A multiphysics phase field model on melting and kinetic superheating of aluminum nanolayer and nanoparticle

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A multiphysics phase field model on melting and kinetic superheating of aluminum nanolayer and nanoparticle

by

Yong Seok Hwang

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
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Major: Engineering Mechanics

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Iowa State University
Ames, Iowa
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DEDICATION

I would like to dedicate this thesis to my wife Chanmi, to my daughter Soyeon, to my son Ilhwan, and to my parents.
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ABSTRACT

It has been found during the last decade that a nanoscale melting of metal has very distinctive features compared to its microscale counterpart. It has been observed that a highly non-equilibrium state can result in extreme superheating of a solid state, which cannot be explained well by thermodynamic theories based on equilibrium or nucleation. An endeavor to find the limit temperature of superheating becomes more complicated when various physical phenomena interact in a similar scale. The main goal of this research is to establish a multiphysics model and to reveal the mechanism of melting and kinetic superheating of a metal nanostructure at high heating rates. The model includes elastodynamics, a fast heating of metal considering a delayed heat transfer between electron gas and lattice phonon and couplings among physical phenomena, and phase transformation incorporated with thermal fluctuation. The model successfully reproduces two independent experiments, and several novel nanoscale physical phenomena are discovered. For example, the depression of the melting temperature of Al nanolayer under plane stress condition, the threshold heating rate, $10^{11}$ K/s, for kinetic superheating, a large temperature drop in a 5 nm collision region of the two solid-melt interfaces, increase in solid temperature by dissipation of thermal fluctuation and resultant acceleration of homogeneous melting, and a strong effect of geometry on kinetic superheating in Al core-shell nanostructure at high heating rate.
CHAPTER 1. INTRODUCTION

During the last decade, it has been found that nanoscale melting of metal has very distinctive features compared to its microscale counterpart[6]. For example, the melting of a metal nanoparticle can occur at several hundred Kelvin lower than its bulk melting temperature or can be suppressed to a higher temperature by treatments such as coherent interface and negative curvature[6]. The nanolayer under a plane stress or strain condition has an equilibrium melting temperature several tens of Kelvin below that of stress free structure[1]. Some physics have been revealed so that it can be described by a fundamental model, for example the depression of the melting point for a nanoparticle. However, many physical phenomena are still not well understood. This is especially true at high heating rates which can be realized by short pulse laser irradiation; it has been observed that a highly non-equilibrium state can result in extreme superheating of a solid state[5, 7], which cannot be explained well by thermodynamic theories based on equilibrium or nucleation. For example, an irradiation of a femtosecond laser into a 20 nm thick aluminum nanolayer can temporarily heat up the nanolayer to 1400 K which is several hundred Kelvin above its equilibrium melting temperature, 898.1 K, without melting it[1, 7, 4]. This temperature is much higher than the theoretically predicted limit temperature of an aluminum solid state, for example, $1.38 T_{eq} = 1288.5 K$ with entropy catastrophe if $T_{eq} = 933.67 K$[8].

The limit of superheating solid and melting mechanisms at very high heating rates is a fundamental problem among numerous applications, which are under intense study[9, 10, 11, 12, 13, 14, 15, 5]. Melting induced by irradiation of the ultrafast laser has been researched for the last several decades and has been widely used for industrial manufacturing processes even without a full understanding of melting mechanisms[16]; among several applications are reforming micron particles and hence producing nanoparticles[17], producing hollow nanoparticles[18], laser-
induced forward transfer (LIFT)\cite{19} and nano-structuring\cite{20}. Ultra fast heating and melting are also parts of more complex phenomena such as fast combustion of metallic nanoparticles\cite{21} and LIFT of a nanolayer\cite{19}.

In order to explain the superheating limit, various catastrophes (isochoric, isenthalpic, isentropic) and Lindemann and shear instabilities\cite{22, 8, 23} have been suggested and explored. Entropy catastrophe\cite{8} suggested a $1.38T_{eq}$ superheating for Al, isochoric condition\cite{24} predicted $1.28T_{eq}$, and homogeneous nucleation theory\cite{25} gave a value around $1.21T_{eq}$ as the limit of superheating. Mei and Lu\cite{6} well summarized these models. MD simulation for homogeneous nucleation showed a similar melting temperature for a cubic Al sample confined by periodic boundary conditions; for example, $1.3T_{eq}$ was simulated by Forsblom and Grimvall\cite{26} and $1.22T_{eq}$ by Jin and Lu\cite{27} for the same potential. Many researchers have described the limit of kinetic superheating with homogeneous nucleation theory\cite{25, 9, 10, 11, 12}, but at a high heating rate, the homogeneous nucleation theory is not in good agreement with experiments (see Ref. 5 and chapter 3). Since the temperature may exceed the lattice instability temperature $T_i$, the density-functional and phase-field approach (PFA) result in zero energy of the critical nucleus\cite{28, 29, 30}, and homogeneous nucleation theory based on a sharp interface is conceptually unacceptable; thus, barrierless melting should be considered. For this case, the solid phase does not possess a local energy minimum and represents a transitional state that melts barrierlessly at the ps time scale.

