface edges.
From 5ps to 15ps, surface edges become smoother and broader and contain mostly liquid
atoms. Liquid regions are then created by the joining of neighboring liquid atoms and the
solid facets shrink in size with mostly atoms belonging to \{111\} planes left. From 15ps to
30ps, the remaining \{111\} planes continue to shrink in size and disconnected liquid
regions finally coalesce into one contiguous layer containing almost all the surface liquid
atoms (percolation). This observation is similar to results in our constant temperature
equilibrium melting simulations of Au nanoparticles in which \{111\} planes are also
found to be more stable against surface premelting in contrast with \{110\} or \{100\}
planes. It is also consistent with the stability of \{111\} planes on flat surfaces of bulk Au
up to the bulk melting temperature [30] found in simulations using the glue potential.
Figure 5.6b examined quantitatively our observations in Figure 5.6a. For each liquid
surface atom in successive atomic configurations during ultrafast laser melting, we traced
back to its local crystallographic plane in the initial configuration. At each time step, the
number of liquid surface atoms originating from the same local crystallographic plane of
the initial configuration is then normalized by the total number of atoms on that plane.
Typical results are presented in Figure 5.6b ($\sigma_1=150\text{fs}$, $E_0=25\text{kJ/mol}$). Only the first 30ps is shown because after that inner atoms start to melt and surface atoms in the initial configuration may move into the inner region. Clearly, atoms on the initial \{111\} planes present a lower fraction of liquid atoms during surface premelting, whereas atoms on the other two local crystallographic planes or from vertices and surface edges have similar probability to be premelted. Thus our conclusion visually obtained from Figure 5.6a is justified.

Similar calculations are repeated in Figure 5.7 for the smaller 456-atom Au nanoparticle. Again, melting is initiated on vertices or surface edges and spreads to other regions. Surface atoms on the initial \{111\} planes are still relatively more stable against surface premelting than those on other local planes. However, the distinction between different initial local planes is not as clear as in the larger 7,164-atom Au nanoparticle. This may be attributed to two effects: first, temperature fluctuations are inversely proportional to the square root of the number of atoms and thus are much stronger for small nanoparticles; second, the number of surface atoms in the 456-atom Au nanoparticle is only one seventh of that in the 7,164-atom Au nanoparticle so that the determination of local crystalline planes is more affected by random fluctuations.
Figure 5.6: Evolution of 7,164-atom Au nanoparticle after ultrafast laser irradiation (pulse duration $\tau_L=150$fs, absorbed energy $E_0=25$kJ/mol).  

a) (Color online) Snapshots of atomic configurations in the orthographic projection. Blue: solid atoms on $\{111\}$ planes; Green: solid atoms on $\{100\}$ planes; Black: solid atoms on $\{110\}$ planes; White: solid atoms on vertices and surface edges; Red: liquid atoms. 

b) Time variations of fraction of liquid atoms at different crystallographic planes: surface atoms on $\{111\}$ planes are more stable. 

c) Time variations of lattice temperature $T_l$ and fraction of solid atoms $\eta$. As in Figure 5.1 and Figure 5.3, $T_l$ oscillates with a period of approximately 2ps due to breathing vibrations of nanoparticles.
Figure 5.6 continued

\[ \sigma_L = 150 \text{fs}, \ E_0 = 25 \text{kJ/mol} \]

**b)**

Fraction of liquid atoms

\[
\begin{align*}
\text{Time (ps)} & \\
0 & \quad \text{0.0} \\
10 & \quad \text{0.2} \\
20 & \quad \text{0.4} \\
30 & \quad \text{0.6} \\
40 & \quad \text{0.8} \\
50 & \quad \text{1.0} \\
\end{align*}
\]

**c)**

Lattice Temperature (K)

\[
\begin{align*}
\text{Time (ps)} & \\
0 & \quad \text{400} \\
10 & \quad \text{600} \\
20 & \quad \text{800} \\
30 & \quad \text{1000} \\
40 & \quad \text{1200} \\
\end{align*}
\]
Figure 5.7: Same as in Figure 5.6 but for the 456-atom Au nanoparticle at lower absorbed laser energy $E_0=18$kJ/mol. a) (Color online) Snapshots of atomic configurations in the orthographic projection. Blue: solid atoms on {111} planes; Green: solid atoms on {100} planes; Black: solid atoms on {110} planes; White: solid atoms on vertices and surface edges; Red: liquid atoms. b) Time variations of fraction of liquid atoms at different crystallographic planes: surface atoms on {111} planes are more stable. c) Time variations of lattice temperature $T_l$ and fraction of solid atoms $\eta$. 

Continued
Figure 5.7 continued

\[ \sigma_L = 150 \text{fs}, \ E_0 = 18 \text{kJ/mol} \]

- **(b)** Fraction of liquid atoms
  - \{111\} planes
  - \{100\} planes
  - \{110\} planes
  - Vertices & Surface edges

- **(c)** Lattice Temperature (K)
  - \( T_L \)
  - Fraction of Solid Atoms \( \eta \)
5.4.3 Partial and complete surface premelting: percolation study

As discussed in the previous section, surface premelting starts with a formation of small islands on the nanoparticle surface which grow with time (lattice temperature) both in area and depth. A percolation theory has been applied on surfaces of nanoparticles to study quantitatively the transition (percolation) from disconnected liquid regions (partial surface premelting) to a contiguous liquid layer (complete surface premelting). Figure 5.8 presents conditions (fraction of surface liquid atoms \( p \), lattice temperature \( T_l \), and time) at this surface premelting transition of the 7,164-atom Au nanoparticle under ultrafast laser irradiation (\( \sigma_L = 150\text{fs} \)) at different absorbed laser energy \( E_0 = 25\text{~}40\text{kJ/mol} \). (Below 25kJ/mol, complete surface premelting is not achieved). Figure 5.8a demonstrates a fundamental result: regardless of \( E_0 \), complete surface premelting is achieved at the same fraction of liquid surface atoms \( p = 0.69 \). We will return to this observation later. Lattice temperature \( T_l \) at complete surface premelting is always above the particle melting temperature \( T_m \) and increases with \( E_0 \) (Figure 5.8b). This is consistent with the superheating of nanoparticles discussed later in Section 5.4.4. However, the slope of the curve in Figure 5.8b decreases with \( E_0 \), indicating that a greater fraction of inner atoms is melted at complete surface premelting at higher \( E_0 \). Figure 5.8c compares the time to reach complete surface premelting and to reach maximum lattice temperature. At \( E_0 = 25\text{kJ/mol} \), both phenomena occur at the same time. At any higher \( E_0 \), complete surface premelting always occurs earlier. \( T_l \) starts decreasing mainly due to the inner region melting of nanoparticles, as has also been observed in Figure 5.5. This is because surface premelting needs much less latent heat of fusion than the melting of inner regions, and thus has less effect on changes of \( T_l \).
Figure 5.8: Conditions of the complete surface premelting (percolation) for the 7,164-atom Au nanoparticle under ultrafast laser irradiation (pulse duration $\sigma_L=150\text{fs}$, absorbed energy $E_0=25\text{~}40\text{kJ/mol}$) a) Fraction of liquid surface atoms $p$; b) Lattice temperature $T_l$; c) Time to reach percolation, and to reach maximum $T_l$ which occurs always later. Notice that domains marked by “solid-liquid coexistence” or “liquid” refer to the equilibrated state of nanoparticles as shown in Figure 5.3 and Figure 5.4.
Figure 5.8a suggests that the percolation threshold $p_c (=0.69)$ of complete surface premelting is a universal factor and is not related to surface premelting history. To further explore this issue, we have expanded our study by two different approaches. In the first approach, constant temperature equilibrium melting simulations were performed for the same Au nanoparticle. At each temperature, we recorded fraction of liquid surface atoms $p$ averaged over 100 configurations and fraction of those configurations in which complete surface premelting is achieved. As shown in Figure 5.9, when $T_1$ increases from 1036K to 1038K, $p$ increases from 0.64 to 0.74. At the same time, fraction of configurations in which complete surface premelting is achieved jumps from 0.61 to 0.98. Thus, the percolation threshold $p_c$ in constant temperature equilibrium melting simulations should be between 0.64 and 0.74, and its average is just 0.69. In the second approach, we used simulated atomic configurations as above. However, instead of determining the state of liquid surface atoms by structural characterization methods, we
randomly assigned some surface atoms to be liquid-like with an increasing fraction $p$ from 0 to 1 and examined at which fraction $p$ complete surface premelting was achieved. This approach decouples the $p_c$ value from any particular melting process. At each temperature this approach is repeated 100 times to obtain average percolation threshold $p_c$. It varies in the range between 0.68 and 0.72, again close to 0.69. These studies confirmed our hypothesis that the percolation threshold $p_c$ is a pure geometric parameter independent of surface premelting history or distribution of liquid-like surface atoms. The orientation dependence of surface premelting discussed in Section 5.4.3 is not significant enough to affect the percolation threshold $p_c$.

Figure 5.9: Fraction of liquid surface atoms $p$ and fraction of configurations in which complete surface premelting is achieved versus temperature for the 7,164-atom Au nanoparticle. Results are for constant temperature equilibrium melting simulations.
Figure 5.10 reports similar calculation results for the smaller 456-atom Au nanoparticle. In contrast to Figure 5.8, the percolation threshold $p_c$ (i.e., complete surface premelting) occurs only at conditions such that the whole nanoparticle is melted in its equilibrated state; for this size of nanoparticles $p_c$ is not reached if the solid-liquid coexistence is the equilibrated state. Despite heated by ultrafast laser, this observation is consistent with our previous results obtained by constant temperature equilibrium melting simulations in Section 4.6.3. In that work, we have demonstrated that for larger Au nanoparticles like N=7,164, the surface is completely premelted at a temperature 5K below the particle melting temperature whereas for smaller nanoparticles like N=456, it is only partially premelted. The percolation threshold $p_c$ shown in Figure 5.10a is 0.63, independent of absorbed laser energy. This value is slightly lower than that for the larger 7,164-atom Au nanoparticle ($p_c=0.69$) because of the relative ease to reach percolation in a smaller surface. Figure 5.10b suggests again that lattice superheating is needed to achieve complete surface premelting. At higher absorbed laser energy $E_0$, complete surface premelting occurs at higher lattice temperature and earlier time. Note that in Figure 5.10c we didn’t include results between $E_0=18.5$~$19.5$kJ/mol. This energy level is close to the transition from solid-liquid coexistent state to pure liquids. The melting process takes a much longer time to reach an equilibrated state and is very sensitive to initial configurations. The time to reach the percolation threshold $p_c$ scatters so much from configuration to configuration that its average value is meaningless and was excluded from Figure 5.10c.
Figure 5.10: Same as Figure 5.8 but for the 456-atom Au nanoparticle. Conditions of the complete surface premelting (percolation) under ultrafast laser irradiation (pulse duration \( \sigma_L = 150\text{fs} \), absorbed energy \( E_0 = 15\text{~40kJ/mol} \)). a) Fraction of liquid surface atoms \( p \); b) Lattice temperature \( T_l \); c) Time to reach percolation. The complete surface premelting is not reached at the equilibrated “solid-liquid coexistence” state. It is reached only for nanoparticles in an equilibrated liquid state.
5.4.4 Temporary lattice superheating

Two competitive processes contribute to variations of lattice temperature $T_l$ in our simulations. On the one side, due to weak energy coupling factor $G$ in Au, restoration of electron-lattice temperature equilibrium after ultrafast laser excitation may take several tens of picoseconds and the lattice continues to be heated during that period. On the other side, the melting of nanoparticles tends to decrease $T_l$. Temporary superheating above the nanoparticle melting temperature $T_m$ occurs at intermediate $E_0$ when the time scales for above two processes—the electron-lattice temperature equilibrium and the solid-liquid phase transition—become comparable. The initial energy transfer rate $G(T_e-T_l)$ between electrons and the lattice is very high due to their large temperature difference, and thus there is no sufficient time for nanoparticles to go through the solid-liquid phase transition before being superheated. Since the formation rate of critical liquid nuclei increases with temperature, superheating accelerates surface premelting and leads to subsequent lattice
temperature drop as fraction of liquid phase increases. This temperature drop doesn’t necessarily cease at the particle melting temperature $T_m$. Finally, a solid-liquid coexistent or supercooled nanoparticle state would be formed. Ivanov and Zhigilei [112] have observed temporary superheating in their simulations of Au thin film ablation. Supercooled amorphous Au thin films have also been reported in both experiments [118] and simulations [119]. At $E_0$ above this intermediate range, the heat input before complete solid-liquid phase transition is sufficient, and a monotonic increase of $T_l$ occurs. At lower $E_0$, melting of inner regions is not initiated and temperature of nanoparticles also monotonically increases to the equilibrated value below $T_m$.

To study quantitatively conditions of temporary lattice superheating, we have simulated a wide absorbed laser energy range $E_0$ from 5 to 40kJ/mol and laser pulse duration $\sigma_L$ from 150fs to 100ps for the 7,164-atom Au nanoparticle. Curves like those in Figure 5.3a are smoothed to determine maximum $T_l (T_{l_{\text{max}}})$ and time to reach it. The superheating is observed in the intermediate energy range $E_0=25$~$35$kJ/mol. But for the longest laser pulse $\sigma_L=100$ps, the superheating is observed in a narrower energy range $E_0=26$~$32$kJ/mol. A further increased $\sigma_L$ may approach the time scale of the equilibrium melting and eliminate any temporary superheating.
Figure 5.11: Conditions of temporary superheating for the 7,164-atom Au nanoparticle after laser irradiation: a) maximum lattice temperature $T^{\text{max}}_l$; b) time to reach $T^{\text{max}}_l$. The laser pulse duration varies from 150fs to 100ps and absorbed laser energy $E_0$ varies from 25 to 35kJ/mol. Notice that domains marked by “solid-liquid coexistence” or “liquid” refer to the equilibrated state of nanoparticles as shown in Figure 5.3 and Figure 5.4.
Compared results are shown in Figure 5.11. For a given laser pulse duration $\sigma_L$, $T_i^{\text{max}}$ increases in proportion to $E_0$ and is reached roughly at the same time regardless of $E_0$. For short pulses $\sigma_L<10\text{ps}$ at a given absorbed laser energy $E_0$, $T_i^{\text{max}}$ is practically independent of pulse duration and is reached at approximately the same time. However, for the longest pulse $\sigma_L=100\text{ps}$, $T_i^{\text{max}}$ is significantly lower and the time required to reach it increases greatly. These observations suggest that at higher lattice heating rates (shorter laser pulses $\sigma_L=150\text{fs}$~$10\text{ps}$), the electron-lattice temperature equilibration process dominates $T_i$ for the time range prior to its reaching $T_i^{\text{max}}$. The effect of the solid-liquid phase transition on nanoparticle temperatures becomes stronger at lower lattice heating rate (longer $\sigma_L=100\text{ps}$) and leads to decreased $T_i^{\text{max}}$. Note that the superheating phenomenon occurs before reaching any equilibrated states: solid-liquid coexistent or supercooled liquid states as indicated by the vertical dashed line separating two domains.

5.4.5 Melting front velocity and catastrophic solid inner core melting

At high absorbed laser energy $E_0$, the inner region would be melted besides surface premelting. Figure 5.5 allows for an estimation of the melting front velocity $V_m$ during ultrafast laser irradiation. The equivalent liquid layer thickness $\delta$ is defined as the summation of fractions of liquid-like atoms in all the atomic layers multiplied by average atomic layer thickness $\bar{h}$ ($=R/n_L$, where $R$ is radius of Au nanoparticles and $n_L$ is the number of atomic layers). Time variations of $\delta(t)$ are plotted in Figure 5.12 by solid lines at $E_0=28$~$40\text{kJ/mol}$ and $\sigma_L=150\text{fs}$. $V_m(t)$ is then calculated by taking the derivative of $\delta(t)$. Several findings from Figure 5.12 are summarized here.
First, when the stabilized state of Au nanoparticles is solid-liquid coexistent \((E_0<28\text{kJ/mol})\), only one peak could be found on the curve of \(V_m(t)\). This indicates the initiation of surface premelting and its subsequent propagation into inner regions. From 28kJ/mol to 28.2kJ/mol, the slightly increased \(E_0\) causes catastrophic solid inner core melting and leaves supercooled nanoparticles. The equivalent liquid layer thickness \(\delta\) jumps accordingly from 1.5nm to 3.2nm for fully melted nanoparticles. On the melting front velocity curve \(\delta(t)\), a second peak appears representing the solid inner core melting. With a further increase of \(E_0\), this second peak becomes stronger, i.e., the solid inner core collapses more quickly. This second peak also appears earlier and moves towards the first peak. Finally, at \(E_0=40\text{kJ/mol}\), the melting proceeds so fast that it is no longer possible to separate two melting front velocity peaks.