Trying to find the limit temperature of superheating becomes more complicated when various physical phenomena are involved in a similar scale. Hydrostatic pressure, deviatoric stress conditions, and heating rate can be major parameters to determine an achievable superheating temperature during the melting process\cite{1}. Thermal expansion in constraint conditions generates compressive pressure, which should increase the equilibrium melting temperature according to the Clausius-Clapeyron relation. At the same time, for nanoparticles, surface premelting and melting are observed below the melting temperature at slow heating, and the melting temperature is reduced with the particle size\cite{31, 32, 33}. For the fast heating of nanoparticles, premelting and superheating compete \cite{14, 34, 35, 36}, and consequently barrierless surface melting may contribute to the mechanism of superheating\cite{37}. Moreover, a melting mechanism
under such high heating rates is governed by a combination of thermodynamics, kinetics, thermal conduction, mechanics, and several nanoscale effects, as well as their coupling. The melting of metal induced by irradiation of a femtosecond laser would be one of the best examples. Heating rate which exceeds several hundred $K/\text{ps}$ can produce an elastic wave in the sample which has a time scale similar to that of melting even for a sample as small as several tens of nanometers\cite{38}; for example, if an aluminum nanolayer is 20 nm in thickness the time required for the elastic wave to travel from one side to the other is about $20[\text{nm}]/4000[\text{m/s}] \sim 5.0 \text{ ps}$ which is comparable with 3.5 ps for complete melting time with femtosecond laser irradiation\cite{5}. Ultrafast heating of metal featured by time lagging between electron gas and lattice\cite{9} also has a similar time scale of about a few ps with the melting time scale\cite{4,7}. High temperature induced by superheating implies that the sample is in the metastable state or above the instability state where thermal fluctuation has a major role on melting through nucleation or homogeneous melting; the time scale of the thermal fluctuation, usually several hundred femtoseconds\cite{39}, is only one order smaller than the melting time scale. Phase transformation is coupled to thermal conduction, in particular through latent heat and the effect of temperature on the kinetics of melting. As will be shown, the spatial nanoscale effects are related to the width of a sample ($w = 25 \text{ nm}$), the width of a pre-molten surface layer (1 nm) where melt nucleates, the width of a propagating solid-melt interface (3 nm) within which all transformation-related processes occur, the size of the interface collapse region (5 nm) where temperature drops drastically, and the distance between moving interfaces where a standing elastic wave is localized. Coupled models for the melting of metals irradiated by an ultrafast laser that include mechanics and the two temperature model (TTM) for heating have been suggested in Ref. 38, 40; however, they did not include kinetics of melting and were not able to resolve superheating or the coupling of phase transformation with temperature evolution. The melting models coupled to TTM for a heating and interface tracking model based on melt nucleation kinetics was developed in Ref. 41, 42; however, it did not include mechanics and coupling between temperature evolution and mechanics. The model in Ref. 43 was focused on the heating process without the kinetics of melting and elastic waves.

The experiment for ultrafast heating of an aluminum nanolayer with a femtosecond laser
showed at least $1.5 T_{eq}$ superheating\[7\], which is far beyond the limit described by the above criteria. It is still difficult to observe these combined physics in experiments in-situ. Theoretical and numerical approaches which combine involving multiphysics are some of the possible approaches to analyzing the details of melting and kinetic superheating at an extremely high heating rate.

The main purpose of the research is to establish a multiphysics model so as to reveal the mechanism of melting and kinetic superheating of a metal nanostructure at a high heating rate which can be created by irradiation of an ultrafast laser; a continuum framework is selected to deal with a wider range of temporal and spatial scales than a molecular dynamic simulation. The model includes elastodynamics, a fast heating of metal considering a delayed heat transfer between electron gas and lattice phonon and couplings among physics, and phase transformation incorporated with thermal fluctuation. The Ginzburg-Landau equation for phase transformation is augmented by Newton’s equation to describe an elastic wave and the two temperature model which can explain the picosecond time delay of the heat transfer between electron gas and lattice phonon in metals\[4, 1\]. The lattice heat transfer equation is reinforced with coupling terms which can incorporate thermo-elastic coupling, coupling between temperature and phase transformation, and coupling with dissipation of phase transformation\[1\]. A random fluctuation term produced as white noise is added to the conventional Ginzburg-Landau equation to explain the thermal fluctuation of the order parameter and its effect on melting. The magnitude of the fluctuation is formulated by the fluctuation-dissipation theorem which is based on a random force of the Langevin equation\[44, 45\]. A discretized time step is selected to resolve the relaxation process of fluctuation which provides a physical guideline to selecting the magnitude of the order parameter fluctuation that depends on discretization\[39\].

The model is applied to simulate nanoscale melting and kinetic superheating of aluminum nanostructures; i.e. melting and kinetic superheating of an aluminum nanolayer at a high heating rate created by irradiation of a pico- and femtosecond laser, and melting and kinetic superheating of an aluminum nanoparticle which has an oxide shell. The simulation of melting the aluminum nanolayer successfully replicates experimentally measured melting time up to the
order of 3.5 picoseconds. Several novel nanoscale physics are discovered; the depression of the melting temperature to $898.1 \, K$ when the aluminum nanolayer is under plane stress condition, the threshold heating rate, $10^{11} \, K/s$, for kinetic superheating of the aluminum nanolayer with free surfaces, and a temperature drop up to several hundred Kelvin in a 3 nm solid-melt interface and a 5 nm collision region between the two interfaces for a fast heating rate of $6.9 \times 10^{12} \, K/s$. Also, it is found that melting and kinetic superheating of an aluminum nanoparticle which has a core-shell structure have unique features under a fast heating rate; the suppression of the core melting by high pressure, an interaction between the elastic wave, temperature, and melting for a higher heating rate than $1 \times 10^{12} K/s$, and a profound effect of the shell on melting are newly revealed. It is confirmed that a thermal fluctuation with a sufficiently small $\Delta t$ to resolve the relaxation process can describe barrierless homogeneous melting in a superheated metal solid above its instability temperature so that the simulation can replicate experimentally-observed melting time.

Chapter 2 shows mathematical formalism for a multiphysics phase field approach including the phase transformation, fast heat transfer, and elastodynamics. Chapter 3 includes the simulation of melting and kinetic superheating of an aluminum nanolayer irradiated by a picosecond and femtosecond laser with the multiphysics model without couplings and thermal fluctuation. Chapter 4 is about the internal stress-induced melting of an aluminum nanolayer below melting temperature and threshold heating rate for kinetic superheating. Chapter 5 explains extraordinary behaviors of nanoscale melting and kinetic superheating of an aluminum nanolayer irradiated by a picosecond laser. Chapter 6 describes the effect of the thermal fluctuation of the order parameter on the simulation of melting and kinetic superheating in femtosecond time scales. Finally, Chapter 7 describes the effect of fast heating on melting of an aluminum nanoparticle which has a core-shell structure.
CHAPTER 2. MATHEMATICAL MODEL FOR GOVERNING PHYSICS

2.1 Governing equations for metal

Governing equations are comprised of the Ginzburg-Landau equation with thermal fluctuation for melting, equation of elastodynamics or elastostatics, and the two temperature model (TTM) which includes contributions due to heat of fusion, thermoelastic effects, and dissipation due to melting. We designate contractions of tensors $A = \{A_{ij}\}$ and $B = \{B_{ji}\}$ over one and two indices as $A \cdot B = \{A_{ij} B_{jk}\}$ and $A : B = A_{ij} B_{ji}$, respectively; $I$ is the unit tensor, $\nabla$ and $\nabla_0$ are the gradient operators in the deformed and undeformed states, and $\otimes$ designates the dyadic product of vectors.

2.1.1 Kinematics, free energy, and stresses

**Kinematics.** Total strain tensor $\varepsilon = (\nabla_0 u)_s$ is decomposed into elastic $\varepsilon_e$, transformation $\varepsilon_t$, and thermal $\varepsilon_\theta$ strains in an additive way, where $u$ is the displacement vector, and the subscript $s$ designates symmetrization;

$$\varepsilon = \varepsilon_e + \varepsilon_t + \varepsilon_\theta; \quad \varepsilon = 1/3 \varepsilon_0 I + \varepsilon; \quad (2.1)$$

$$\varepsilon_{in} = \varepsilon_{in} I = \varepsilon_t + \varepsilon_\theta; \quad \varepsilon_t = 1/3 \varepsilon_{0t} (1 - \phi (\eta)) I; \quad (2.2)$$

$$\phi = \eta^2 (3 - 2\eta) \text{ for } 0 \leq \eta \leq 1;$$

$$\varepsilon_\theta = \alpha_s (T_{eq} - T_0) I + (\alpha_m + \Delta \alpha \phi (\eta)) (T - T_{eq}) I; \quad (2.3)$$

where $\eta$ is the order parameter in which 1 represents solid and 0 is melt, $\alpha_s$ and $\alpha_m$ are the linear thermal expansion coefficients for solid and melt, respectively; $\Delta \alpha = \alpha_s - \alpha_m$, $T_0$ is the initial temperature, $\varepsilon_0$ is the total volumetric strain, $\varepsilon_{0t}$ is the volumetric transformation strain for complete melting, $e$ is the deviatoric strain, and $\phi$ is the interpolation function for variation...
of any material property between solid and melt. $\phi$ satisfies conditions $\phi(0) = d\phi(0)/d\eta = d\phi(1)/d\eta = 0$, $\phi(1) = 1$.

**Free energy.** Free energy per unit undeformed volume is formulated as in Ref. 4, 36:

$$
\psi = \psi^e + J\psi^\theta + \psi^\theta + J\psi^\nabla; \quad \psi^\theta = A\eta^2(1-\eta)^2;
$$

$$
\psi^e = 0.5K\varepsilon_0^2 + \mu\varepsilon_0 : \varepsilon_0; \quad \psi^\theta = H(T/T_{eq} - 1)\phi(\eta);
$$

$$
\psi^\nabla = 0.5\beta|\nabla\eta|^2, \quad A := 3H(1 - T_c/T_{eq}),
$$

where $\psi^\theta$, $\psi^e$, $\psi^\theta$, and $\psi^\nabla$ are the double-well, elastic, thermal, and gradient energy respectively; $\rho_0$ and $\rho$ are the mass densities in the undeformed and deformed states, respectively, $J = \rho_0/\rho = 1+\varepsilon_0$, $K(\eta) = K_m + \Delta K\phi(\eta)$ and $\mu(\eta) = \mu_s\phi(\eta)$ are the bulk and shear moduli, $\Delta K = K_s - K_m$, $\beta$ is the gradient energy coefficient, $H$ is latent heat of fusion, $\nabla$ is the gradient operator in the deformed state, $T_{eq}$ is bulk equilibrium temperature, 933.67K, and $T_c = 0.8T_{eq}$ is the melt instability temperature.

**Stresses.** A thermodynamic procedure in Ref. 46, 47, 48 leads to the following equations for the stress tensor $\sigma$:

$$
\sigma = \frac{\partial \psi}{\partial \varepsilon} - J^{-1}\nabla\eta \otimes \frac{\partial \psi}{\partial \nabla\eta} = \sigma^e + \sigma_{st};
$$

$$
\sigma^e = K\varepsilon_0^e I + 2\mu\varepsilon_0; \quad \sigma_{st} = (\psi^\nabla + \psi^\theta)I - \beta\nabla\eta \otimes \nabla\eta,
$$

where $\sigma^e$ and $\sigma_{st}$ are the elastic stresses and interface stresses (interface tension). Correct expression for the interface stresses are obtained by using the gradient operator in the deformed state in the gradient energy $\psi^\nabla$ and by multiplying $\psi^\theta$ and $\psi^\nabla$ by the Jacobian $J$.

### 2.1.2 Ginzburg-Landau equation with thermal fluctuation

The explicit expression for the thermodynamic driving force $X$, work-conjugated to the $\dot{\eta}$, can be obtained using the thermodynamic procedure. Linear relationship between $X$ and $\dot{\eta}$
results in the Ginzburg-Landau equation for melting:

\[
\frac{1}{L} \frac{\partial \eta}{\partial t} = X = -J^{-1} \frac{\partial \psi}{\partial \eta} \bigg|_\varepsilon + \nabla \cdot \left( J^{-1} \frac{\partial \psi}{\partial \nabla \eta} \right) = J^{-1} \{-\varepsilon_0 p_e + 3 p_e \Delta \alpha (T - T_{eq})\} \frac{\partial \phi}{\partial \eta} - J^{-1} \{0.5 \Delta K \varepsilon_0^2 + \mu e_e : \varepsilon_e + H \left( \frac{T}{T_{eq}} - 1 \right) \} \frac{\partial \phi}{\partial \eta} - 4 A \eta (1 - \eta)(0.5 - \eta) + \beta \nabla^2 \eta - \frac{\varsigma}{L} + \frac{\omega(x, t)}{L},
\]

(2.8)

where \( L \) is the kinetic coefficient, \( \varsigma \) is the term of bulk perturbation that mimics thermal fluctuations by amplifying numerical error, \( \omega(x, t) \) is thermal fluctuation of the order parameter, \( p_e = \sigma_e : I/3 = -\bar{p} \) is the mean elastic stress, and \( \bar{p} \) is the pressure. \( \omega(x, t) \) is derived by the statistical relationship:

\[
\langle \omega(x, t) \omega(x', t') \rangle = 2 L k_B T \delta(x - x') \delta(t - t'),
\]

(2.9)

where \( k_B \) is Boltzmann constant and \( \delta \) means Dirac’s delta function. The statistical relationship for thermal fluctuation is developed by the fluctuation-dissipation theorem[44, 45]. Discretized form of the equation, Eq. (2.10), provides standard deviation of fluctuation, \( \sigma_{s, \omega} \) which is used for white noise generator. Thus random fluctuation of the order parameter which has Gaussian distribution can be added into the computational domain in terms of space and time.

\[
\sigma_{s, \omega} = \sqrt{\frac{2 L k_B T}{\Delta V \Delta t}},
\]

(2.10)

where \( \Delta V \) and \( \Delta t \) are discretized volume and time respectively.