Second, in the neighboring energy range where solid inner core collapse from the coexistent state to pure liquids occurs \((E_0\approx28.2\text{kJ/mol})\), the melting process greatly slows down and takes more than 600ps to finish. As shown in Figure 5.12b, between the first and second melting front velocity peak, a period of plateau exists in which the equivalent liquid layer thickness \(\delta\) barely changes. The nanoparticle is waiting for sufficient thermal fluctuations to overcome entropy barriers between the locally maximum coexistent state and the globally maximum pure liquid state, and induce catastrophic solid inner core melting.

Third, as shown in Figure 5.13, the maximum melting front velocity of the first peak varies significantly from 21m/s at \(E_0=25\text{kJ/mol}\) to 174m/s at \(E_0=40\text{kJ/mol}\), due to an increasing degree of lattice superheating \(T/T_m\) from 1.03 to 1.22. The data points can be fitted well by a second order polynomial, indicating a speeding increase of the maximum
melting front velocity at higher $E_0$. Several authors argued that in a sufficiently superheated crystal, homogeneous nucleation of liquid nuclei may play a dominant role in the melting kinetics [120][121]. Unlike heterogeneous nucleation in which liquid nuclei appear on the surface, grain boundaries or internal defects, nucleation sites in homogeneous nucleation appear in both inner and surface regions of materials simultaneously. The crystal can then be melted very fast at a speed only limited by its sound velocity. However, our calculations showed that, at least up to a superheating degree of $T/T_m=1.22$, melting is still initiated on the surface and then propagates into the inner regions. Au nanoparticles are thought to be more stable against homogeneous melting than their bulk counterparts because surface-to-volume ratio is much higher in nanoparticles so that surface premelting is easier to occur to provide enough liquid nucleation sites. Besides, $V_m$ in our calculations (174m/s at $T/T_m=1.22$) is less than 5% of the sound velocity of bulk Au at room temperature (3,376m/s). Ivanov and Zhigilei [122] calculated velocity of melting front for Au plane surfaces recently. At the same degree of superheating, our results are comparable to their propagation velocities. They attributed this relatively low propagation speed to local cooling of the melting front when latent heat of fusion is spent to melt inner atoms.
Figure 5.12: Time variations of equivalent liquid layer thickness \( \delta \) and melting front velocity \( V_m \) at the absorbed laser energy \( E_0 = 28 \text{–} 40 \text{kJ/mol} \) (7,164-atom Au nanoparticle, laser pulse duration \( \sigma_L = 150 \text{fs} \)). Simulation time is longer at \( E_0 = 28 \) and 28.2kJ/mol.
Figure 5.12 continued

**E₀ = 30 kJ/mol**

- **c)**: Equivalent liquid layer thickness $\delta$(nm) vs. Time (ps) for $E₀ = 30$ kJ/mol.
- **d)**: Melting front velocity $V_m$(m/s) vs. Time (ps) for $E₀ = 40$ kJ/mol.

**E₀ = 40 kJ/mol**

- **c)**: Equivalent liquid layer thickness $\delta$(nm) vs. Time (ps) for $E₀ = 40$ kJ/mol.
- **d)**: Melting front velocity $V_m$(m/s) vs. Time (ps) for $E₀ = 40$ kJ/mol.
Figure 5.13: The maximum melting front velocity of the first peak in Figure 11 as a function of overheating. \((E_0=25-40\text{kJ/mol}, N=7,164\text{-atom}, \sigma_L=150\text{fs})\). The data points can be fitted well by the second order polynomial, as plotted by the straight line.

5.4.6 Equilibrated state: Independence of laser pulse duration

We have simulated the melting process of Au nanoparticles under ultrafast laser irradiation over a wide absorbed energy range \(E_0\) from 5 to 40kJ/mol and pulse duration range \(\sigma_L\) from 150fs to 100ps. Figure 5.14 presents for the 7,164-atom Au nanoparticle comparative results of equilibrated lattice temperature and fraction of remaining solid atoms. Both quantities are dependent only on absorbed laser energy \(E_0\), but not on laser pulse duration \(\sigma_L\). This means nanoparticles reach the thermodynamic equilibrium state which is independent of the particular kinetic path achieved at different \(\sigma_L\). It is not obvious \textit{a priori} since longer laser pulse produces lower \(T_i^{\text{max}}\), which may lead to a slower formation rate of liquid nuclei, a larger remaining solid core and a higher lattice temperature and the final nanoparticle state in simulations might be a quasi-equilibrium.
However, our simulations indicate that the same $E_0$ gives the same equilibrated lattice temperature and fraction of solid atoms, regardless of laser pulse duration, i.e. the equilibrated state of Au nanoparticles is not related to any kinetic melting process.

As mentioned in Section 5.2.2, in our simulations total energy in the system remains constant after the laser pulse terminates and the system then evolves in a microcanonical ensemble (NVE). Thus, for the purpose of comparisons, we have also performed constant energy equilibrium melting simulations of Au nanoparticles with the same size. As shown in Figure 5.14, it gives the same values as those from ultrafast melting simulations, supporting the conclusion that the thermodynamically equilibrated state is reached. This finding also indicates that to obtain the final state of nanoparticles, a single constant energy equilibrium melting simulation (NVE) could replace multiple lengthy ultrafast melting simulations at different $\sigma_L$. The NVE curve in Figure 5.14 also shows that the 7,164-atom Au nanoparticle is in the solid-liquid coexistent state at $E_0=28\text{kJ/mol}$ with 24% of solid atoms left. However, it suddenly melts completely with a slight increase of $E_0$ by 0.2kJ/mol, i.e. catastrophic solid inner core melting occurs. The lattice temperature of supercooled liquids drops to 950K, 100K lower than the particle melting temperature $T_m$ (≈1045K).
Figure 5.14: a) Equilibrated lattice temperature and b) Equilibrated fraction of solid atoms versus absorbed laser energy $E_0$ for the 7,164-atom Au nanoparticle after laser irradiation. Laser pulse duration varies from 150fs to 100ps and absorbed laser energy $E_0$ from 5 to 40kJ/mol. When $E_0$ is less than 28kJ/mol, the nanoparticle is in the solid-liquid coexistent state; at higher energies it transforms into pure liquid. Results from constant energy equilibrium melting simulations (NVE) are shown by solid line.
We have found that microcanonical droplet theory (MCD) [39][123] gives a good explanation of above observations. Briefly speaking (the detailed results will be reported elsewhere), in constant energy equilibrium melting simulations, entropy should be maximized while maintaining total energy constant. (In contrast, the particle melting temperature $T_m$ is calculated from constant temperature equilibrium melting simulations, in which the Helmholtz free energy should be maximized while maintaining particle temperature constant.) Since, after absorption of laser energy, the nanoparticle remains a closed microcanonical system, its equilibrated lattice temperature and fraction of solid atoms could be predicted from the microcanonical droplet theory, and becomes independent on laser pulse duration. Catastrophic solid inner core melting and the supercooled state occur because it is no longer beneficial in terms of entropy to maintain a small solid core instead of having it fully melted.

Figure 5.15 compares constant energy equilibrium melting simulations of Au nanoparticles with different sizes ranging from 456-atom to 7,164-atom. All five curves start at the same initial temperature and begin to deviate from the straight line when $E_0>10$KJ/mol, due to the initiation of surface premelting and the creation of a solid-liquid coexistent state. Lattice temperature starts to decrease after reaching the particle melting temperature $T_m$. At two smaller sizes, it is followed immediately by catastrophic solid inner core melting. At other larger sizes, nanoparticles may remain in the solid-liquid coexistent state in a range of $E_0$ before catastrophic solid inner core melting. Nanoparticles then transform to supercooled liquids and could remain stable in this state for a very long time. After becoming pure liquids, nanoparticle temperature will resume increasing linearly with $E_0$, at a slope equaling constant energy heat capacity of Au. At
the same $E_0$, larger nanoparticles have a lower lattice temperature. This is because smaller nanoparticles have a lower latent heat of fusion [20].

Figure 5.15: Equilibrated temperature $T_1$ obtained by constant energy equilibrium melting simulations for nanoparticles of different sizes (from 456-atom to 7,164-atom). Nanoparticle energy corresponds to the absorbed laser energy $E_0$ used in previous figures. All sizes of nanoparticles reach the maximum temperature which equals nanoparticle melting temperature $T_m$ and after that decrease. At limited range of energies $E_0$, all nanoparticles melt in a supercooled liquid state (our simulations indicate that they remain in this state for a very long time; not shown in the figure).

5.5 Summary and Conclusions

An integrated MD+TTM computational model has been applied in this chapter to study the microscopic mechanism of ultrafast laser irradiation of Au nanoparticles at low laser intensity where surface premelting and solid-liquid phase transition are major
interests. Energy is conserved after the laser pulse terminates and the system evolves like a microcanonical ensemble. Thus, our simulations best represent cases for free-standing nanoparticles in the inertia gas or nanoparticles on the amorphous substrate with rather slow heat conduction. A wide combination of laser pulse durations $\sigma_L$ from 150fs to 100ps, absorbed laser energies $E_0$ from 5kJ/mol to 40kJ/mol, and nanoparticle sizes $N$ from 456 to 7,164 atoms have been considered. Several conclusions regarding kinetic melting processes were drawn from our simulations.

1) Lattice temperature $T_l$ doesn’t increase monotonically. Temperature oscillations are associated with breathing vibration mode of nanoparticles.

2) Temporary superheating occurs at intermediate $E_0$ when the time scales for two competitive processes—the electron-lattice temperature equilibrium and the solid-liquid phase transition—become comparable.

3) For a given laser pulse duration $\sigma_L$, maximum temperature of superheating $T_{l, max}$ increases in proportion to $E_0$ and is reached roughly at the same time regardless of $E_0$. For short pulses $\sigma_L<10$ps at a given $E_0$, $T_{l, max}$ is practically independent of pulse duration, but decreases significantly for the longest pulse $\sigma_L=100$ps. These observations suggest that at short $\sigma_L (=150$fs$\sim10$ps), for temperatures below $T_{l, max}$, the lattice temperature is dominated by the electron-lattice temperature equilibration process. The effect of the solid-liquid phase transition on nanoparticle temperatures becomes stronger at longer $\sigma_L$ (100ps), leading to the significantly decreased $T_{l, max}$.

4) Nonhomogeneous surface premelting was observed in both equilibrium and ultrafast melting of Au nanoparticles. With temperature increase, liquid-like atoms appear first
in local surface crystallographic planes like {110} or {100}; and surface liquid-like regions can grow deep into the inner region before the formation of a contiguous premelted surface layer.

5) The transition (percolation) from disconnected liquid regions (partial surface premelting) to a contiguous liquid layer (complete surface premelting) occurs at a fraction of liquid surface atoms that is only weakly dependent on particle size. The percolation threshold $p_c$ is a universal factor and is not related to surface premelting history, i.e. applied laser pulse energy or its duration. The complete surface premelting occurs above the particle melting temperature $T_{m}$, but before $T_{l}^{\text{max}}$ is reached. The subsequent decrease from $T_{l}^{\text{max}}$ is mainly driven by the melting of the nanoparticle inner volume.

6) For smaller 456-atom Au nanoparticles, complete surface premelting occurs only when the entire nanoparticle is melted in its equilibrated state, whereas for larger 7,164-atom nanoparticles, it is reached both in the equilibrated solid-liquid coexistent state and pure liquid state. This is consistent with our previous observations in equilibrium melting simulations. In that work, we have demonstrated that for larger Au nanoparticles like $N=7,164$, the surface is completely premelted at a temperature 5K below the particle melting temperature whereas for smaller nanoparticles like $N=456$, it is only partially premelted.

7) The equilibrated state (lattice temperature and fraction of remaining solid atoms) of Au nanoparticles in simulations is determined solely by absorbed laser energy $E_{0}$, and is independent of any kinetic melting path resulting from different laser pulse
durations $\sigma_L$. Thus thermodynamic equilibrium is achieved at the end of our simulations.

8) There exists a range of absorbed laser energy, in which nanoparticles undergo catastrophic solid inner core melting, transform to supercooled liquids and remain stable in that state for a very long time.
Chapter 6. Melting under Ultrafast Laser Irradiation: Microcanonical Droplet (MCD) Theory

6.1 Representative MD Simulation Results

We have simulated the melting process of Au nanoparticles under ultrafast laser irradiations over a wide absorbed energy range $E_0$ from 5 to 40kJ/mol and pulse duration range $\sigma_L$ from 150fs to 100ps. The size of nanoparticles varies from 456-atom ($R=1.22$nm) to 7,164-atom ($R=3.07$nm). An extensive report on our MD simulation results are presented in Chapter 5. This section reviews several important findings which triggers our thoughts in explaining MD simulation results using the microcanonical droplet (MCD) theory.

6.1.1 Ultrafast melting instability

At each absorbed laser energy $E_0$, our ultrafast melting simulations were repeated five times using different initial atomic configurations. These different atomic configurations are all dumped from our constant temperature melting simulations at 300K, and their atomic velocities have been normalized to ensure the same total energy before the laser irradiation. As shown by Figure 6.1a, at laser pulse duration $\sigma_L=150$fs, when $E_0$ is lower than 28kJ/mol or greater than 30kJ/mol, different runs follow similar time variations of fraction of solid atoms $\eta$. However, at $E_0$ between 28kJ/mol and 30kJ/mol, both time variations and the equilibrated state of $\eta$ could be different from configuration
to configuration. A representative example of $E_0 = 28.2 \text{kJ/mol}$ is presented in Figure 6.1b, where simulation time has been extended from 200ps to 800ps. Five curves using different initial configurations start to diverge at $\eta = 0.40$. In two curves, fraction of solid atoms stabilizes at $\eta = 0.20$ for more than 200ps, and then the nanoparticle is suddenly melted within 100ps. Note that snapshots of atomic configurations for one curve are shown in Figure 6.2, where the outer liquid shell is rendered as transparent so that time variations of the inner solid core could be revealed. In a third curve, fraction of solid atoms continuously drops to pure liquids within 400ps. Its melting speed clearly slows down when $\eta$ is between 0.2 and 0.4, and returns to normal speed later. The other two curves of fraction of solid atoms fluctuate between 0.2 and 0.4. Longer simulations till 10ns have been performed but the nanoparticles are still not completely melted. Thus, ultrafast melting instability of nanoparticles at absorbed laser energy $E_0 = 28.2 \text{kJ/mol}$ is found in both the kinetic melting path and the thermodynamic equilibrated state.
Figure 6.1: Ultrafast melting instability: a) at the absorbed laser energy $E_0=28$ and 30kJ/mol, different initial atomic configurations gave the same kinetic melting path and the same equilibrated state (fraction of solid atoms); b) at $E_0=28.2$kJ/mol, ultrafast melting is instable and depends on the initial atomic configuration. Simulation results are obtained from the 7,164-atom Au nanoparticle at the laser pulse duration $\sigma_L=150$fs.
Figure 6.2: Snapshots of atomic configurations of the 7,164-atom Au nanoparticle under ultrafast laser irradiation $E_0=28.2\text{kJ/mol}$ and $\sigma_L=150\text{fs}$: outer red shadow region is liquid-like atoms and inner white concrete region is solid-like atoms. The inner solid core decreases a lot from 20ps to 200ps. But it barely changes from 200ps to 400ps due to its metastable state. After 400ps, catastrophic inner solid core melting occurs, and the nanoparticle becomes pure liquids before 600ps.

6.1.2 Equilibrated state: Independence of laser pulse duration

As discussed in Section 5.4.6 and illustrated in Figure 5.14, equilibrated lattice temperature $T_l$ and fraction of solid atoms $\eta$ in ultrafast melting of Au nanoparticles don’t depend on laser pulse duration $\sigma_L$ or any particular kinetic melting process, as long as the same amount of absorbed energy $E_0$ is applied. That is to say, ONE constant energy melting simulation (NVE) could replace MANY lengthy ultrafast melting simulations at different $\sigma_L$ to predict the equilibrated state of nanoparticles. The NVE curves in Figure 5.14 also show that the 7,164-atom Au nanoparticle is in the solid-liquid coexistent state
at $E_0=28\text{kJ/mol}$ with 24% of solid atoms left. However, it suddenly melts completely with a slight increase of $E_0$ by 0.2kJ/mol, i.e. catastrophic solid inner core melting. The lattice temperature of supercooled liquids drops to 950K, 100K lower than the particle melting temperature $T_m$ (=1045K). In the following sections, we will apply microcanonical critical droplet theory (MCD) to explain these two findings.

6.2 Microcanonical Critical Droplet Theory (MCD)

6.2.1 Review of the MCD theory

Microcanonical critical droplet theory (MCD) [46][123] predicts the thermodynamic equilibrium state of nanoparticles when the total energy in the whole system is conserved (a.k.a. microcanonical ensemble). In our ultrafast melting simulations, total energy in the system remains constant after ultrafast laser pulse terminates, and the system (including melting processes) then evolves likes a microcanonical ensemble (NVE). Thus, the MCD theory is applicable to interpret the equilibrated state of our ultrafast melting simulations.

The solid-liquid coexistent nanoparticle is usually described in the shape of a spherical solid core of radius $R_s$ surrounded by a liquid outer shell of radius $R$ (see Figure 6.6a). The fraction of remaining solid atoms is $\eta=(R_s/R)^3$. The total energy per atom $e$ in nanoparticles (internal energy plus surface/interfacial energy) is a function of two variables: lattice temperature $T$ and fraction of solid atoms $\eta$. $e$ is expressed as

$$
e(T, \eta) = \eta e_s + (1-\eta)e_l + \frac{3}{\rho R} \bigg\{ \gamma_I + [\gamma_{sl} + \Delta \gamma \text{EXP}] \eta^{2/3} \bigg\}$$  \hspace{1cm} (6.1)
Here $e_s$ and $e_l$ are solid and liquid internal energy per atom at the temperature $T$. They are linked to $e_s^{\text{m}}$ and $e_l^{\text{m}}$ (internal energy per atom at the size-dependent particle melting temperature $T_m$) as:

$$e_s = e_s^{\text{m}} + c_v (T - T_m)$$

$$e_l = e_l^{\text{m}} + c_v (T - T_m)$$

$c_v$ is specific constant volume heat capacity, $\rho$ is density, $\gamma_s$ and $\gamma_l$ are solid and liquid surface energy, and $\gamma_{sl}$ is solid-liquid interfacial energy. The excessive surface energy is defined as:

$$\Delta \gamma = \gamma_s - \gamma_l - \gamma_{sl}.$$  

The larger $\Delta \gamma$, the easier surface premelting. The exponential term $\text{EXP}$ is expressed as:

$$\text{EXP} = e^{-2(1- \eta^{1/3}) R/\xi}$$  \hspace{1cm} (6.2)

This term characterizes short-range interactions between solid-liquid and liquid-vapor interfaces and $\xi$ is the correlation length. The inclusion of $\Delta \gamma \text{EXP}$ in Eq. (6.1) ensures that $e \rightarrow e_s + 3 \gamma_s / \rho R$ for the pure solids $\eta \rightarrow 1$. Similarly, the total entropy per atom $s$ of the solid-liquid coexistent nanoparticle is also a function of $T$ and $\eta$, and written as:

$$s(T, \eta) = \eta s_s + (1-\eta) s_l$$  \hspace{1cm} (6.3)

Here $s_s$ and $s_l$ are solid and liquid entropy per atom at the temperature $T$. They are linked to $s_s^{\text{m}}$ and $s_l^{\text{m}}$ (entropy per atom at the temperature $T_m$) as:

$$s_s = s_s^{\text{m}} + c_v \ln T / T_m$$

$$s_l = s_l^{\text{m}} + c_v \ln T / T_m.$$  

In a microcanonical ensemble with constant total energy $e$, total entropy $s$ should be maximized with respect to $T$ and $\eta$. (In contrast, the particle melting temperature $T_m$ is calculated from the canonical ensemble melting simulations, in which the Helmholtz free energy should be maximized while maintaining particle temperature constant.) Thus, thermodynamic equilibrium state of nanoparticles is deterministic at any given total energy $e$, regardless of laser pulse durations or specific kinetic melting processes.
Extremizing RHS of Eq. (6.3) under the constraint of Eq. (6.1), we can solve the equilibrated fraction of solid atoms \( \eta \) (0 \( \leq \eta \leq 1 \)) for total energy \( e \) through the equation:

\[
\eta^{4/3} - \frac{3}{\rho RL_m} (\gamma \sl + \Delta \gamma EXP) \eta
+ \left( \frac{e-e_i^m}{L_m} - \frac{3\gamma_i}{\rho RL_m} + \frac{2cT_m \Delta \gamma EXP}{\rho \xi L_m} \right) \eta^{1/3} + \frac{2cT_m}{\rho RL_m} (\gamma \sl + \Delta \gamma EXP) = 0
\]  
(6.4)

where \( L_m = e_i^m - e_s^m = T_m (s_i^m - s_s^m) \) is the latent heat of fusion. The equilibrated lattice temperature \( T \) is then calculated as

\[
T = T_m + \frac{e-e_i^m - \frac{3}{\rho R} \left( \gamma_i + \gamma \sl \eta^{2/3} + \Delta \gamma EXP \eta^{2/3} \right) + \eta L_m}{c_v}
\]  
(6.5)

For the further analysis, it is convenient to reformulate Eq. (6.4) and (6.5) by choosing total energy per atom \( e \) before laser irradiation (at \( T=300K \)) as 0. As a result, \( e \) is equal to absorbed laser energy \( E_0 \) after ultrafast laser pulse terminates, and internal energy at the particle melting temperature \( e_i^m = \Delta E - 3\gamma_i / \rho R \) (\( \Delta E \) is input energy needed to increase the particle temperature from 300K to \( T_m \)). In this manner, Eq. (6.4) and (6.5) becomes

\[
E_0 = -L_m \eta + \frac{3}{\rho R} \left( \gamma \sl + \Delta \gamma EXP \right) \eta^{2/3}
- \frac{2cT_m}{\rho RL_m} (\gamma \sl + \Delta \gamma EXP) \eta^{-1/3} - \frac{2cT_m \Delta \gamma EXP}{\rho \xi L_m} \Delta E
\]  
(6.6)

\[
T = T_m + \frac{E_0 - \Delta E - \frac{3}{\rho R} \left( \gamma \sl + \Delta \gamma EXP \right) \eta^{2/3} + L_m \eta}{c_v}
\]  
(6.7)

6.2.2 Interpretation of the MCD theory

In evaluating Eq. (6.6) and (6.7), material parameters of Au nanoparticles are mainly calculated from our own MD simulations using the Quantum Sutton-Chen
potential (see Section 4.3 and 4.4). They are: \( L_m = 12.68 \text{kJ/mol} \), \( c_v = 31.925 \text{J/mol} \), \( \gamma_s = 0.85 \text{N/m} \), \( \gamma_l = 0.61 \text{N/m} \), \( \Delta E = 31.9 \text{kJ/mol} \) and \( R = 3.16 \text{nm} \) for the 7,164-atom Au nanoparticle, and \( \rho \) is calculated directly from \( R \). Besides, experimental values \( \Delta \gamma = 0.0466 \text{N/m} \) and \( \xi = 0.39 \text{nm} \) are taken from [124].

6.2.2.1 Catastrophic solid inner core melting

By varying fraction of solid atoms \( \eta \) from 0 to 1, RHS of Eq. (6.6) is represented in Figure 6.3a as a parabolic-like curve, whereas LHS (constant absorbed laser energy \( E_0 \)) is represented as vertical dotted lines. The intersection points (grey dots) illustrate the solution of Eq. (6.6) straightforwardly: the equilibrated fraction of solid atoms \( \eta \) at any \( E_0 \).

1) At \( 10.3 \text{kJ/mol} < E_0 < 23.9 \text{kJ/mol} \): each vertical dotted line has two intersection points with the parabolic-like curve, representing two possible solutions of Eq. (6.6).

   However, only the intersection point with the upper solid part is physically possible because the entropy there is locally maximized. The intersection point with the lower dashed part is physically impossible because the entropy there is locally minimized.

   Within this absorbed laser energy range, nanoparticles are partially melted. The increasing \( E_0 \) leads to a gradually decreased equilibrated fraction of solid atoms \( \eta \).

2) At \( E_0 < 10.3 \text{kJ/mol} \): the vertical line doesn’t intersect with the upper solid part of the parabolic-like curve. Au nanoparticles remain pure solid and \( \eta = 1 \).

3) At \( E_0 > 23.9 \text{kJ/mol} \): similarly, Au nanoparticles become pure liquids and \( \eta = 0 \).

4) At the focus point of the parabolic-like curve \( (E_{cr} = 23.94 \text{kJ/mol} \text{ and } \eta_{cr} = 0.2) \), the solid-liquid coexistent nanoparticle becomes critical. Any slight increase of absorbed laser energy \( E_0 \) could cause catastrophic solid inner core melting and transform solid-liquid coexistent Au nanoparticles into pure liquids. This instability is interpreted as:
to convert an amount of solid atoms into liquid ones, latent heat of fusion is provided and total entropy increases; to maintain the solid-liquid interface, interfacial energy is provided, also leading to entropy increase. When the size of the remaining solid core is small enough, it is no longer beneficial in terms of entropy to keep an explicit solid-liquid interface and catastrophic solid inner core melting occurs.

Catastrophic solid inner core melting is revealed also in Figure 6.3b, where the equilibrated lattice temperature $T_1$ versus $E_0$ is plotted by calling Eq. (6.7). At $E_0<10.3\text{kJ/mol}$, $T_1$ increases linearly with $E_0$. Keep in mind that $T_1$ is slightly above 300K at $E_0=0\text{kJ/mol}$ (no laser irradiation) because heat capacity at the particle melting temperature was used in the evaluation. When surface premelting occurs, lately absorbed laser energy is partially consumed in the form of latent heat of fusion. Lattice temperature increase slows down, reaches the peak temperature $T_p=895\text{K}$, and then starts to drop with further $E_0$ increase. Finally, at $E_0=23.94\text{kJ/mol}$, a sharp decrease of $T_1$ from 855K to 796K leaves supercooled nanoparticles. After that, $T_1$ returns to increase with $E_0$ linearly. This S-shape caloric curve is typical in the microcanonical ensemble (constant energy simulations) and very different from that in the canonical ensemble (constant temperature simulations), where $T_1$ monotonically increases with $E_0$. In the microcanonical ensemble, only $E_0=23.94\text{kJ/mol}$ and $T_1=796\text{K}$ are needed to completely melt the 7,164-atom Au nanoparticle, much lower than $E_0=31.9\text{kJ/mol}$ and $T_1=1045\text{K}$ in the canonical ensemble. Some authors called the temperature in this critical point (796K) in Figure 6.3b as the microcanonical melting temperature, in order to differ from the (canonical) melting temperature obtained from constant temperature simulations.
Both critical fraction of solid atoms $\eta_{cr}$ and microcanonical melting temperature $T_{cr}$ can be found directly from the MCD theory. Taking the derivate of $E_0$ with respect to $\eta$ in Eq. (6.6), we obtained the equation for $\eta_{cr}$:

\[
\frac{dE_0}{d\eta} \bigg|_{\eta=\eta_{cr}} = 0 = \frac{2}{\rho R} (\gamma_{sl} + \Delta \gamma \text{EXP}) \eta_{cr}^{-1/3} - \frac{4}{3} \frac{c_v T_m \Delta \gamma R}{\rho \xi^2 L_m} \text{EXP} \eta_{cr}^{-2/3} + \frac{4}{3} \frac{c_v T_m \Delta \gamma}{\rho \xi L_m} \text{EXP} \eta_{cr}^{-1} + \frac{2}{3} \frac{c_v T_m}{\rho R L_m} (\gamma_{sl} + \Delta \gamma \text{EXP}) \eta_{cr}^{-4/3} + \frac{2}{3} \frac{\Delta \gamma}{\rho \xi} \text{EXP} - L_m
\] (6.8)

$T_{cr}$ is then calculated by substituting $\eta_{cr}$ into Eq. (6.7).

To calculate fraction of solid atoms $\eta_p$ at peak temperature $T_p$ before catastrophic solid inner core melting, RHS of Eq. (6.7) is maximized under the constraint of Eq. (6.6). This leads to

\[
\eta_p^{2/3} + \frac{\xi}{R} \eta_p^{1/3} - \frac{\xi^2}{2 \Delta \gamma R^2} \left( \frac{\gamma_{sl}}{\text{EXP}} + \Delta \gamma \right) = 0
\] (6.9)

$T_p$ is then calculated by substituting $\eta_p$ into Eq. (6.7).
Figure 6.3: a) Plot of Eq. (6.6): the intersection points (grey dots) of vertical lines with the upper solid curve indicate the equilibrated fraction of solid atoms at any absorbed laser energy $E_0$. The intersection points with the lower dashed curve are physically impossible because they have locally minimized entropy instead of locally maximized entropy. b) Plot of Eq. (6.7): the equilibrated lattice temperature at any $E_0$. 

---

Lattice temperature $T_l$ (K)

Critical point
$\text{(E}_{cr}, T_{cr})$

$T_m$ (canonical) melting temperature

$T_p$ peak temperature

$T$ microcanonical melting temperature
Figure 6.4: Total entropy per atom $s$ versus fraction of solid atoms $\eta$ at different absorbed laser energy $E_0$: a) 10kJ/mol, b) 22kJ/mol, c) 23kJ/mol, and d) 30kJ/mol. The grey dots in each figure indicate the equilibrated state.
Figure 6.4 continued

![Graph showing total entropy vs. fraction of solid atoms for two scenarios. The upper graph illustrates a total entropy of 23 kJ/mol with 7,164 atoms, and the lower graph shows a total entropy of 30 kJ/mol with 7,164 atoms.]
6.2.2.2 Global stable to metastable state transition

Figure 6.3 doesn’t reveal another form of instability when nanoparticles gradually melt. In Figure 6.4 total entropy per atom $s$ of the nanoparticle versus fraction of solid atoms $\eta$ for several absorbed laser energy is compared. At $E_0=10$ or $22$kJ/mol, locally maximum entropy achieved at $\eta=1$ or $\eta=0.51$ is also the globally maximum entropy. It means the equilibrated state of the solid-liquid coexistent nanoparticle is globally stable. However, when $E_0$ increases to $23$kJ/mol, total entropy $s$ at the local maximum $\eta=0.4$ is actually lower than that at $\eta=0$ (pure liquids). In other words, the equilibrated state of the solid-liquid coexistent nanoparticle is only locally stable (metastable). The entropy difference between $\eta=0$ and $\eta=0.4$ in this case prevents the metastable particle from collapse. The transition of the equilibrated state from globally stable to locally stable occurs at $E_0=22.68$ and $\eta=0.435$. With increasing $E_0$, the entropy barrier between two stable states diminishes, and finally leads to the catastrophic solid inner core melting at $E_0=23.94$kJ/mol.

6.2.3 Compare the MCD theory with MD simulations

Now let us revisit Figure 6.1 of the ultrafast melting of nanoparticles with a knowledge of two forms of instability reveled by the MCD theory (globally stable to metastable state and metastable to catastrophic solid inner core melting). The MCD theory predicts the 7,164-atom Au nanoparticle becomes metastable at the fraction of solid atoms $\eta=0.435$ and collapses into pure liquids at $\eta=0.2$. In Figure 6.1b, five curves start to diverge at $\eta=0.40$ as soon as entering the metastable state. Thermal fluctuations in three initial configurations are strong enough to make them across entropy barriers and become pure liquids within 800ps. Keep in mind that when the solid-liquid coexistent
nanoparticles are in the metastable state, their melting speed slows down. In the other two cases, nanoparticles are simply constrained in the metastable state and the corresponding \( \eta \) stabilizes at the value very close to that causing catastrophic solid inner core melting (\( \eta = 0.2 \)).