**Reinforced free energy potential for order parameter out of range.** The thermal fluctuation can cause the order parameter to grow larger than unity when \( T > 1.2 T_{eq} \) once \( \eta > 1 \). This happens because the traditional definition of \( \phi \), \( \phi = \eta^2 (3 - 2\eta) \), while fully satisfactory for \( 0 \leq \eta \leq 1 \), creates a unphysical minimum of the local order parameter-dependent part of the energy, \( \tilde{\psi}^9 + \psi^9 \) for \( \eta > 1 \), as shown in Fig. 2.1 (a). To prevent the unphysical minimum for outranged order parameter, Ginzburg Landau equation with only local order parameter-dependent part, Eq. (2.11), can be used.
\[
\frac{1}{L} \frac{\partial \eta}{\partial t} = -J^{-1} H \left( \frac{T}{T_{eq}} - 1 \right) \frac{\partial \phi}{\partial \eta} - 4A\eta(1 - \eta)(0.5 - \eta). \tag{2.11}
\]

In order to restore \( \eta \) to 1 in case that \( \eta > 1 \), \( \frac{\partial \eta}{\partial t} < 0 \) in any case when \( \eta > 1 \). Since the second term in right hand side of Eq. (2.11) is always negative for \( \eta > 1 \), the negative first term for \( \eta > 1 \) will satisfy the condition. Therefore, Eq. (2.12) is the condition of reinforced \( \phi(\eta) \) for \( \eta > 1 \).

\[
\frac{\partial \phi}{\partial \eta} > 0 \quad \text{for} \quad T > T_{eq}; \tag{2.12}
\]

\[
\frac{\partial \phi}{\partial \eta} < 0 \quad \text{for} \quad T \leq T_{eq}.
\]

Since the \( \phi \) should be continuous at \( \eta = 1 \), Eq. (2.13) satisfies the condition of Eq. (2.12) for \( \eta > 1 \).

\[
\phi = 2 - \eta^2(3 - 2\eta) \quad \text{for} \quad \eta > 1 \quad \text{and} \quad T > T_{eq}; \tag{2.13}
\]

\[
\phi = \eta^2(3 - 2\eta) \quad \text{for} \quad \eta > 1 \quad \text{and} \quad T \leq T_{eq}.
\]

The same logic can be applied to the case of \( \eta < 0 \), and the condition becomes \( \frac{\partial \eta}{\partial t} > 0 \) in any case when \( \eta < 0 \) at this time. Eq. (2.14) is found to satisfy the condition and eliminate unphysical minimum as shown in Fig. 2.1 (b).

\[
\phi = \eta^2(3 - 2\eta) \quad \text{for} \quad \eta < 0 \quad \text{and} \quad T > T_{eq}; \tag{2.14}
\]

\[
\phi = -\eta^2(3 - 2\eta) \quad \text{for} \quad \eta < 0 \quad \text{and} \quad T \leq T_{eq}.
\]

Fig. 2.1 shows the comparison of the thermal part of free energy, \( \psi^\theta + \psi^\tilde{\theta} \), between the conventional and reinforced potential for possible \( T \) conditions. The reinforced function \( \phi \) also produces a higher barrier of potential, leading higher driving force to return \( \eta \) to the range \( \eta \leq 1 \) for \( T_{eq} < T \leq 1.2T_{eq} \) and to the range \( \eta \geq 0 \) for \( 0.8T_{eq} \leq T < T_{eq} \) in Fig. 2.1 (c) and (d) respectively.
Figure 2.1: Comparison of thermal part of the free energy, $\tilde{\psi}^\theta + \psi^\theta$, landscape corresponding to traditional function $\phi = \eta^2(3 - 2\eta)$ (solid lines) and reinforced definition of $\phi$ in Eqs.(2.13), (2.14) for (a) $T \geq 1.2T_{eq}$, (b) $T \leq 0.8T_{eq}$, (c) $T = 1.05T_{eq}$, and (d) $T = 0.95T_{eq}$ (dashed lines).

2.1.3 The equation of motion

The equation of motion is written in a traditional form

$$\rho \frac{\partial^2 u}{\partial t^2} = \nabla \cdot \sigma.$$  

(2.15)

It allows to describe elastodynamics caused by fast heating and melting. When melting occurs at a time scale much larger than that for an elastic wave, static equilibrium equation, $\nabla \cdot \sigma = 0$, is used instead.
2.1.4 Two-temperature model with couplings

The TTM describes that energy absorbed by electron gas near the metal surface spreads all of electron gas by collisions of electrons in the femtosecond time scale and later transfers to a phonon by electron-phonon coupling[49]. The heat transfer mechanism can be represented by the lattice conduction equation, the electron conduction equation, and their coupling:

\[ C_l \frac{\partial T}{\partial t} = \nabla \cdot (\kappa_l \nabla T) + G (T_e - T) - 3T (\alpha_m + \Delta \alpha \phi) \frac{\partial p_e}{\partial t} + \left( \frac{\partial \eta}{\partial t} \right)^2 / L - \left[ 3p_e \Delta \alpha - \frac{H}{T_{eq}} \right] T \frac{\partial \phi}{\partial \eta} \frac{\partial \eta}{\partial t}, \tag{2.16} \]

\[ C_e \frac{\partial T_e}{\partial t} = \nabla \cdot (\kappa_e \nabla T_e) + I - G (T_e - T), \tag{2.17} \]

where \( T \) and \( T_e \) are the temperature of lattice and electron gas respectively, \( \kappa_l \) and \( \kappa_e \) are the lattice and electron thermal conductivity coefficients respectively, \( I \) is the laser power absorbed by the electrons, \( G \) is the electron-phonon coupling coefficient, \( C_l = C_{lm} + (C_{is} - C_{lm}) \phi(\eta) \) is the lattice heat capacity where \( C_{lm} \) and \( C_{is} \) are the heat capacities for melt and solid respectively. In the lattice heating equation (2.16), the second term in the right hand side is due to electron-phonon coupling, the third term describes thermoelastic coupling (e.g., cooling in an expansion wave or heating in a compression wave), the fourth term is the dissipation rate due to melting, and the last term is the heat source due to melting. Usually, only heat of fusion is included in the temperature evolution equation[30]. Also, since entropy of fusion \( H/T_{eq} \) is considered to be constant, heat of fusion reduces for melting below \( T_{eq} \) at slow heating and increases for the high heating rates with overheating. TTM model can be replaced to traditional heat conduction model in case that governing physics has sufficiently larger time scale than several picoseconds. In this case, Eq. (2.17) can be neglected and \( \kappa_l = \kappa_e \).

2.2 Governing equations for metal oxide

Phase transformation of an aluminum oxide is not considered so that Eq. (2.1), (2.2), (2.3), (2.7) are replaced by Eq. (2.18) and (2.19):

\[ \varepsilon = \varepsilon_e + \varepsilon_{\theta}; \quad \varepsilon_{\theta} = \alpha_{ox} (T - T_0) I, \tag{2.18} \]
\[ \sigma = \sigma_e = K_{ox}\varepsilon_0 I + 2\mu_{ox}e_e. \] (2.19)

Equation of motion, Eq. (2.15), is used for dynamic case, and static equilibrium equation, \( \nabla \cdot \sigma = 0 \), is used when melting occurs at a time scale much larger than that for an elastic wave. Only lattice heat conduction equation with thermoelastic coupling is used for heat transfer;

\[ C_2 \frac{\partial T_2}{\partial t} = \nabla \cdot (\kappa_2 \nabla T_2) - 3T_2\alpha_{ox} \frac{\partial p_{2,e}}{\partial t}, \] (2.20)

where subscript 2 represents an aluminum oxide.
The limits of superheating of solids and melting mechanisms at very high heating rates are fundamental problems with numerous applications, which are under intense study\cite{9, 10, 11, 12, 13, 14, 15, 5}. Experimentally, melting induced by irradiation of the ultra-fast laser has been researched for the last several decades and has been widely used for industrial manufacturing processes\cite{16}. Various catastrophes (isochoric, isenthalpic, isentropic) and Lindemann and shear instabilities\cite{22, 8, 23} have been suggested and explored to predict the superheating limit. Many researchers have described the limit of kinetic superheating with homogeneous nucleation theory\cite{25, 9, 10, 11, 12}, but at higher heating rates the homogeneous nucleation theory is not in good agreement with experiments (see Ref. 5 and below). Also, since the temperature may exceed the lattice instability temperature $T_i$, the density-functional and phase-field approach (PFA) result in zero energy of the critical nucleus\cite{28, 29, 30}, and homogeneous nucleation theory based on sharp interface is conceptually unacceptable; thus, barrierless melting should be considered. For this case, solid phase does not possess a local energy minimum and represents a transitional state that melts barrierlessly at the ps time scale. At the same time, for nanoparticles, surface premelting and melting are observed below the melting temperature at slow heating, and the melting temperature is reduced with the particle size\cite{31, 32, 33}. For fast heating of nanoparticles, premelting and superheating compete\cite{14, 34, 35, 36}, and consequently barrierless surface melting may contribute to the mechanism of superheating\cite{37}. Recent molecular dynamics (MD) simulations\cite{50} have revealed two mechanisms, surface-induced melting
and propagation of solid-melt interfaces (for slower heating) and homogeneous melting (for faster heating), which compete for the intermediate heating rates. However, MD simulations have well-known time and space limitations. It is known that phase field approach (PFA) to melting\cite{35, 36, 30} can be applied for larger size and time scales, which makes it favorable for practical applications. However, we are not aware of any applications of PFA to laser-induced melting. Mechanical strains and stresses have also been found to be important\cite{13, 38, 35, 36}.

The goal of this work is to develop a simple PFA to kinetic superheating and melting under irradiation by ps and fs lasers and verify it by comparison with known experiments and MD simulations. For this purpose, we used an advanced PFA to melting coupled to mechanics\cite{35, 36} and combined it with the two-temperature model (TTM)\cite{49}. Our PFA\cite{35, 36} described well the surface-induced melting (namely, the width of the surface molten layer vs. temperature) and the melting temperature of nanoparticles vs. particle radius, both for very slow heating of Al samples. Information about the kinetics of melting is included in terms of a single kinetic parameter $L$ in the Ginzburg-Landau equation, which is related to interface mobility. In the current work, we used $L = 532 m^2/Ns$ justified by MD simulation for Al for small overheating (See below) and did not change any terms or other parameters in the PFA model\cite{35, 36}. Still, we obtained a good agreement with known experiments\cite{3, 5} in terms of the time for complete melting for the heating rates $Q$ from 1 to 1290 $K/ps$. This means that in the first approximation the information about melting kinetics at high superheating is present in the model for slow heating. Two major melting mechanisms were reproduced, in an agreement with MD results\cite{50}. In all cases, surface premelting and melting represent the initial stage of the process. At $Q \leq 79.04 \ K/ps$, two-sided barrierless surface melting forms two solid-melt interfaces, which propagate toward each other and meet near the center of a sample; melting time, and consequently superheating, increase with the sample width. The temperature for complete melting has a cubic relation on $\log Q$, while the surface melting temperature is a linear function of $\log Q$ and for given $Q$ is independent of fluence, pulse duration, and sample size. At $Q \geq 300 \ K/ps$, barrierless homogeneous melting (without nucleation) at sample center occurs faster than due to interface propagation. Melting time, and consequently superheating, are independent of the sample width in this regime and depend on heating rate only. They
represent the upper bounds for melting time and superheating temperature.

### 3.1 Governing equations

The system of equations is composed of PFA to melting coupled with mechanics[35, 36] and TTM[49]. Total strain tensor, \( \varepsilon \), free energy per unit undeformed volume, \( \psi \), and the stress tensor, \( \sigma \), are described by Eq. (2.1), Eq. (2.4) and Eq. (2.7) respectively. Melting of layer is described by Ginzburg-Landau equation, Eq. (2.8) with \( \varsigma = 0 \) and \( \omega (x, t) = 0 \). Conventional TTM model is used to describe the heating process.

\[
C_l \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left( \kappa_l \frac{\partial T_e}{\partial x} \right) + G (T_e - T) ;
\]  
(3.1)

\[
C_e \frac{\partial T_e}{\partial t} = \frac{\partial}{\partial x} \left( \kappa_e \frac{\partial T_e}{\partial x} \right) + I - G (T_e - T) ,
\]  
(3.2)

where, \( I \) is the irradiated laser power.