Further comparisons suggest that current MCD theory only qualitatively, but not quantitatively, explain our MD simulation results. Similar to analytical calculations of Figure 6.3, surface premelting in MD simulations of Figure 5.14 initiates at around \( E_0 = 10 \text{kJ/mol} \). It ends up with catastrophic solid inner core melting at \( E_0 = 28.2 \text{kJ/mol} \), higher than \( E_0 = 23.94 \text{kJ/mol} \) predicted by the MCD theory. Moreover, in MD simulations peak temperature \( T_p \) reached before catastrophic solid inner core melting is very close to particle melting temperature \( T_m \). This finding is observed not only for the 7,164-atom Au nanoparticle, but also for other smaller nanoparticle sizes. However, \( T_p \) in the MCD theory is 150K lower than \( T_m \).

Part of above inconsistency can be entitled with uncertain material properties. In evaluating Eq. (6.6) and (6.7), temperature dependence of surface energy \( \gamma_s \) and \( \gamma_l \) is omitted. In fact, \( \gamma_s \) and \( \gamma_l \) are obtained by comparing energy difference between our MD simulations of the 7,164-atom Au nanoparticle and bulk Au at 300K and 1400K respectively. Keep in mind that in bulk Au simulations, application of periodic boundary conditions outside the 6,192-atom simulation cell ensures zero surface energy. Simulation temperatures of 300K or 1400K are chosen because nanoparticles are then pure solids or pure liquids. In intermediate temperatures, surface premelting prevents a reliable determination of surface energy. It is known that surface energy always decreases with temperature increase. Experimental thermal gradient of surface energy is \(-4.33 \times 10^\ldots\).
$4 \text{J/m}^2/\text{K}$ for $\gamma_s$ and $-1 \times 10^{-4} \text{J/m}^2/\text{K}$ for $\gamma_l$ [17]. Thus, in evaluating Eq. (6.6) and (6.7) $\gamma_s$ is overestimated and $\gamma_l$ is underestimated. When temperature increases, both effects could reduce interfacial energy $\gamma_{sl}$, leading to a higher $E_0$ at the catastrophic solid inner core melting and higher peak temperature $T_p$. As illustrated in Figure 6.5a, when $\gamma_s-\gamma_l$ decreases from 0.24N/m to 0.14N/m, $E_0$ at the catastrophic solid inner core melting increases from 23.94kJ/mol to 27.13kJ/mol, and $T_p$ increases from 895K to 969K. In Figure 6.5b, we have also studied the effects of solid-liquid interfacial energy $\gamma_{sl}$. This value is taken directly from experimental data, and may be inconsistent with our MD simulations. However, it has less pronounced effect.
Figure 6.5: Effects of material parameters on evaluations of the MCD theory a) decrease solid surface energy $\gamma_s$ or increase liquid surface energy $\gamma_l$ b) vary solid-liquid interfacial energy $\gamma_{sl}$. The grey dots in each curve indicate the peak temperature $T_p$. 
6.2.4 Extension of the MCD theory: surface nonpremelting \{111\} planes

Varying uncertain material properties partly mitigate, but could not eliminate, differences between our MCD theoretical calculations and MD simulations. Using Eq. (6.9), and combining it with Eq. (6.6) and (6.7), we derived a simple equation to relate $T_p$ with $\eta_p$ when peak temperature is reached.

$$\frac{T_p}{T_m} = 1 - \frac{2\gamma_{s1}}{R\rho L_m \eta_p} \frac{1}{2 + 2A - A^2}, \text{ where } \frac{\varepsilon_r}{R/\eta_p^{1/3}} = A$$

(6.10)

Clearly unless interfacial solid-liquid energy $\gamma_{s1}$ reduces to 0 (which is impossible for Au), peak temperature $T_p$ in the current MCD theory is always lower than particle melting temperature $T_m$, which is contrary to our MD simulations. We hypothesized that this difference comes from the phenomenon of nonhomegeneous surface premelting. It is known that in bulk Au plane surfaces, \{110\} surfaces were completely premelted and have positive excessive surface energy $\Delta \gamma$ [40]. \{111\} surfaces remained stable up to the bulk melting temperature and have negative $\Delta \gamma$, indicating a complete lack of surface premelting [30]. A liquid layer was also generated on \{100\} surfaces, but its thickness did not increase with temperature [31]. Our recent MD simulations on Au nanoparticles (Chapter 4 and Chapter 5) confirmed that part of local \{111\} surfaces are most stable against surface premelting, and remain solid till $T_m$. However, the current MCD theory assumes that solid-liquid coexistent nanoparticles melt in a layer by layer form. An improvement to current MCD theory is needed to take into account of surface nonpremelting \{111\} planes.

Schebarchov and Hendy [47] developed a spherical cap model to include \{111\} planes and negative $\Delta \gamma$. As illustrated in Figure 6.6b, when surface premelting starts, the
liquid layer grows from top to bottom of the sphere, with its thickness $h$ changing from 0 to $2R$. At any moment of $h<2R$, part of surfaces will not be premelted yet. The fraction of remaining solid atoms is

$$
\eta = \frac{4R^3 - h^2(3R-h)}{4R^3} = 2\left(\frac{h}{2R}\right)^3 - 3\left(\frac{h}{2R}\right)^2 + 1 = 2x^3 - 3x^2 + 1 \quad (6.11)
$$

where $x=h/2R$ is relative liquid cap height ($0 \leq x \leq 1$). The total energy per atom $e$ in nanoparticles is expressed as

$$
e (T, \eta) = \eta e_s + (1-\eta) e_l + \frac{2\pi R(2R-h)\gamma_s + 2\pi Rh\gamma_l + \pi h(2R-h)\gamma_{sl}}{4\pi^3 R^3 \rho} \quad (6.12)
$$

Here short-range interactions between solid-liquid and liquid-vapor interfaces are omitted. The total entropy per atom $s$ in nanoparticles is still Eq. (6.3). Following the same procedure as in Section 6.2.2, we can calculate relative liquid cap height $x$ ($0 \leq x \leq 1$) for any absorbed laser energy $E_0$ through the equation:

$$
E_0 = \Delta E - (2x^3 - 3x^2 + 1)L_m + \frac{3}{\rho R} \left( \Delta \gamma - \Delta \gamma x + \gamma_{sl} - \gamma_{sl} x^2 \right) - \frac{c_v T_m}{2\rho RL_m} \frac{(\Delta \gamma + 2\gamma_{sl} x)}{x(1-x)} \quad (6.13)
$$

The lattice temperature $T$ is then obtained as

$$
T = T_m + \frac{E_0 - \Delta E + (2x^3 - 3x^2 + 1)L_m - \frac{3}{\rho R} \left( \Delta \gamma - \Delta \gamma x + \gamma_{sl} - \gamma_{sl} x^2 \right)}{c_v} \quad (6.14)
$$

Figure 6.7 evaluates Eq. (6.13) and (6.14) using the same material parameters as in Section 6.2.2 and Figure 6.3, except for $\Delta \gamma$ where a negative value of $-0.0466$N/m is applied. The presence of surface nonpremelting planes and negative $\Delta \gamma$ significantly elevates the peak temperature $T_p$ from 895K to 1023K, but leaves critical $E_0$ at the inner
core collapse almost unchanged. As explained by Schebarchov and Hendy, surface energy term in Eq. (6.12) increases with \( h \) only when \( h > h^* = -\Delta \gamma R / \gamma_{sl} \) is satisfied. Negative \( \Delta \gamma \) adds additional stability to delay occurrence of surface premelting until sufficient energy is accumulated to create a liquid cap of thickness \( h^* \) at once. At the same time, the peak temperature \( T_p \) is also increased. On the other side, critical \( E_0 \) is more related to energy difference between \( \gamma_s \) and \( \gamma_l \), and is barely changed comparing to Figure 6.3. In Figure 6.6c, representative MD simulated configuration of the solid-liquid coexistent nanoparticle is shown, in which part of local \{111\} surfaces are not premelted yet. Compared with MD simulations, none of two MCD models, concentric sphere model and spherical cap model, are adequate in the representation of complex geometries of liquid regions on outer surfaces of nanoparticles. However, both models qualitatively explained how the equilibrated temperature and fraction of solid atoms will follow changes of absorbed laser energy \( E_0 \).
Figure 6.6: MCD models of solid-liquid coexistent nanoparticles (gray region is liquids, and white region is solids): a) concentric sphere model w/o surface nonpremelting planes; b) spherical cap model w/ surface nonpremelting plane. In c), representative MD simulated configuration of the solid-liquid coexistent nanoparticle is shown, in which part of local {111} surfaces are not premelted yet. Clearly, none of two MCD models are adequate in the representation of complex geometries of liquid regions on outer surfaces of nanoparticles.
Figure 6.7: Spherical cap model with surface nonpremelting plane  

**a)** Plot of Eq. (6.13): the intersection points (grey dots) of vertical lines with the solid curve indicate the equilibrated fraction of solid atoms at any absorbed laser energy $E_0$. The intersection points with the dashed curve are physically impossible because they have locally minimized entropy instead of locally maximized entropy.  

**b)** Plot of Eq. (6.14): the equilibrated lattice temperature at any $E_0$. 

\[ \text{Absorbed laser energy } E_0 (\text{kJ/mol}) \]

\[ \text{Fraction of solid atoms } (\eta) \]

\[ \text{Critical point } (E_{cr}, \eta_{cr}) \]

\[ \text{Local max} \]

\[ \text{Local min} \]

\[ \text{Microcanonical melting temperature } T_{cr} \]

\[ \text{Peak temperature } T_p \]

\[ \text{Lattice temperature } T_L (\text{K}) \]
6.3 Size Dependent Ultrafast Nanoparticle Melting

6.3.1 Interpret MCD curves for various nanoparticle sizes

In Section 6.1 and 6.2, we have discussed MD simulation results and compared them with analytical calculations using the MCD theory for the 7,164-atom Au nanoparticle only. It showed that the MCD theory could qualitatively explain our simulation results. In this section, we applied the MCD theory to several different nanoparticle sizes, and to understand the size-dependence melting behavior of nanoparticles under ultrafast laser irradiation.

Figure 6.8 presents fraction of solid atoms $\eta$ as a function of absorbed laser energy $E_0$ for eleven different sized Au nanoparticles with smallest 276 atoms to largest 7,164 atoms. When calculating these curves, size-dependent nanoparticle radius $R$, melting temperature $T_m$ and $\Delta E$ have been used (see Table 6.1). With particle size increase, $E_0$ at the start of surface premelting $E_{st}$, at the transition into metastable state $E_{tr}$ (black dots) and at the catastrophic solid inner core melting $E_{cr}$ (black squares) all increase significantly. For example, the 276-atom Au nanoparticle collapses into pure liquids at $E_0=2.62\text{kJ/mol}$ whereas the 7,164-atom Au nanoparticle didn’t collapse until $E_0=23.94\text{kJ/mol}$. The curvature of these curves also increases with particle size. For larger nanoparticles, energy difference between $E_{st}$ and $E_{cr}$ is larger, indicating a more gradually occurring surface premelting process. However, energy difference between $E_{tr}$ and $E_{cr}$ becomes smaller with particle size increase, indicating that larger nanoparticles try to avoid the metastable state.

Figure 6.8 is a valuable reference in choosing appropriate laser pulse fluence in processing nanoparticles, especially considering that nanoparticles in experimental
conditions are not monosized but usually have a wide size distribution. Morphological changes of nanoparticles are preferred to be induced in the solid state with the aid of surface premelting. This is because when laser fluence is high enough to melt nanoparticles, coalescence occurs and mechanical properties of nanoparticles are degraded due to subsequent grain size growth. Laser pulse fluence should be carefully adjusted so that absorbed laser energy is within the range of the start of surface premelting $E_{st}$ and the transition into metastable state $E_{cr}$ for all possible nanoparticle sizes in experiments.

<table>
<thead>
<tr>
<th>$N$</th>
<th>$R$ (nm)</th>
<th>$T_m$ (K)</th>
<th>$\Delta E$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>276</td>
<td>1.06</td>
<td>805</td>
<td>18.52</td>
</tr>
<tr>
<td>456</td>
<td>1.25</td>
<td>835</td>
<td>21.79</td>
</tr>
<tr>
<td>736</td>
<td>1.47</td>
<td>915</td>
<td>25.41</td>
</tr>
<tr>
<td>1088</td>
<td>1.68</td>
<td>945</td>
<td>26.77</td>
</tr>
<tr>
<td>1556</td>
<td>1.90</td>
<td>965</td>
<td>27.78</td>
</tr>
<tr>
<td>2112</td>
<td>2.10</td>
<td>985</td>
<td>28.93</td>
</tr>
<tr>
<td>2808</td>
<td>2.31</td>
<td>1005</td>
<td>29.88</td>
</tr>
<tr>
<td>3604</td>
<td>2.51</td>
<td>1015</td>
<td>30.34</td>
</tr>
<tr>
<td>4664</td>
<td>2.73</td>
<td>1025</td>
<td>30.92</td>
</tr>
<tr>
<td>5768</td>
<td>2.93</td>
<td>1035</td>
<td>31.41</td>
</tr>
<tr>
<td>7164</td>
<td>3.16</td>
<td>1045</td>
<td>31.90</td>
</tr>
</tbody>
</table>

Table 6.1: Spherical Au nanoparticles studied in this paper: the number of atoms $N$, radius at room temperature $R$, their size-dependent melting temperatures $T_m$ and total energy difference $\Delta E$ between 300K and $T_m$. 
6.3.2 Limiting nanoparticle sizes $R_1$ and $R_2$

For very small nanoparticles $R < R_2$, black dots $\eta_{tr}$ in Figure 6.8 (global stable to metastable state transition) will intersect with the horizontal line $\eta = 1$ (i.e., $\eta_{tr} = 1$).

Physically speaking, nanoparticles become metastable as soon as entering into the solid-liquid coexistent state. For any absorbed laser energy $E_0$ and its stabilized fraction of solid atoms $\eta$, local maximum entropy of the coexistent state $s_m(\eta, E_0)$ is always not greater than that of the pure liquid state $s_l(0, E_0)$. The equal sign is reached only at the initiation of surface premelting ($\eta_{st} = 1, E_{st}$). Thus, at the critical radius $R_2$, the following equation holds:
\[ s_m(\eta, \eta, E_{st}) = s_i(0, E_{st}) \]  

(6.15)

Setting \( \eta = 1 \) in Eq. (6.6), \( E_{st} \) is obtained as

\[ E_{st} = -L_m + \frac{3}{\rho R} (\gamma_{sl} + \Delta \gamma) - \frac{2c_sT_m}{\rho R L_m} (\gamma_{sl} + \Delta \gamma) - \frac{2c_sT_m \Delta \gamma}{\rho \xi L_m} + \Delta E \]  

(6.16)

Setting \( \eta = 1 \) in Eq. (6.7) and substituting \( E_0 \) with \( E_{st} \) in Eq. (6.16), the particle temperature \( T_{st}(\eta=1, E_{st}) \) becomes:

\[ T_{st}(\eta=1, E_{st}) = T_m - \frac{2T_m}{\rho R L_m} (\gamma_{sl} + \Delta \gamma) - \frac{2T_m \Delta \gamma}{\rho \xi L_m} - \frac{L_m}{c_v} \]  

(6.17)

Similarly, the particle temperature \( T(\eta=0, E_{st}) \) becomes:

\[ T(\eta=0, E_{st}) = T_m + \frac{3}{\rho R c_v} (\gamma_{sl} + \Delta \gamma) - \frac{2T_m}{\rho R L_m} (\gamma_{sl} + \Delta \gamma) - \frac{2T_m \Delta \gamma}{\rho \xi L_m} - \frac{L_m}{c_v} \]  

(6.18)

According to Eq. (6.3), the total entropy per atom is

\[ s = \eta \left[ s^m + c_v \ln \left( T / T_m \right) \right] + (1-\eta) \left[ s^m + c_v \ln \left( T / T_m \right) \right] \]  

(6.19)

Substituting Eq. (6.19) into Eq. (6.15), it has

\[ s^m + c_v \ln \frac{T_{st}(\eta=1, E_{st})}{T_m} = s^m_i + c_v \ln \frac{T(\eta=0, E_{st})}{T_m} \]

\[ \Rightarrow T_{st}(\eta=1, E_{st}) = e^{-L_m/c_v T_m} \]  

(6.20)

Finally, \( R_2 \) is obtained by substituting Eq. (6.17) and (6.18) into Eq. (6.20)

\[ R_2 = \frac{L_m}{\rho L_m} \left( \frac{3L_m - 2c_sT_m \left( 1 - e^{-L_m/c_v T_m} \right)}{L_m - c_sT_m \left( 1 - e^{-L_m/c_v T_m} \right)} \right) \]  

(6.21)

Using size dependent material properties of the 276-atom or 7,164-atom Au nanoparticle in Table 1, \( R_2 \) is 0.78nm and 0.82nm respectively. In Figure 6.9, we plotted \( R_2 \) for each
nanoparticle size and found the extrapolated point $R_2$ as 0.73nm, close to our calculations using Eq. (6.21).