Static equilibrium equation is used for mechanics, \( \nabla \cdot \sigma = 0 \).

### 3.2 Problem formulation, boundary and initial conditions

An infinite layer of the width \( w \) is subjected to penetrating laser fluence orthogonal to the right surface, which is modeled as a distributed heat source with thermal isolation at surfaces. No fluctuations on bulk are included—i.e., barrierless melting is considered. Plane boundaries are stress-free, and one of the boundaries are fixed to prevent translation and rotation of a sample. Because the radius of the irradiated spot was much larger than \( w \), \( mm \) vs. \( nm \), the problem can be safely considered as a 1-D problem with zero displacements orthogonal to the laser axis, with all parameters varying along the laser axis only. Thus the sample is described with 1-D coordinate system and Fig. 3.1 shows the schematic of a computational domain.
The boundary condition for the order parameter $\eta$ at the surface with the unit normal $\mathbf{n}$ is

$$J \frac{\partial \psi}{\partial \nabla_\eta} \cdot \mathbf{n} = \beta \nabla \eta \cdot \mathbf{n} = -\frac{d\gamma}{d\eta},$$

(3.3)

where $\gamma(\eta) = \gamma_m + (\gamma_s - \gamma_m)\phi(\eta)$, $\gamma_s$ and $\gamma_m$ are the solid-vapor and melt-vapor surface energies. It takes into account reduction in the surface energy of the external surface during melting. Since energy irradiated by the laser is included as a volumetric heat source according to Beer-Lambert law in Eq. (3.4), the heat flux was zero at both plane boundaries. Attenuation of the laser irradiated is modeled as

$$I = I_0 \exp(-\zeta(w - x)); \quad I_0 = \zeta W / (1 - \exp(-\zeta w));$$

$$W = (1 - R) F_0 / t_p,$$

(3.4)

where $\zeta$ is the absorption coefficient, which is $1.21 \times 10^8 m^{-1}$ for the 1064-nm laser in the picosecond experiment and $1.4616 \times 10^8 m^{-1}$ for the 700-nm laser in the femtosecond experiment; $w$ is thickness of a sample, which is 25 nm for the picosecond experiment and 20 nm for the femtosecond experiment; $R$ is the reflectance, which is 0.87 for fs experiment[5] and 0.0 for ps experiment since absorbed fluence was reported for ps case[3]; $t_p$ is the pulse duration; $F_0$ is the fluence of laser.

The initial temperature was $T_0 = 293.15 K$ and $\eta = 0.999$ for all cases. The finite-element code
COMSOL Multiphysics was used for the simulations[51].

### 3.3 Kinetic coefficient and material properties

To determine kinetic coefficient $L$, we utilize an analytical solution for interface velocity, $c$, in Ref. 52:

$$c = \frac{6L\rho_0\Delta G^T(T)}{k}; \quad k = \sqrt{\frac{6H(T_{eq} - T_c)}{\beta T_{eq}}}; \quad \Delta G(T) = \frac{H}{\rho_0 T_{eq}}(T - T_{eq}). \quad (3.5)$$

Then the interface mobility is:

$$\mu = \frac{dc}{dT} = \sqrt{\frac{6H\beta}{T_{eq}(T_{eq} - T_c)}} L. \quad (3.6)$$

Substituting $\mu = 1.7 \text{ m/(sK)}$ obtained with MD simulation in Ref. 53, we obtain $L = 532 \text{ m}^2/\text{Ns}$.

**Material properties.** The lattice heat capacities are described by the following equations[54]:

$$C_s = (2434.86 + (3308.87 - 2434.86)/(900.0 - 300.0) \times (T - 300.0)) \times 10^3 \text{ J/(m}^3\text{K})$$

for $T < 900.0 K$;

$$C_{ls} = 3308.87 \times 10^3\text{ J/(m}^3\text{K}) \quad \text{for} \quad T > 900.0 K;$$

$$C_m = (2789.1 + (2713.72 - 2789.1)/(1173.0 - 933.0) \times (T - 933.0)) \times 10^3 \text{ J/(m}^3\text{K}). \quad (3.7)$$

The heat capacity of electron gas is $C_e = \tilde{\gamma}T_e$, where $\tilde{\gamma} = 91.2 \text{ J/(m}^3\text{K}^2)$ is the electron heat capacity constant[55]. The electron thermal conductivity is approximated as $\kappa_e = \kappa_{e,eq}T_e/T$ to take into account the non-equilibrium effect[56, 57]:

$$\kappa_e^{eq} = \kappa_{em}^{eq} + \phi(\eta)(\kappa_{es}^{eq} - \kappa_{em}^{eq}), \quad (3.8)$$

where $\kappa_{es}^{eq} = 208 W/(mK)$ for solid and $\kappa_{em}^{eq} = 102 W/(mK)$ for melt[54]. The lattice thermal conductivity is $\kappa_l = 0.01\kappa_e$[58].

For the electron-phonon coupling coefficient $G$, the theoretically calculated data is used[55]:

$$G = (3.663 - 1.218/(1 + (T_e \times 10^{-4}/0.221)^{2.294})) \times 10^{17}. \quad (3.9)$$
Table 3.1: Properties of aluminum[1]

<table>
<thead>
<tr>
<th>$\rho_0$ (kg/m$^3$)</th>
<th>$T_{eq}$ (K)</th>
<th>$H$ (J/m$^3$)</th>
<th>$K_m$ (GPa)</th>
<th>$K_s$ (GPa)</th>
<th>$\mu$ (GPa)</th>
<th>$\varepsilon_{01}$</th>
<th>$\alpha_m$ (K$^{-1}$)</th>
<th>$\alpha_s$ (K$^{-1}$)</th>
<th>$\gamma_s$ (J/m$^2$)</th>
<th>$\gamma_m$ (J/m$^2$)</th>
<th>$\beta$ (N)</th>
<th>$L$ (m$^2$/Ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2700.0 $\times 10^6$</td>
<td>933.67</td>
<td>933.57</td>
<td>41.3</td>
<td>71.1</td>
<td>27.3</td>
<td>0.06</td>
<td>4.268 $\times 10^{-5}$</td>
<td>3.032 $\times 10^{-5}$</td>
<td>1.050</td>
<td>0.921</td>
<td>3.21</td>
<td>532</td>
</tr>
</tbody>
</table>

Coefficients, constants, and properties used for the simulation are presented in Table 3.1[1]. They correspond to the width, energy, and mobility of a plane solid-melt interface of $\delta_{sm} = 2.02\text{nm}$, $\gamma_{sm} = 0.14\text{J/m}^2$, and $\lambda_{sm} = 1.7\text{ms}^{-1}\text{K}^{-1}$.