For even smaller nanoparticles $R<R_1<R_2$, black squares $\eta_{cr}$ in Figure 6.8 (metastable solid-liquid coexistent to pure liquid state transition) will intersect with the horizontal line $\eta=1$ (i.e., $\eta_{cr}=1$). Physically speaking, surface premelting won’t exist for small nanoparticles at any $E_0$. They only possess two possible states: pure solids or pure liquids. To calculate $R_1$, let $\eta=1$ in Eq. (6.8):

$$\frac{\Delta \gamma}{\xi} R^2_1 + A\xi R_1 - \frac{B}{2} \xi = 0 \quad (6.22)$$

Here $A = \left(\frac{3\rho L_{sl}^2}{4c_v T_m} + \frac{\Delta \gamma}{\xi} \frac{3L_m \Delta \gamma}{2c_v T_m \xi}\right)$ and $B = (\gamma_{sl} + \Delta \gamma) \left(1 + \frac{3L_m}{c_v T_m}\right)$. Then

$$R_1 = \frac{\xi^2}{2\Delta \gamma} \left(-A + \sqrt{A^2 + 2B\Delta \gamma / \xi^2}\right) = \frac{B}{A + \sqrt{A^2 + 2B\Delta \gamma / \xi^2}} \quad (6.23)$$

The same equation was obtained in [46] with corrections of an obvious misprint. Using size dependent material properties of the 276-atom or 7,164-atom Au nanoparticle in Table 1, $R_1$ is 0.35nm and 0.49nm respectively. In Figure 6.9, we plotted $R_{cr}$ for each nanoparticle size and found the extrapolated point $R_1$ as 0.40nm, just in the middle of our calculation results using Eq. (6.23).

Combining Eq. (6.21) and (6.23), following conclusions of the size-dependent MCD theory are reached: 1) When $R<R_1$, solid-liquid coexistent state doesn’t exist for any $E_0$. Nanoparticles are in the solid state initially, and suddenly become pure liquids above a certain absorbed laser energy. 2) When $R_1<R<R_2$, there exist a range of energies in which nanoparticles are in the coexistent state. However, this coexistent state is always
metastable. When the remaining solid inner core is smaller than $R_{cr}$, it collapses into pure liquids at infinitesimal $E_0$ increase. 3) When $R > R_2$, nanoparticles change from global stable coexistent state, to metastable coexistent state, and finally collapse into pure liquids.

Figure 6.9: Size-dependent $R_{cr}$ (solid-liquid coexistent to pure liquid state transition) and $R_{tr}$ (global stable to metastable state transition). Their extrapolated points with the nanoparticle radius $R$ determine $R_1$ and $R_2$ respectively.

6.4 Summary and Conclusions

The microcanonical droplet (MCD) theory has been applied in this chapter to understand ultrafast melting simulation results presented in Chapter 5 and to understand nanoparticle size effects on the ultrafast melting process. The MCD theory predicts the thermodynamic equilibrium state of nanoparticles when the total energy in the whole
system is conserved (a.k.a. microcanonical ensemble). In our ultrafast melting simulations, total energy in the system remains constant after ultrafast laser pulse terminates, and the system (including melting processes) then evolves like a microcanonical ensemble (NVE). Several conclusions were drawn from this study and are summarized here:

1) Two types of ultrafast melting instability are identified in both MD simulations and the MCD theory. They are global stable to metastable state transition and catastrophic solid inner core melting.

2) The equilibrated state (lattice temperature and fraction of remaining solid atoms) of nanoparticles after ultrafast laser irradiation could be predicted from the MCD theory, and is independent of any kinetic melting path resulting from different laser pulse durations $\sigma_L$.

3) Current MCD theory only qualitatively, but not quantitatively, explains our MD simulation results. This is due to inconsistent material properties and lack of taking into account of surface nonpremelting $\{111\}$ planes.

4) Larger nanoparticles have a more gradually occurring surface premelting process, and avoid staying in the metastable state.

5) Two limiting nanoparticle sizes $R_1$ and $R_2$ are determined from the MCD theory: a) When $R<R_1$, solid-liquid coexistent state doesn’t exist for any $E_0$. Nanoparticles are in the solid state initially, and suddenly become pure liquids above certain absorbed laser energy; b) When $R_1<R<R_2$, there exist a range of energies in which nanoparticles are in the coexistent state. However, this coexistent state is always metastable. When the remaining solid inner core is smaller than $R_{cr}$, it collapses into
pure liquids at infinitesimal $E_0$ increase; c) When $R>R_2$, nanoparticles change from global stable coexistent state, to metastable coexistent state, and finally collapse into pure liquids.
Chapter 7. Nanoparticles’ Sintering and Coalescence

7.1 Introduction

Sintering/coalescence process is accepted as a thermal treatment for bonding particles into a coherent, predominantly solid structure via mass transport events that often occur on the atomic scale [125]. It is traditionally used for manufacturing ceramic objects or in the field of powder metallurgy. Recently, this technique shows an increasing importance in synthesizing nanoparticles with the desired morphology and chemical purity from the vapor-phase [126], or building nanostructures through the cluster-deposition technique [7]. However, the sintering/coalescence mechanism in nanoparticles is still poorly understood. According to the continuum theory, the driving force is believed to be the excess surface free energy in the system. While various mass transport models have been proposed to describe the sintering process for microparticles [125], high sintering rates observed at low temperatures for nanoparticles cannot be explained by any diffusion-based model. Due to the high surface-to-volume ratio, the nanoparticle temperature can be significantly altered by surface energy release, which turns out to accelerate the sintering/coalescence process. Besides this, the melting temperature of nanoparticles is well known to be size-dependent, leading to a complex melting/solidification process when coalescence of nanoparticles is initiated at the temperature slightly below a nanoparticle melting temperature.
In this study, to provide additional insight and to better understand sintering and coalescence processes of nanoparticles, molecular dynamics (MD) simulations using the Quantum Sutton-Chen potential have been employed. Gold nanoparticles were selected as an example of a typical material system. MD simulations of sintering have been performed at constant energy and under a femtosecond laser pulse irradiation. During sintering in the liquid phase, the initial neck growth can be well described by the viscous flow model. For two particles with initial temperature just below the single particle melting temperature, the initial neck growth is initially controlled by viscous flow and then later by grain boundary diffusion. At initial temperatures well below melting, the sintering process occurs very rapidly and ends with a non-spherical oval particle shape. Remarkably, the initial growth rate of the neck region at these temperatures is similar to that in the liquid state. The transient response and sintering of two free Au nanoparticles irradiated by the femtosecond laser pulse is also simulated by combining the two-temperature model with the MD model. It is shown that by increasing laser input energy, nanoparticles can be melted, forming a single larger nanoparticle.

This chapter is organized as follows: Section 7.2 outlines the continuum sintering/coalescence theory developed for microparticles. Section 7.3 reviews the past MD simulation results of the nanoparticle sintering/coalescence. Section 7.4 presents a systematic constant energy MD simulation study of Au nanoparticles sintering and coalescence over a broad initial temperature range with special emphasis on the growth and structural evolution of the neck region between nanoparticles. Section 7.5 extends our simulation studies to the sintering induced by ultrafast laser irradiation. Section 7.6 summarizes our findings.
7.2 Continuum Theory of Sintering and Coalescence

7.2.1 Mass transport mechanism

The driving force for sintering/coalescence process is believed to be the excess surface free energy in the system. Local curvature changes during the coalescence process create the corresponding gradients in vapor pressure, chemical potential or surface stress over neighboring surfaces, and promote the motion of atoms and vacancies [125]. Various mass transport models are proposed to describe ways of material migration in the sintering particles. In the solid-state, these include surface diffusion (SF), grain boundary diffusion (GBD), evaporation & condensation (EC), and volume diffusion from the surface of the particle (VDS) and from the interior of the particle (VDV). In the liquid or amorphous material, viscous flow (VF) is often considered as the dominant mechanism. These models have been extensively reviewed in the dissertation of Lunden [127], and are illustrated in Figure 7.1 together with their transport paths.
Generally speaking, the material migration mechanisms during the sintering process can be grouped into two categories. In the EC, SD and VDS models, material is transported from the particle surface toward the neck, simply filling the area between particles. However, the particle mass centers remain at the same location. These mechanisms are called adhesion mechanisms. On the other hand, in the GBD, VDV and VF models, materials are moved from the region between the particles toward the neck, causing the particle mass centers approach one another. These mechanisms are called densification mechanisms.

7.2.2 Morphology evolution of sintering particles

The morphology evolution of two sintering particles can be divided into two stages. In the initial growth stage, two spherical particles approach each other driven by various gradients between them and the neck region is created. This process is shown in Figure 7.2, where $x_n$ is the neck radius and $R_0$ is the initial particle radius. A larger
spheroidal particle is formed in the end. In the second coalescence stage, the non-spherical particle gradually changes into a spherical particle.

![Figure 7.2: The geometry of two sintering nanoparticles. The shaded area is the neck region](image)

The initial growth stage of sintering is best described by the neck growth in terms of the neck radius. Frenkel [128] and Kuczinski [129] pioneered studies in this direction. For two tangent spherical particles with the equal size, the neck growth equation resulted by any individual mass transport mechanism is given as

$$\left(\frac{x_n}{R_0}\right)^n = \frac{B(T)}{R_0^m} t$$

(6.24)

where $B(T)$ is a term depending on the sintering temperature and relevant material properties and $t$ is the time. The exponent $m$ and $n$ depend on the specific dominant mass
transport mechanism. The characteristic coalescence time $\tau_f$ is defined from Eq. (6.24) as the time at which the neck radius to the particle initial radius ratio reaches 1 or 0.83 (corresponding to the largest possible neck to radius ratio of two sintering spheres). For the surface diffusion, Nichols and Mullins [130][131] showed that

$$B(T) = \frac{25D_s \gamma_f \delta^4}{k_B T}; \quad m = 4; \quad n = 6; \quad \tau_f = R_0^3 / B(T)$$  \hspace{1cm} (6.25)

where $D_s$ is the surface diffusion coefficient and $\delta$ is the atomic size. For the grain boundary diffusion, Coblentz et al. [132] gave the expression

$$B(T) = \frac{192D_g \gamma_f \delta^3}{k_B T}; \quad m = 4; \quad n = 6; \quad \tau_f = R_0^4 / B(T)$$  \hspace{1cm} (6.26)

where $D_g$ is the grain boundary diffusion coefficient and $b$ is the width of the grain boundary. While for the viscous flow, Frenkel [128] developed a simple model as

$$B(T) = \frac{3\gamma_f}{2\pi \eta}; \quad m = 1; \quad n = 2; \quad \tau_f = R_0 / B(T)$$  \hspace{1cm} (6.27)

where $\eta$ is the viscosity.

Many experiments were performed in the past to obtain neck growth data. Curves were fitted to determine the exponents $m$ and $n$, and thus which mass transport mechanism is dominant in the sintering process. However, this method can be problematic for two reasons [127]. First, generally several mass transport mechanisms work together during the sintering process of particles. They are close in the magnitude so it is hard to say which one is dominant. Another difficulty comes from the derivation of Eq. (6.24). Simplified geometric assumptions about the particle system are often used; particularly the particle radius is set to be the same during the sintering, thus violating
volume conservation. This restricts the use of Eq. (6.24) to the initial growth stage only, i.e. \( x_n/R_0 \leq 0.3 \).

There exist several attempts to model the evolving morphology of two sintering particles after the initial growth stage. Recently, a computational model solving the geometry of the bi-sphere system was presented by Lunden [127]. This model allows for the integration of various mass transport mechanisms into the flux equation. It is stable only when \( x_n/R_0 \geq 0.1 \). By comparing this model with other literature data, Lunden [127] concluded that, for at least silicon and copper, surface and grain boundary diffusion were the dominant transport sintering mechanisms for solid-like particles and surface diffusion became more important when temperature increased.

For the multi-particle sintering, an effort was made by Koch and Friedlander [133] to describe the agglomerate coalescence in the initial growth stage in terms of surface area reduction. The coalescence rate of agglomerates is directly proportional to its excess surface energy, written as

\[
\frac{dA}{dt} = -\frac{1}{\tau_f}(A - A_{sph})
\]

(6.28)

where \( A_{sph} \) is the surface area of the final sphere. This work is based on the assumption that the viscous flow is the dominant mass transport mechanism. Later on, Friedlander and Wu [134] extended this method to the coalescence stage. Solid-state surface and grain boundary diffusion were assumed to be the controlling mechanism. The characteristic coalescence time \( \tau_f \) for the solid-state sintering is

\[
\tau_f = \frac{k_B T R_0^3}{16 \gamma_s D_v}
\]

(6.29)
where $D$ is the surface or grain boundary diffusion coefficient and $v$ is the atomic volume.

For the liquid stage, we have

$$\tau_f = \frac{2\eta R_s}{\gamma_f}$$

(6.30)

where $\eta$ is the viscosity.

The coalescence rate also has a significant impact on the final morphology observed during the multi-particle sintering. The sintering starts from the initial touch of particles via the collision. A competition exists between the characteristic time for particle-particle collisions and that for the particle coalescence. At relatively high temperatures when the collision time $\tau_c$ is much shorter than the coalescence time $\tau_f$, we mainly get larger spherical particles. However, at low temperatures when particles don’t have the enough time to finish the coalescence before the next collision, a collection of smaller attached particles (aggregates) is produced [126][135].

### 7.2.3 Energy balance equation

Temperature in the sintering particles may increase due to energy release by the surface reduction. Hence the coalescence rate may be increased. They may also lose energy by the collision with surrounding air molecules or the heat exchange with the substrate. This sintering process can be analyzed using an energy balance equation [136][137]. Considering a system containing two identical spherical particles with $N$ atoms each in the gas phase, the total energy $E$ of this system is the summation of the bulk energy term $E_b$ and the surface energy term $E_s$

$$E = E_b + E_s = 2N[E_{\text{coh}}(0) + C_v T_p] + \gamma A$$

(6.31)
where $E_{coh}(0)$ is the bulk cohesive energy per atom at the absolute zero, $T_p$ is the particle temperature and $C_v$ is the constant volume heat capacity. Any changes in the total energy would result from gains or losses to the surrounding in the form of heat convection or conduction or radiation. For particles in the gas phase,

$$\frac{dE}{dt} = 2NC_v \frac{dT_p}{dt} + \gamma \frac{dA}{dt} = -ZC_gA_{sph}(T_p - T) - \varepsilon\sigma_{SB}A_{sph}(T_p^4 - T^4) \quad (6.32)$$

This equation can be combined with Eq. (6.28) to establish the relationship between the particle temperature $T_p$ and the particle surface area $A$.

$$2NC_v \frac{dT_p}{dt} = \frac{\gamma}{\tau_f} (A - A_{sph}) - ZC_gA_{sph}(T_p - T) - \varepsilon\sigma_{SB}A_{sph}(T_p^4 - T^4) \quad (6.33)$$

Where $C_g$ is the heat capacity of gas molecules, $\varepsilon$ is the emissivity, $T$ is the environment temperature, $\sigma_{SB}$ is the Stefan-Boltzmann constant and

$$Z = \frac{p}{\sqrt{2\pi m_k b T}} \quad (6.34)$$

is the collision rate with gas molecules.

If the energy loss is negligible (as in constant energy MD simulations) or the cooling time $\tau_{cool}$ due to heat transfer is much longer than the coalescence time $\tau_f$, Eq. (6.33) can be simplified as

$$2NC_v \frac{dT_p}{dt} = \frac{\gamma}{\tau_f} (A - A_{sph}) \quad (6.35)$$

Lehtinen and Zachariah [136] used Eq. (6.35) to show that the heat release associated with the particle sintering could reduce the coalescence time by as much as a few orders of magnitude. They also derived a dimensionless “coalescence heating number” which was used to evaluate if the sintering process could be considered as an
adiabatic process. In a later study [137], the same authors used Eq. (6.33) to study the particle sintering in the gas phase at the low pressure or high volume loading condition. In both systems, time was insufficient for particles to relax to the gas temperature before another collision event took place. The released surface energy was accumulated and the resulting particle temperature was increased further.

7.3 Literature Review of MD Simulation Results

There have been several computational studies to understand the sintering process of nanoparticles from the atomistic point of view. Due to the large surface area to volume ratio, nanoparticles can be significantly heated by the released surface energy. We will discuss this in Section 7.3.1, followed by reviewing papers on two equal-sized nanoparticles’ sintering, with a focus on efforts to determine dominant mass transport mechanisms in different sintering stages. In Section 7.3.3, the sintering of differently oriented or unequal-sized nanoparticles is discussed.

7.3.1 Temperature increase in nanoparticles

Zachariah and Carrier [126] studied the coalescence of two silicon nanoparticles using constant energy MD simulation. They first pointed out that initial rapid temperature increase was unique to nanoparticles’ sintering and speeded up the coalescence. This fact was especially true for the final coalescence stage of the gradual transformation to a spherical particle [136].

Hendy et al. [138] studied the coalescence of two 565-atom icosahedron at various initial temperatures using constant energy MD simulations. By equating the
thermal energy increase of the sintering nanoparticles with the surface energy reduction, they estimated the temperature increase in the complete coalescence as

\[ \Delta T = 3 \left(1 - 2^{-1/3}\right) \frac{\gamma}{\rho C_v R} \]  

(6.36)

where \( \rho \) is the density. This expression was applicable until an initial coalescence temperature \( T_i = 340 \text{K} \). After that, since the melting temperature of nanoparticles is size-dependent, the final coalesced nanoparticle was molten and a drop in the final temperature was observed due to the latent heat of fusion. However, if the final temperature fell between the melting point of the larger cluster and that of the smaller clusters, a metastable molten droplet was formed first and then froze.

7.3.2 Two equal-sized nanoparticles’ sintering

Zhu and Averback [139] published one of the earliest papers on MD simulations of nanoparticles’ sintering. By studying the sintering at 700K of two single crystal Cu nanoparticles containing 4,688 atoms each, they attributed the initial rapid sintering to plastic deformation caused by dislocation mechanism. The relative center-to-center shrinkage \( \Delta L_{cc}/2R \) after 25ps was found to be 12% while the value induced by any diffusion mechanisms should be less than 0.1%. Meanwhile, the shear stress in the neck region at 5ps was calculated to be 8GPa, sufficient to induce the dislocation. The grain-boundary dislocation was actually shown by authors on atomic configuration plots. On the contrary, by studying the sintering of Al nanoparticles containing 1,014 atoms, 1,966 atoms and 2,439 atoms respectively, Raut et al. [140] concluded that the shear stress in the contact region was too small to induce plastic deformation, although the atomic
mobility in that region is mainly due to the convective flow of atoms, rather than the diffusive motion.

Lewis et al. [41] considered the coalescence of two Au nanoparticles in liquid-liquid, liquid-solid and solid-solid states. Constant temperature MD simulations were performed. Thus this simulation was relevant to the study of supported nanoparticles that are loosely bound to the substrate [7]. Their results showed that the macroscopic sintering theory via diffusion failed to account for the sintering behavior of nanoparticles since the presence of facets in nanoparticles greatly reduced the atomic flux [7][41].

Small silicon nanoparticles having no more than 500 atoms were modeled by Zachariah and Carrier [126] over a broad temperature range using constant energy MD simulations. It was shown that the nanoparticles’ coalescence time was very sensitive to size and temperature at lower initial temperatures when particles were clearly solid-like but considerably less sensitive at higher initial temperatures when they were liquid-like. The coalescence time for solid-state particles is predicted pretty well by the diffusion model using Eq. (6.29) [133][63]. For liquid particles, the viscous flow model using Eq. (6.30) [128] gave the generally right trend but the predicted coalescence time was ten times quicker than the simulated values. This may be caused by an inaccurate viscosity data for nanoparticles.

The size-dependent particle melting temperature was taken into account by Arcidiacono et al. [141] in applying the grain boundary diffusion mechanism in a study of Au nanoparticle coalescence. A similar fast initial growth stage (within 0.3ns), independent of the particle size and the initial temperature, was detected. Contrary to Lewis’s results [41], they found that, at least for nanoparticles larger than 2nm, the
analytic model could generally predict the initial neck growth rate obtained via MD simulations.

7.3.3 The effect of orientation and unequal-sized nanoparticles’ sintering

The sintering of two differently oriented nanoparticles, which is common in experiments, has also been studied. Two particles would rotate with respect to each other to find a low-energy grain boundary between them [139]. Since the surfaces of particles are nanoscopically rough, the different orientation does not strongly affect their contact area and therefore the potential gradient. The shrinkage rate was similar to that of the same oriented nanoparticles although the surface diffusivity was different, resulting in a different neck size [140].

While the analytic models in Section 7.2 are only valid for two equal-sized nanoparticles, MD simulations can also be used to study the sintering between two unequal-sized nanoparticles. Zeng et al. [142] simulated the sintering of unequal-sized Cu nanofibers, and found that the smaller fiber that was sub-critical to support crystallinity could become amorphous and exhibit the accelerated bulk diffusion activity. Hawa and Zachariah [143] presented thorough studies of the silicon nanoparticles. They concluded that the deformation of the smaller particle and convection processes dominated the liquid-phase coalescence, whereas diffusion processes dominated the coalescence in near solid-like particles. Coalescence processes became faster when the size ratio of two particles (smaller/larger) went to zero.
7.4 Sintering of Au nanoparticles: Constant Energy and Constant Temperature MD Simulations

In this section, the sintering process of two equal-sized Au nanoparticles is systematically studied. Each nanoparticle contains 456 atoms with a radius of 1.22nm at 300K, or 7,164 atoms with a radius of 3.07nm at 300K. Constant energy MD simulations were conducted to model the sintering process occurring when nanoparticles are free or loosely attached to a substrate. Constant temperature MD simulations were conducted to model the sintering process occurring when nanoparticles have sufficient heat exchange with the underlying substrate or surroundings. Results are presented at various initial temperatures to cover both solid-state sintering and liquid phase coalescence. At each initial temperature, five independent simulations are performed to obtain the average value.

7.4.1 Initial configuration preparation

To prepare a reliable initial configuration for two sintering Au nanoparticles at initial temperature $T_0$, the following procedure is applied:

1) Take the final nanoparticle configuration at $T_0$ from the Au nanoparticle equilibrium melting simulation.

2) Using the above nanoparticle configuration, run additional constant temperature simulations in the equilibrium stage (100ps) and in the statistical data collection stage (100ps). In the second stage, instantaneous nanoparticle configurations are dumped every 0.5ps, so total 200 configurations are stored.
3) Select from the second step those nanoparticle configurations which have instantaneous temperature \( T_{\text{ins}} \) as \(|T_{\text{ins}} - T_0| < 5\text{K}\) and average temperature \( T_{\text{avg}} \) as \(|T_{\text{avg}} - T_0| < 10\text{K}\).

4) Take any two of those nanoparticle configurations selected in the third step. Align them such that the closest distance is 0.3nm, slightly larger than the atomic distance in FCC Au (0.2885nm at 300K). The initial translational momentum and angular momentum are also removed during the alignment.

7.4.2 Two 456-atom Au nanoparticles

7.4.2.1 Liquid phase coalescence (1200K)

Figure 7.3 shows the reduced moment of inertia in the collision direction \( I_x/I_{\text{sph}} \), together with the particle temperature versus time. Morphologies of two sintering nanoparticles at different times are also plotted, where black beads denote the left nanoparticle and grey beads denote the right nanoparticle.

As shown by Figure 7.3, the nanoparticle temperature rapidly increases during the sintering process within the first 30ps. After that, it fluctuates due to atomic thermal fluctuations in the finite system. Since constant energy MD simulations are applied, the energy released from surface area reduction can only be converted to the kinetic energy of nanoparticles. When two particles completely coalesce into one, the final temperature is 1295.88±4.86K by averaging over five simulations. Using solid surface energy at 300K \( \gamma = 0.61\text{N/m} \) and constant volume heat capacity \( C_v = 35.14\text{J/mol/K} \) at 1200K for the 456-atom Au nanoparticle, both of which are obtained from our previous MD simulations, Eq. (6.36) gives a prediction of 1300.8K, pretty close to our simulated values.
Figure 7.3: Reduced moment of inertia in the collision direction and the particle temperature versus time at initial temperature 1200K. Morphology changes of nanoparticles are also shown.
Several ways are available to characterize morphology changes of two coalescing nanoparticles. The reduced moment of inertia approaches unity when the coalesced particle becomes perfectly spherical, and is commonly used to specify different stages of the sintering. In the first 2ps, the two particles gradually approach each other driven by the potential gradient between them. The reduced moment of inertia generally remains constant at this stage. After that, as shown in Figure 7.3b, a collision occurs between two particles. A non-zero initial neck radius is created immediately after the collision and grows very fast, indicating two particles enter into the initial growth stage. This stage is illustrated in Figure 7.3c to f. From 2ps to 30ps, the reduced moment of inertia sharply decreases with approximately exponential decay. Most of the energy release, as indicated by the rapid temperature increase, also occurs in this stage. By the end of 30ps, a spheroidal particle is formed. The coalescence stage begins after this, and the system gradually changes into a spherical shape with no further temperature increase. The coalescence finishes when the reduced moment of inertia reaches 1.0. This turns out to be 60ps in the current case.

Morphology changes of two coalescing particles can also be characterized by the aspect ratio of the system. Here we define the aspect ratio as

$$C = \frac{2R_x}{R_y + R_z}$$

(6.37)

where \(x\) is the collision direction and \(R_\alpha (\alpha = x, y, z)\) is the gyration radius at different directions. This property is presented in Figure 7.4 as a function of time. The coalescence time is found as 66ps, close to our previous finding (60ps).
Figure 7.4: Aspect ratio of the 456-atom Au nanoparticle as a function of time at the initial temperature 1200K

The reduced center-to-center distance $\Delta L_{cc}/L_{cc}$ between two particles is useful to determine important mass transport mechanisms since only the densification mechanism can lead to the decrease of $L_{cc}$. This property is presented in Figure 7.5 as a function of time. By comparing with Figure 7.3, we find that in the initial growth stage (first 30ps), the coalescence proceeds by optimizing the particles’ contact region, like in the viscous flow mass transport mechanism driven by surface tension. After that, we observe a different decrease rate of $L_{cc}$. This decrease continues even after the end of the complete coalescence, indicating that the interdiffusion phenomenon in which atoms of one particle diffuse into another particle. Finally, when two particles are perfectly mixed, a zero $L_{cc}$ will be obtained, however, in the current case it is not reached within 500ps.
Figure 7.5: The reduced center-to-center distance $\Delta L_{cc}/L_{cc}$ as a function of time at the initial temperature 1200K

The same conclusion can be reached by plotting mass center velocity of the left particle in the collision direction. This is presented in Figure 7.6 till the end of the complete coalescence (60ps). Finite velocity observed in the first 30ps indicates that two particles approach each other by the viscous flow mechanism. After that, velocity fluctuates around zero and interdiffusion begins.
Figure 7.6: Mass center velocity of the left particle in the collision direction as a function of time at the initial temperature 1200K

In our MD simulations, neck atoms are defined as those located within 0.15nm away from the system geometrical center in the collision direction. The neck radius is then calculated from neck atoms by using Eq. (4.9). For the liquid phase coalescence evolving based on the viscous flow mechanism, Frenkel [128] developed a simple model to describe the neck growth rate. It is expressed as

$$\left(\frac{x_n}{R_0}\right)^2 = \frac{3\gamma_l}{2\pi\eta R_0} t$$

where $x_n$ is the neck radius, $R_0$ is the initial particle radius, $\gamma_l$ is the liquid surface energy, $\eta$ is the particle viscosity and $t$ is the time. The characteristic coalescence time $\tau_f$ is defined when $x_n/R_0$ reaches unity as
\[ \tau_f = \frac{2\pi \eta R_0}{3\gamma_i} \]  

(6.39)

To compare Eq. (6.38) and (6.39) with our MD simulations, \( \gamma_i \) is chosen as 0.61N/m and the viscosity for Au at 1200K (\( \eta = 8.77 \times 10^{-3} \text{Pa\cdots} \)) is obtained from simulations of Qi et al. [144] using the same Q-SC metal potential. This generates a viscous flow mechanism driven coalescence time of 39.2ps, which is in good agreements with the length of the initial growth stage determined from MD simulations (30ps). Note that only the initial growth stage is dominated by the viscous flow, as explained in the previous section.

In Figure 7.7, we illustrate time evolution of the reduced neck radius \( x_n/R_0 \) and compare this with the prediction made by the Frenkel’s model. Because nanoparticles are not perfectly spherical but faceted, this leads to a non-zero initial neck radius. For this reason to compare with the model we have shifted in Figure 7.7 the MD simulated neck radius by this non-zero initial value. One can see that the calculated neck radius is described well by the viscous flow model to 30ps. Then interdiffusion replaces viscous flow as the dominant transport mechanism.
Figure 7.7: Time evolution of the neck radius compared with the analytical prediction made by Frenkel [128] at the initial temperature 1200K

7.4.2.2 Sintering at 800K

Sintering at the initial temperature 800K, which is slightly below the melting temperature, takes a much longer time to reach the equilibrium state than that at higher or lower initial temperatures. The reduced moment of inertia in the collision direction and temperature versus time in the first 3ns, together with morphological changes of two sintering particles, are showed in Figure 7.8. The final reduced moment of inertia is 1.26, indicating that the resulted particle has a spheroidal shape. Note that the final particle average temperature (893K) is higher than the melting temperature of the initial 456-atom Au nanoparticle (835K) but is lower than that of the combined, 912-atom, Au nanoparticle (920K). Thus, although the final product is still solid, it may undergo a
melting-solidification cycle due to surface energy release and increase of temperature during sintering.

A closer look at the growth rate of the neck region can reveal more details about the sintering mechanism. This is illustrated in Figure 7.9 (as in Figure 7.7, the simulated results have been shifted due to the non-zero initial contact area). The growth rate predicted from analytical models is also shown. From Figure 7.9, we observe that the viscous flow model is sufficient to describe the initial neck growth up to 15ps, which suggests the initial neck region behaves like liquids or amorphous solids. After 20ps the slope changes, indicating a different neck growth mechanism is dominating. For the solid-state sintering, the grain boundary diffusion mechanism is often used [132]. The initial neck growth rate is

\[
\left( \frac{x_n}{R_0} \right)^6 = \frac{192D_b \gamma_s \delta^3}{k_BT_R^4} t
\]

(6.40)

and the characteristic coalescence time is

\[
\tau_f = \frac{k_BT_R^4}{192D_b \gamma_s \delta^3}
\]

(6.41)

where \(D_b\) is grain boundary diffusion coefficient, \(b\) is grain width, \(\gamma_s\) is solid surface energy (0.85N/m), \(\delta\) is atomic size (2.56Å), \(k_B\) is Boltzmann constant and \(T\) is temperature. Surface energy \(\gamma_s\) is obtained from our MD simulations and \(D_b\) from the Boltzmann-Arrhenius dependence

\[
D_b = D_{b0} \exp\left(- \frac{E_a}{RT} \right)
\]

(6.42)

The parameters \(D_{b0}b = 9.44 \times 10^{-15}\) m/s and \(E_a = 83.0T_m\) J/mol were obtained from Brown and Ashby’s [145][146] empirical relations valid for all FCC metals. The predicted
change of reduced neck radius with time in Eq. (6.40) is shown by solid line in Figure 7.9. The grain boundary diffusion model gives a correct exponential dependence after 20ps. The applicability of the model in this sintering stage is especially evident if one adjusts the parameter $D_{gb}$ to a lower value ($6.17 \times 10^{-17} \text{ m/s}$) or activation energy $E_a$ to a higher value ($123.0T_m \text{ J/mol}$) to fit the experimental data (dashed line). The necessity to adjust $D_{gb}$ or $E_a$ indicates that the grain boundary diffusion coefficient calculated from [145][146] may not valid for nanoparticles or is not consistent with MD simulations using the Q-SC potential.
Figure 7.8: Reduced moment of inertia in the collision direction and the particle temperature as a function of time during the sintering process at the initial temperature 800K. Morphology changes of nanoparticles are also shown.
Figure 7.9: Time evolution of the neck radius compared with analytical predictions made by Frenkel [128] and Coblentz et al. [132] for the first 2ns. The initial temperature is 800K.