### 3.4 Melting induced by picosecond laser irradiation

The melting of a 25-nm, thin Al nanolayer irradiated by an ultrafast laser was simulated to replicate the melting time measured in the experiments[3]. Conditions and results are shown in Table 3.2. In each simulation, the melting of a sample starts from the surface because of the reduction in surface energy during melting. The surface melting temperature $T_{sm}$ was defined as the temperature at which the order parameter first reached 0.5. Despite the promoting effect of the surface, for fast heating the surface melting occurred above $T_{eq}$. A solid-melt interface propagated from each surface toward each other, and met at the melting center. This mechanism represents heterogeneous melting.

The melting center is shifted to the left from the sample center because of the one-sided heating and heterogeneous temperature (Fig. 3.2a). When the temperature exceeds $T_i$, barrierless melting starts at each point of the solid for any initial deviation from $\eta = 1$. It is called a homogeneous melting, because it does not require interfaces. It has nothing to do with homogeneous nucleation, which does require interface and thermal fluctuations. The heating rate at each point is practically constant during laser irradiation and can be defined, for example, as $Q = (T_{sm} - T_0)/t_{sm}$, where $t_{sm}$ is the time of surface melting. For $Q \leq 79.04\text{K/ps}$, homogeneous melting is negligible before the two interfaces meet, even for the highest fluence of ps laser irradiation (Fig. 3.2b). The time for complete melting, $t_m$, is defined as time from the moment of laser irradiation to the instant when the two interfaces meet each other, and the interface position is defined by $\eta = 0.5$. Table 3.2 shows good agreement between calculated and experimentally determined $t_m$ within the reported range of experimental error.
Figure 3.2: Distribution of the order parameter for some time instants for absorbed fluence of 11 $mJ/cm^2$ (a), 13 $mJ/cm^2$ of ps laser (b), and for irradiated fluence of 70 $mJ/cm^2$ of fs laser (c).
The maximum superheating temperature, $T_s$, is defined as the temperature reached for the given heating rate during the time for complete melting $t_m$; i.e., $T_s \approx Q t_m + T_0$. Because irradiation for the two strongest fluences, 11 and 13 mJ/cm$^2$, was ended before the melting was completed, $T_s$ was not reached in these simulations. To find $T_s$, we added two more cases with fluences of 14.67 mJ/cm$^2$ during 80 ps and 19.5 mJ/cm$^2$ during 30 ps, which have a longer duration of irradiation but same heating rates, 23.15 and 79.04 K/ps. As shown in Table 3.2, much higher superheating temperature, 1784.8 and 2524.7 K, respectively, reached, while $T_{sm}$ did not change. The maximum superheating temperatures for heterogeneous melting, $T_s$, is well described by a cubic polynomial ($R^2 = 0.9999$), $T_s(K) = 1041.54 + 252.29 \log Q + 42.08(\log Q)^2 + 124.83(\log Q)^3$.

Our results for the melting time, while in agreement with the experiments[3], differ significantly from the previous models based on homogeneous nucleation theory. For example, in Refs. 10, 11 the following $\theta - \beta - Q$ model is suggested $\beta = (A_0 - b \log_{10}Q)\theta_c(\theta_c - 1)^2$, where $\beta$ is a constant that depends on the material, $A_0$ and $b$ are constants, and $\theta_c = T_s/T_{eq}$. In our study of heterogeneous melting, maximum superheating for any heating rate depends not only on the material but also on $w$ because the interface velocity and $w$ determine the melting time, which controls the maximum superheating. The homogeneous nucleation model[9] predicted $t_m = 1$ ps for $\theta_c = 1.31$, but our prediction was 296.8 ps for the similar superheating $\theta_c = 1.27$. The homogeneous nucleation model[12] predicted $t_m = 10$ ps for $\theta_c = 1.936$ in contrast to 63.5 ps for $\theta_c = 1.91$ in our simulations; also $t_m = 10$ ns for $\theta_c = 1.33$ vs. 296.8 ps for $\theta_c = 1.27$ in our model. These contradictions confirm the inapplicability of the homogeneous nucleation model above lattice instability temperature for very high heating rates. Even MD simulations[11], which did not consider surface melting, showed $\theta_c = 1.19$ superheating for 5 K/ps, which should be between $\theta_c = 1.33$ and $\theta_c = 1.54$ for this heating rate in our simulations and experiment.
Table 3.2: Summary of simulation results of melting of Al nanolayer without coupling terms

<table>
<thead>
<tr>
<th>Fluence (mJ/cm²)</th>
<th>t&lt;sub&gt;exp&lt;/sub&gt; (ps)&lt;sup&gt;1&lt;/sup&gt;</th>
<th>t&lt;sub&gt;m&lt;/sub&gt; (ps)</th>
<th>Q (K/ps)</th>
<th>T&lt;sub&gt;sm&lt;/sub&gt; (K)</th>
<th>T&lt;sub&gt;s&lt;/sub&gt; (K)</th>
<th>θ&lt;sub&gt;c&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>1000</td>
<td>789.8</td>
<td>0.95</td>
<td>942.9</td>
<td>1035.5</td>
<td>1.11</td>
</tr>
<tr>
<td>8</td>
<td>350</td>
<td>296.8</td>
<td>3.03</td>
<td>1055.5</td>
<td>1187.0</td>
<td>1.27</td>
</tr>
<tr>
<td>9</td>
<td>180</td>
<td>161.5</td>
<td>6.51</td>
<td>1158.5</td>
<td>1344.5</td>
<td>1.44</td>
</tr>
<tr>
<td>10</td>
<td>115</td>
<td>106.4</td>
<td>11.21</td>
<td>1234.4</td>
<td>1491.0</td>
<td>1.60</td>
</tr>
<tr>
<td>11</td>
<td>60</td>
<td>63.6</td>
<td>23.15</td>
<td>1397.5</td>
<td>1703.0</td>
<td>1.82</td>
</tr>
<tr>
<td>14.67&lt;sup&gt;2&lt;/sup&gt;</td>
<td>–</td>
<td>63.5</td>
<td>23.15</td>
<td>1397.5</td>
<td>1784.8</td>
<td>1.91</td>
</tr>
<tr>
<td>13</td>
<td>20</td>
<td>27.7</td>
<td>79.04</td>
<td>1573.6</td>
<td>1921.4</td>
<td>2.06</td>
</tr>
<tr>
<td>19.5&lt;sup&gt;2&lt;/sup&gt;</td>
<td>–</td>
<td>26.8</td>
<td>79.04</td>
<td>1573.6</td>
<td>2524.7</td>
<td>2.70</td>
</tr>
</tbody>
</table>

1 Pulse duration is same as t<sub>exp</sub> in the experiment.
2 Additional simulation cases to attain maximum superheating temperature at the same heating rate; an 80 ps pulse for 14.67 mJ/cm² and an 30 ps pulse for 19.5 mJ/cm² were used.