7.4.2.3 Solid state sintering (300~700K)

In Figure 7.10, the reduced moment of inertia in the collision direction $I_x/I_{sph}$ at the initial temperature 300K and 700K is plotted as a function of time. Other intermediate temperatures have similar curves. As a result of the solid state sintering, two sintering particles will end up with a dumbbell-like shape instead of a larger spherical particle as in the liquid phase. The coalescence time $\tau_f$ is defined as the time after which the reduced moment of inertia becomes stable and is listed in Table 7.1. Theoretical predictions made from the grain boundary diffusion mechanism (see Eq. (6.41)) are also included. Although the sintering is incomplete, it finishes in less than 20ps, much faster than predictions made from solid state diffusion models.
Another interesting finding is that the decrease of reduced moment of inertia with time is not monotonic. A local minimum and peak around 10ps can be found at all initial temperatures, followed by a rapid decrease in the reduced moment of inertia and several oscillations. We associate this oscillating pattern with vibration of nanoparticles during the sintering. For lower initial temperature (300K), this effect is more pronounced because nanoparticles are stiffer at lower initial temperatures.

![Graph showing reduced moment of inertia in the collision direction versus time at initial temperatures 300K and 700K](image)

Figure 7.10: Reduced moment of inertia in the collision direction versus time at initial temperatures 300K and 700K
<table>
<thead>
<tr>
<th>Initial temperature (K)</th>
<th>$\tau_f$, simulation (ps)</th>
<th>$\tau_f$, theory (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>140</td>
<td>$4.08 \times 10^8$</td>
</tr>
<tr>
<td>400</td>
<td>40</td>
<td>$5.29 \times 10^4$</td>
</tr>
<tr>
<td>500</td>
<td>18.1</td>
<td>$1.04 \times 10^4$</td>
</tr>
<tr>
<td>600</td>
<td>17.6</td>
<td>786.46</td>
</tr>
<tr>
<td>700</td>
<td>26.4</td>
<td>128.77</td>
</tr>
</tbody>
</table>

Table 7.1: Comparison of simulated coalescence time with theoretical prediction

The reduced neck radius versus time is presented at the initial temperature 300K and 700K in Figure 7.11 and Figure 7.12 respectively. Within the first 10ps, the calculated neck radius grows so fast that it can’t be explained by any known solid-state diffusion models. After that, at 300K the neck radius oscillates several times and then becomes stable. But at 700K, the neck region continues to grow for more than 500ps; the growth rate is so slow that it also can’t be described by any known diffusion models.
Figure 7.11: Time evolution of the neck radius at the initial temperature 300K

Figure 7.12: Time evolution of the neck radius at the initial temperature 700K
The rapid solid-state sintering can be partially understood by calculating global bond-orientational order parameters (BOP) over neck atoms and compare with those obtained over atoms in the other region of two sintering particles. In Figure 7.13 and Figure 7.14, we overlap plots of the reduced moment of inertia and the global BOP parameter \(Q_6\) for atoms in the neck region (\(\text{NQ}_6\)) and for atoms in the other regions (\(\text{BQ}_6\)) of the two sintering particles. Beginning from 2ps, the reduced moment of inertia decreases rapidly. A large amount of surface energy is released and accumulated in the neck region. The neck is heated up, becomes softer as indicated by a sharp decrease in the \(\text{NQ}_6\) and by a local minimum in the reduced moment of inertia. The liquid-like neck region can facilitate the approach of two particles, and hence reduce the coalescence time by several orders of magnitude. The heat can’t accumulate in the neck region for very long, instead diffusing into other regions of the nanoparticles. Then, a typical increase of the reduced moment of inertia followed by a sharp decrease is observed. In a recent review of experimental observations of nanoparticles’ coalescence [147], authors also mention that the liquid-like mobility of surface layers and the contact region is essential in the understanding of the coalescence mechanism. In Section 7.4.3, the local BOP method is applied to study initial neck regions in the larger 7,164-atom Au nanoparticle. A better understanding of formation of liquid-like atoms and their distributions in the neck regions at different initial temperatures could be reached.
Figure 7.13: Reduced moment of inertia and BOP versus time at initial temperature 300K. NQ₆ and BQ₆ are neck and the other regions correspondently.

Figure 7.14: Reduced moment of inertia and BOP versus time at initial temperature 700K. NQ₆ and BQ₆ are neck and the other regions correspondently.
7.4.2.4 **Comparisons between constant energy and constant temperature simulations**

The results presented in the previous sections were calculated from constant energy MD simulations to model the sintering process when nanoparticles are free or loosely attached to a substrate. In this case, nanoparticle temperature increases due to surface area reduction and surface energy release. Constant temperature MD simulations are also often conducted to model the sintering process when nanoparticles have sufficient heat exchange with the underlying substrate or surroundings. In that case, nanoparticle temperature is kept to be the same as initial sintering temperature $T_0$. Figure 7.15 compared results calculated using both MD simulations. At solid state sintering ($T_0=300$–$700K$) or liquid phase coalescence ($T_0=1200K$), similar time variations of reduced moment of inertia are observed. Note that due to particle temperature increase in constant energy simulations, final reduced moment of inertia at solid state sintering ($T_0=300K$) is slightly lower than that in constant temperature simulations. The main difference between two MD simulations occurs at intermediate initial temperature 800K. As explained in Section 7.4.2.2, in constant energy simulations, although the final product is still solid, the sintering nanoparticles may undergo a melting-solidification cycle due to surface energy release and increase of temperature. From Figure 7.15b, it is also clear that two simulated curves start to diverge in accompany with significant particle temperature increase above the 456-atom Au nanoparticle melting temperature $835K$ in constant energy simulations.
Figure 7.15: Comparisons of constant energy and constant temperature MD simulation results on time variations of reduced moment of inertia at different initial temperatures: a) 300K; b) 800K; c) 1200K. Particle temperature in constant energy MD simulations is also shown.
7.4.3 Two 7164-atom Au nanoparticles

Several new analysis tools are applied in this section to study initial neck regions during the solid state sintering. A quantitative understanding of formation of liquid-like atoms in the neck region and its important role in explaining rapid solid-state sintering could be reached. The larger 7,164-atom Au nanoparticle is selected because of more atoms in its neck region and less statistical fluctuations in calculated properties. These statistical fluctuations make analysis tools discussed below difficult to be applied to the smaller 456-atom Au nanoparticle to obtain any conclusive answers. Only constant temperature simulation results at the initial temperature 900K, well below the particle melting temperature 1045K, are presented. Other initial temperatures like 1000K and 1020K gave similar findings. As shown in Section 7.4.2.4, constant energy and constant temperature simulations give close results at the solid state sintering.
Like smaller 456-atom Au nanoparticles, the solid state sintering in larger 7,164-atom Au nanoparticles also proceeds very fast. The reduced neck radius versus time is presented in Figure 7.16. From 10ps to 22ps, the calculated neck radius grows so fast that it can’t be explained by any known solid-state diffusion models. After that, a very slow increase rate of reduced neck radius is also detected. The local BOP method is applied to analyze fraction of liquid-like atoms in different regions of two sintering nanoparticles. In Figure 7.17, the surface of the neck region is represented by thick solid line; the bulk of the neck region is represented by thick dashed line; the surface of regions other than the neck is represented by thin solid line, and the bulk of regions other than the neck is represented by thin dashed line. Cross sections of the neck region at several different sintering times are also shown in the same figure, with liquid-like atoms colored as red and solid-like atoms colored as blue. Figure 7.18 presents time variations of reduced
moment of inertia and neck region temperature during the sintering. A rich knowledge of solid state sintering is obtained by studying these two figures together.

Figure 7.17: Time variations of fraction of liquid-like atoms in different regions of two sintering nanoparticles at initial temperature $T_0=900$K. Morphology of atoms in the neck
region is also shown, where red stands for liquid-like atoms and blue stands for solid-like atoms.

Figure 7.18: Time variations of reduced moment of inertia and neck region temperature of two sintering 7,164-atom Au nanoparticles at initial temperature 900K. Before the completion of the sintering (30ps), neck region temperature is higher than the whole nanoparticle temperature which is fixed as 900K in constant temperature simulations.

In the first 4ps, two nanoparticles gradually approach each other driven by the potential gradient between them to form the initial neck region. The reduced moment of inertia generally remains constant at this stage. The neck region contains few atoms and behaves like amorphous materials with only liquid-like atoms (Figure 7.17a). From 4ps to 10ps, more atoms enter into the neck region, and are subsequently crystallized to form ordered structures. By 10ps, fraction of liquid-like atoms in the neck region is no difference from that in other regions (Figure 7.17b). However, the neck region only remains in this state very shortly. As shown in Figure 7.18, released surface energy
during the sintering is accumulated in the neck region, and neck temperature is consistently higher than the whole nanoparticle temperature which is fixed as 900K in constant temperature simulations. Since 10ps, the crystallized neck region starts to melt. Like other surface premelting phenomenon we have discussed in previous chapters, the liquid-like atoms in the neck region emerges from surface, with a continuously thickening surface liquid layer (Figure 7.17c-d). At 22ps, the whole neck region is almost completely melted (Figure 7.17e). Decrease of reduced moment of inertia mainly occurs between 10ps and 22ps, i.e., when the neck region becomes liquid-like. High neck temperature lets more heat diffuse into other regions. When the sintering finishes (30ps), the neck temperature drops to nanoparticle temperature 900K and the neck region is recrystallized to have the same fraction of liquid-like atoms as other regions (Figure 7.17f-g). Note that crystallization of the neck region between 4ps and 10ps is only observed at low initial temperatures like \( T_0 = 900K \). At higher initial temperatures, the sintering proceeds faster and enough energy is accumulated to keep the neck region always melted before the sintering finishes.

Atomic trajectory presented in Figure 7.19 provides a direct evidence of dominating diffusion mechanisms in sintering nanoparticles. As explained in Figure 7.1, different mass transport mechanisms have different material transport paths. From 0ps to 4ps (Figure 7.19a), most atoms only vibrate locally. A few atoms close to the contact point of two sintering nanoparticles are drawn together by potential gradient between them to create the initial neck region. Migration of atoms on the surface, which is typical of surface diffusion mass transport mechanism, is also observed, although its effect is negligible. Thus, the reduced moment of inertia barely changes in the first 4ps. Our
previous analysis shows that rapid solid state sintering occurs mainly between 4ps and 30ps. This is attributed to liquid-like neck regions and viscous flow diffusion mechanism. As shown in Figure 7.19b, the collective movement of all the atoms, typically observed in viscous flow diffusion mechanism, is very strong during this period in both inner regions and on the surface. Atomic trajectory also reveals that grain-boundary diffusion is the secondary diffusion mechanism, where atoms migrate along the boundary between two nanoparticles. After 30ps, Figure 7.16 indicates a very slow increase rate of reduced neck size, which doesn’t affect reduced moment of inertia (Figure 7.18) and its origin is unclear from previous analysis. Figure 7.19c shows that surface diffusion is the only reason to this slowly enlarged neck region. As any adhesion mechanisms discussed in Section 7.2.1, in surface diffusion materials is transported from the particle surface toward the neck, simply filling the area between particles. However, the particle mass centers and reduced moment of inertia remain the same.

Continued
Figure 7.19: Atomic trajectory during the sintering of two 7,164-atom Au nanoparticles at initial temperature 900K: a) from 0ps to 4ps; b) from 4ps to 30ps; c) from 30ps to 300ps

Figure 7.19 continued
7.5 Sintering of Au Nanoparticles induced by Ultrafast Laser Irradiation

The integrated MD+TTM computational model developed in Chapter 5 has been applied in this section to study ultrafast laser irradiation of two sintering 7,164-atom Au nanoparticles at low laser intensity where surface premelting and solid-liquid phase transition are major interests. Starting from the same initial temperature 300K, the sintering nanoparticles are subjected to different amounts of absorbed laser energy from 5kJ/mol to 40kJ/mol. At each energy level, five independent runs with different initial Au nanoparticle configurations are performed to obtain average results.

Figure 7.20 compares time evolution of the lattice temperature $T_l$ at different absorbed laser energy $E_0$. Similar to ultrafast melting of single Au nanoparticle, temporary lattice superheating occurs at intermediate $E_0=25$~35kJ/mol when the time scales for two competitive processes—the electron-lattice temperature equilibrium and the solid-liquid phase transition—become comparable. With increasing $E_0$, the equilibrated $T_l$ increases accordingly except for the case between 25kJ/mol and 30kJ/mol, in which both lattice temperatures are close to the particle melting temperature by the end of 200ps. However, as shown below, morphological changes at these two energy levels are very different. At the same absorbed laser energy $E_0$, the equilibrated $T_l$ in two sintering Au nanoparticles is slightly higher than that in single Au nanoparticle. This is due to surface area reduction and surface energy release during sintering processes.
Figure 7.20: Time evolution of lattice temperature $T_l$ of two sintering 7,164-atom Au nanoparticles under different absorbed laser energy $E_0$=5~40kJ/mol.

Figure 7.21 and Figure 7.22 compare time evolution of reduced moment of inertia $I/I_{sp}$ and reduced neck radius $x_n/R_0$ at different absorbed laser energy $E_0$. Before 10ps, all the curves look similar. After 10ps, these curves are separated into three groups. At $E_0$>25kJ/mol, the lattice temperature remains above the particle melting temperature after temporary superheating. The liquid phase coalescence finishes within 100ps and two sintering nanoparticles become one single larger nanoparticle. At $E_0$=25kJ/mol, the lattice temperature is temporarily higher than the particle melting temperature before 40ps, and then drops slightly below it. Similar to Section 7.4.2.2, the sintering in this condition proceeds slowly and didn’t finish within 200ps. The growth rate of neck radius for the first 40ps when its temperature still remains above the particle melting temperature is similar to that in the liquid phase coalescence. A decreased growth rate is observed around 40ps when the lattice temperature drops below the particle melting temperature. At $E_0$<25kJ/mol, the lattice temperature is always below the particle melting temperature.
The solid-state sintering ceases quickly after 40ps. Different $E_0$ gives almost identical reduced moment of inertia, but slightly different neck region sizes.

Figure 7.21: Time evolution of reduced moment of inertia $I_x/I_{sph}$ of two sintering 7,164-atom Au nanoparticles under different absorbed laser energy $E_0=5$~40kJ/mol.

Figure 7.22: Time evolution of reduced neck radius $x_n/R_0$ of two sintering 7,164-atom Au nanoparticles under different absorbed laser energy $E_0=5$~40kJ/mol.
For the sintering induced by ultrafast laser irradiation, it is not easy to determine the dominant mass transport mechanism by simply comparing time evolution of reduced neck radius with continuum sintering models. The main difficulty comes from that particle temperature and diffusion coefficients are not constant. However, as discussed in Section 7.4.3, atomic trajectory reveals mass transport path in sintering nanoparticles and provides a direct evidence of dominant diffusion mechanisms.

Figure 7.23 presents atomic trajectory during solid state sintering at $E_0=20\text{kJ/mol}$. From 0 to 10ps (Figure 7.23a), most atoms vibrate locally. Only a few atoms close to the contact point of two sintering nanoparticles are drawn together to create the initial neck region. Similar plots are obtained in all the other energy levels. Rapid solid state sintering occurs mainly between 10ps and 40ps (Figure 7.23b). The grain boundary diffusion, where atoms migrate along the boundary between two nanoparticles, is very pronounced during this period. The collective movement of atoms is observed only in those areas close to the neck region. This is different from Figure 7.19b, where the collective movement of the whole nanoparticle is found. Note that in ultrafast laser induced sintering, the initial nanoparticle temperature is only 300K, and the neck region may not accumulate enough energy to be completely melted so that the viscous flow mechanism is only secondary compared with grain boundary diffusion. After 40ps, Figure 7.23c shows that surface diffusion is the only mass transport mechanism.
Figure 7.23: Atomic trajectory during solid state sintering of two 7,164-atom Au nanoparticles at absorbed laser energy $E_0=20$kJ/mol: a) from 0ps to 10ps; b) from 10ps to 40ps; c) from 40ps to 200ps
Figure 7.24 presents atomic trajectory at higher absorbed laser energy $E_0=25\text{kJ/mol}$. From 10 to 40ps, the lattice temperature is above the particle melting temperature, thus the whole nanoparticle moves collectively towards the neck region (Figure 7.24a), indicating the viscous flow mechanism. A decreased growth rate is observed after 40ps when the lattice temperature drops below the particle melting temperature. Contrary to what one might expect, the movement as observed through the atomic trajectory (Figure 7.24b) is no longer symmetric. Evidently, the neck grows by surface diffusion on the “top” of the particle, while interior atoms move down to fill in the neck at the “bottom,” developing a flow pattern similar to that reported by Zachariah [126] and Pan [155]. It appears that sintering takes place via both a surface and a grain-boundary diffusion mechanism.
Figure 7.24: Atomic trajectory during the sintering of two 7,164-atom Au nanoparticles at absorbed laser energy $E_0=25\text{kJ/mol}$: a) from 10ps to 40ps; b) from 40ps to 200ps

7.6 Summary and Conclusions

MD simulations have been performed in this chapter to understand microscopic sintering and coalescence mechanisms of Au nanoparticles, and to study the applicability
of continuum sintering theory in nanoscale. Different simulation conditions, like constant energy, constant temperature and ultrafast laser irradiation, have been considered to model different sintering processes. Several conclusions were drawn from this study and are summarized here:

1) In the liquid phase coalescence, the initial neck growth can be well described by the viscous flow model. For two nanoparticles with initial temperature just below the single nanoparticle melting temperature, the initial neck growth is initially controlled by viscous flow and then later by grain boundary diffusion. At initial temperatures well below melting, the sintering process occurs very rapidly and ends with a nonspherical oval particle shape. The rapid solid-state sintering is attributed to formation of liquid-like atoms in the neck region due to accumulated surface energy in the neck region released from surface area reduction.

2) Constant temperature simulations gave similar results as constant energy simulations except for at the initial temperature which is close to the single nanoparticle melting temperature. In that case, although both final products are still solid, the sintering nanoparticles in constant energy simulations undergo a melting-solidification cycle due to surface energy release and increase of temperature, and thus have a much lower reduced moment of inertia than in constant temperature simulations.

3) By adjusting applied absorbed laser energy $E_0$, different sintering degree could be reached. For two 7,164-atom Au nanoparticles, at $E_0>25$kJ/mol, liquid phase coalescence is observed; at $E_0=25$kJ/mol, the neck growth is initially controlled by viscous flow and then later by surface and grain boundary diffusion when the lattice
temperature drops below the particle melting temperature; at $E_0<25\text{kJ/mol}$, the solid state sintering is observed.
Chapter 8. Conclusion

Molecular Dynamics (MD) models have been developed and applied to study the melting/solidification process of a single free Au nanoparticle and the sintering/coalescence process of two free Au nanoparticles with or without ultrafast laser irradiation. A brief summary of our major findings is listed here. The more complete one can be found at the end of each chapter.

**Equilibrium melting and solidification of bulk Au and Au nanoparticles:**

1) Quantum Sutton-Chen (Q-SC) potential is useful to predict material properties of Au bulk and nanoparticles.

2) A remarkable reduction of melting temperature is found for nanoparticles smaller than 3nm and is well accounted by the original Pawlow’s model and the liquid-drop model, both of which predict a decrease of melting temperature proportional to the inverse of the radius of nanoparticles.

3) A reversible nonhomogeneous surface premelting of Au nanoparticles is demonstrated by MD simulations. With temperature increase liquid-like atoms first appear at some vertices and edges of surface facets, then small liquid regions grow and at temperatures close to the particle melting temperature, most of the remaining solid-like surface atoms reside on {111} planes which are most stable against surface premelting. The appearance of a contiguous liquid layer (complete surface premelting) is size dependent and is not observed in very small nanoparticles.
Ultrafast melting of Au nanoparticles:

1) An integrated molecular dynamics (MD) and two-temperature (TTM) computational model has been developed to study ultrafast laser irradiation of Au nanoparticles at low intensity where surface premelting and solid-liquid phase transition are major issues.

2) Conditions for temporary superheating and stable supercooling were examined carefully. Temporary superheating occurs at intermediate $E_0$ when the time scales for two competitive processes, the electron-lattice temperature equilibrium and the solid-liquid phase transition, become comparable. In the stable supercooling, nanoparticles undergo catastrophic solid inner core melting, transform to supercooled liquids and remain in that state for a very long time.

3) A nonhomogeneous surface premelting mechanism similar to that in the equilibrium melting was observed. The appearance of a contiguous liquid layer (complete surface premelting) is size dependent and is not related to surface premelting history.

4) The equilibrated state (lattice temperature and fraction of remaining solid atoms) of nanoparticles after ultrafast laser irradiation could be predicted from the microcanonical droplet (MCD) theory, and is independent of any kinetic melting path resulting from different laser pulse durations $\sigma_L$.

5) Two types of ultrafast melting instability are identified in both MD simulations and the MCD theory. They are global stable to metastable state transition and catastrophic solid inner core melting. The occurrence of ultrafast melting instability is
size dependent. Two limiting nanoparticle sizes \( R_1 \) and \( R_2 \) are determined from the MCD theory.

**Sintering/coalescence process of Au nanoparticles:**

1) Continuum sintering theory is useful in understanding sintering/coalescence processes of nanoparticles, no matter in constant energy/constant temperature simulations or under ultrafast laser irradiation.

2) In constant energy simulations, due to surface reduction and subsequent surface energy release, the sintering of free nanoparticles can lead to a significant temperature increase. In constant temperature simulations, the nanoparticle temperature is always fixed as constant. However, the sintering results in both simulations are very similar, except for the initial temperature which is close to the single nanoparticle melting temperature.

3) In the liquid phase coalescence, the initial neck growth can be well described by the viscous flow model. For two nanoparticles with initial temperature just below the single nanoparticle melting temperature, the initial neck growth is initially controlled by viscous flow and then later by grain boundary diffusion. At initial temperatures well below melting, the rapid solid-state sintering is attributed to formation of liquid-like atoms in the neck region due to accumulated surface energy in the neck region released from surface area reduction.

4) By adjusting applied absorbed laser energy \( E_0 \), different sintering degree could be controlled in two sintering nanoparticles.
Appendix A: Molecular Dynamics (MD) Simulation

A.1 Many-body Metal Potential

Molecular Dynamics (MD) is a computer simulation technique where the atomic forces are calculated through the gradient of a suitable empirical potential and the time evolution of a set of interacting atoms is followed by integrating Newton’s law of motion. A suitable atomic empirical potential is crucial to the success of the simulation. The most commonly used Lennard-Jones potential and other kinds of two-body force potential models are not applicable to simulate metals. For example, $C_{12}/C_{44}$ is the ratio between two elastic constants of a cubic crystal. This ratio is one as predicted by two-body potentials but for Au, the value is very high and is related to the well-known high ductility and malleability of Au [66]. The development of many-body potentials began since the mid 80s, in which atoms are modeled as being embedded into the background electron gas and affected by the local electron density. Belong to this scheme are the Embedded Atom Method (EAM) [148][149] and its extension Modified Embedded Atom Method (MEAM) [150], the Glue model [151], and Finnis-Sinclair Potentials (FS) [152] and its extension Sutton-Chen (SC) [52], which is used in our simulation. Based on the construction of Sutton-Chen potential, the potential energy of finite systems is expressed as a summation over atomic positions [52]

$$U_{tot} = \sum_i U_i = \sum_i \varepsilon \left[ \sum_{j \neq i} \frac{1}{2} V(r_{ij}) - \varepsilon P_i^{1/2} \right]$$

(A.1)
Here $V(r_{ij})$ is a two-body potential to account for the repulsion resulting from Pauli’s exclusion principle,

$$V(r) = \left(\frac{a}{r}\right)^c$$  \hspace{1cm} (A.2)

The local electron density $\rho$ is measured by

$$\rho_i = \sum_{j \neq i} \phi(r_{ij}) = \sum_{j \neq i} \left(\frac{a}{r_{ij}}\right)^m$$  \hspace{1cm} (A.3)

where $r_{ij}$ is the separation distance between atoms, $c$ is a dimensionless parameter scaling the attractive term, $\epsilon$ sets the overall energy scale, $a$ is the lattice parameter and $n, m$ are integer numbers such that $n > m > 6$. This scheme was applied by Sutton and Chen [52] to ten FCC metals (Ni, Cu, Rh, Pd, Ag, Ir, Pt, Au, Pb and Al) and parameters were optimized to describe the experimental lattice parameter, cohesive energy and bulk modulus. It has the advantage of being decomposable into two-body contributions and thus is easily implemented in the programming.

Ikeda et al. [53] reparameterized the Sutton-Chen potential for eight FCC metals and termed it as Quantum Sutton-Chen (Q-SC) potential. In this effort, they included the zero-point energy from quantum corrections and additional experimental properties (photon frequencies, vacancy formation energy and surface energy) into the optimization procedure. The obtained parameters are listed in Table A.1.
<table>
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<tr>
<th></th>
<th>$n$</th>
<th>$m$</th>
<th>$\varepsilon$(eV)</th>
<th>$c$</th>
<th>$a$ (Å)</th>
</tr>
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<tr>
<td>Ni</td>
<td>10</td>
<td>5</td>
<td>7.3767E-3</td>
<td>84.745</td>
<td>3.5157</td>
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<tr>
<td>Cu</td>
<td>10</td>
<td>5</td>
<td>5.7921E-3</td>
<td>84.843</td>
<td>3.6030</td>
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<tr>
<td>Rh</td>
<td>13</td>
<td>5</td>
<td>2.4612E-3</td>
<td>305.499</td>
<td>3.7984</td>
</tr>
<tr>
<td>Pd</td>
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<td>3.2864E-3</td>
<td>148.205</td>
<td>3.8813</td>
</tr>
<tr>
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<td>6</td>
<td>3.9450E-3</td>
<td>96.524</td>
<td>4.0691</td>
</tr>
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</tr>
<tr>
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<td>7</td>
<td>9.7894E-3</td>
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</tr>
<tr>
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<td>8</td>
<td>7.8052E-3</td>
<td>53.581</td>
<td>4.0651</td>
</tr>
</tbody>
</table>

Table A.1: Parameters for the Q-SC potential

A.2 Computational Software and Environment

We use DL_POLY_2 \cite{51}, a parallel molecular dynamics simulation package developed at Daresbury Laboratory in England, to conduct our simulations. The latest version is 2.20. SC and Q-SC potentials have already been implemented in the code. Six kinds of three-dimensional periodic boundary conditions are accommodated. One two-dimensional periodic boundary condition is also included, which can facilitate the surface simulation. The Verlet Leapfrog and the Velocity Verlet integration algorithms are provided. NVE (constant number, volume and energy microcanonical ensemble), NVT (constant number, volume and temperature canonical ensemble), NPT (constant number, pressure and temperature ensemble) and $N\sigma T$ (constant number, stress and temperature
ensemble) are available, with a selection of thermostats and barostats (Hoover or Berendsen type).

Due to the massive number of atoms within nanoparticles (>\(10^4\) for large nanoparticles) and a very long simulation time (typical on the order of several nanoseconds, i.e., one million time steps), parallel computing becomes a necessity. We currently run DL\_POLY\_2 on the IBM Cluster 1350 at the Ohio Supercomputing Center (OSC). DL\_POLY\_2 uses the MPI library and the Replicated Data (RD) strategy to support this parallel environment [153].

We use VMD (Visual Molecular Dynamics) [57][58], a molecular visualization program developed at University of Illinois at Urbana-Champaign, to display and animate atomic configurations throughout this dissertation work.

### A.3 Preparation of Input Files for DL\_POLY\_2

Three input files are required to run MD simulations using DL\_POLY\_2 [154]. They are the CONFIG file, which contains the initial particle configuration; the FIELD file, in which all the interatomic interactions, the particle topology and atomic properties, such as charge and mass are specified; and the CONTROL file, which specifies which kind of simulation you would like to run, how many statistical data you would like generate and the running time for this job.

Several output files are available after MD simulations [154]. These include the OUTPUT file, which provides an extensive report of the job run; the REVIVE file, which contains the accumulated data for a number of thermodynamic quantities and is intended to be used in a restart job; the REVCON file, which contains the restart particle
configuration; and the STATIS file, which contains a time ordered sequence of instantaneous values of thermodynamic and other variables. If specified properly in the CONTROL file, five additional output files are created, including the HISTORY file, which records a time ordered sequence of particle configurations; the RDFDAT file, which contains the Radial Distribution Function (RDF) data; the ZDNDAT file, which contains the Z-density data, the SLAtomRep.out file, which records solid-like or liquid-like status for each atom, and the SLNumRep file, which contains fraction of solid-like and liquid-like atoms in different regions of nanoparticles. For sintering/coalescence simulations of two nanoparticles, a modified DL_POLY_2 execute file is used, and two additional output files are created, including the gyr_temp.out file, which contains the particle gyration radius and center-to-center distance, and the neck.out file, which contains the neck region size. For ultrafast laser irradiation simulations, a modified DL_POLY_2 execute file is used and the laser.out file is created to record electron and lattice temperatures.

The CONFIG file is prepared from the ideal FCC lattice or from the restart REVCON file created at the end of the last simulation. In the latter situation, not only initial atomic positions but also initial atomic velocities and accelerations are provided.

A sample FIELD file suitable to MD simulations of bulk Au is presented below. All the atoms in the periodic cell are grouped into one single “molecule” (molecular types 1; nummols 1). The total number of atoms in the simulation is 500. The atomic weight of Au is 196.97 while the atom charge is 0.0. stch indicates that the type of interatomic potential is Sutton-Chen or Quantum Sutton-Chen, and in the same line potential parameters are given.
We also show a sample CONTORL file suitable to MD simulations of bulk Au. The isobaric-isothermal ensemble (NPT) is used while constant temperature and constant pressure is maintained through the Nose-Hoover type thermostat and barostat (ensemble npt hoover 0.5 1.0). The temperature relaxation time is chosen as 0.5\text{ps} and the pressure relaxation time is chose as 1.0\text{ps}. The longer the relaxation time, the weaker the coupling between the simulated system and the thermostat/barostat. Every MD simulation is divided into two stages: the equilibrium stage in which the system evolve gradually from the initial particle configuration to configurations compatible to given constraints; and the statistical data collection stage in which thermal quantities and other important properties are collected and average values are calculated. In this simulation, the equilibrium step is equilibration 25000 and the total step is steps 50000. The timestep is taken as 0.004\text{ps}, short enough for most of MD simulations. We choose the primary cutoff distance as 7.5000, around 2.5 times larger than the Au atomic distance (2.885\text{Å}), to ensure all the near neighbors are considered in the metal potential calculation. Actually if the cutoff distance is changed from 6.5\text{Å} to

```
Bulk Au with QSC (Quantum Sutton-Chen) Potential
units ev
molecular types 1
Au
nummols 1
atoms 500
Au 196.97 0.0 500
finish
metal 1
Au Au stch 0.0078052 4.0651 11.0 8.0 53.581
close
```
8.5Å, no difference has been observed. The directive `print rdf` means to create the RDFDAT file, while `traj 0 500 2` means to record particle configurations in the HISTORY file every 500 steps.

```
Au with Quantum Sutton-Chen Potential

integrator leapfrog verlet
no link
restart scale

temperature  50.00
pressure     0.000
ensemble npt hoover 0.5 1.0

steps        50000
equilibration 25000
print        50
stats        50
stack        50
rdf          50

timestep     0.0040
cutoff       7.5000
delr width   1.0000
rvdw cutoff  7.5000
no electrostatics
cap force    1000
print rdf
traj 0 500 2

job time     30000
close time   2000

finish
```
References


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