Figure 3.3: Superheating temperature vs. heating rate at the melting center. Rectangular solid symbols represent simulated data in the current research for the experiment[3], triangles are the estimated maximum superheating temperature T<sub>s</sub>, and the red line is the fit to the maximum superheating temperature T<sub>s</sub>. The circular symbols are the superheating temperatures for the stress-free case, and the rectangular hollow symbols represent the surface melting temperature T<sub>sm</sub>. The surface melting temperature, T<sub>sm</sub>, depends linearly on log Q (T<sub>sm</sub> = 912.08+338.50 log Q) and for given Q it is practically independent of fluence, the duration of the laser pulse (Table 3.2), and sample size. The maximum compressive pressure up to 4.5 GPa was observed for the strongest laser fluence. It increases maximum superheating temperature by 305 K (Fig. 3.3), instead of the increase in equilibrium melting temperature by 270 K.
3.5 Melting induced by femtosecond laser irradiation

A 20-nm, thin Al layer\[5, 7\] was irradiated with the fluence 70 mJ/cm$^2$ during 120-fs pulse duration. The simulated heating rate was not constant, with 300 $K/ps$ in average, and maximum value of 1360 $K/ps$. Surface melting started at 4.1 ps, but the homogeneous melting became the dominant mechanism after 5.7 ps until homogeneous melting in the central part completed before the two interfaces meet each other (Fig. 3.2c). For $79.04 K/ps \leq Q \leq 300.0 K/ps$, the mechanism changes from heterogeneous to homogeneous melting as shown in Fig. 3.2. A non-uniform distribution of temperature makes homogeneous melting asymmetric, being faster at the right side. The time and superheating for homogeneous melting for the prescribed heating rates are independent of the sample size.

Fig. 3.4 displays variation of the temperature and the function $\phi(\eta) = \eta^2 (3 - 2\eta)$ of the order parameter, which describes change of any material property during melting in the middle plane of a sample. Superheating up to 1680 K ($\theta_c = 1.80$) was observed. In experiment\[5, 7\], time for initiation and completion of melting is determined by measuring x-ray peaks intensity averaged over the sample thickness. We will use for this purpose the averaged parameter $\bar{\phi} = \int \phi dx/w$, defined in the reference configuration and assume that melting starts at $\bar{\phi} = 0.9$ and completes at $\bar{\phi} = 0.1$. In the experiment\[5\], the time between detected disordering and complete melting was 2 ps. Calculated time for complete melting is $t_{hm} = 2.9 ps$ (for neglected mechanics, it is 1.9 ps), which is in good agreement with experiment. However, the time from the beginning of irradiation to initiation of melting was 1.5 ps in Ref. 5 and 5.2 ps here (for neglected mechanics, it is 4.6 ps). Note that simulation temperature before melting at 1.5 ps is 1400 K, exactly the same as temperature in the experiment\[7\]. Therefore, one has to introduce thermal fluctuations in $\eta$ in order to describe shorter time before initiation of melting. Our preliminary simulations confirmed this conclusion. We would like to keep the current model as simple as possible and to include thermal fluctuations along with thermomechanical coupling, heat of fusion, dynamics and wave propagation\[59\], and stress relaxation via dislocations\[60\] in the future work. Even such a simplified model describes experiments much better that the previous continuum models. In particular, the melting time for the homogeneous nucleation model\[9\] is
more than an order of magnitude shorter than in experiment[5] (which was mentioned in Ref. 5), with lower superheating of $\theta_c = 1.37$ rather than $\theta_c = 1.80$ here.

Figure 3.4: Time evolution of the function $\phi(\eta) = \eta^2 (3 - 2\eta)$ of the order parameter and lattice temperature at a middle plane of sample.

The simulated compressive pressure reached 3.0 GPa. In Fig. 3.4, the onset of melting in the stress-free simulations starts $0.6$ ps earlier than in the case with stresses, and $t_{hm} = 1.9$ ps is shorter than for the stressed case. The temperature for onset of homogeneous melting is practically the same as the final superheating temperature, 1680 K, regardless of stressed or stress-free conditions.

### 3.6 Conclusion

In summary, a good correspondence between the simulated and experimental melting time was obtained for laser heating of the Al nanolayer for the heating rates from 1 to 1290 K/ps using PFA coupled with mechanics and TTM. This did not require modification of the PFA in comparison with the slow-heating regimes. We reproduced and quantified the two main mechanisms found in MD simulation[50], namely (a) heterogeneous melting initiated from surface melting at both surfaces and propagation of two interfaces until they meet, and (b) homogeneous melting without interfaces above $T_i$. These mechanisms substituted for the traditional homogeneous nucleation mechanism, which is not applicable here because $T > T_i$. Note that homogeneous melting under shock loading was also obtained in MD simulations[61]. The same
approach can be applied, e.g., for laser ignition of nano- and micron scale Al particle\cite{62, 63} and nano structuring of thin metal film\cite{64, 65}.
CHAPTER 4. INTERNAL STRESS-INDUCED MELTING BELOW MELTING TEMPERATURE AT HIGH-RATE LASER HEATING

*Modified from the article published in Applied Physics Letters on 2014[1]*

Traditionally, intense laser-induced melting is associated with the possibility of significant kinetic superheating of solids and their melting significantly above the equilibrium melting temperature $T_{eq}$. This was obtained experimentally for heating rates $Q$ in the range $0.95 \sim 1290K/ps[3, 7]$, using molecular dynamics[37], and PFA[4]. E.g., for the heating rate $Q = 1290K/ps$, experimental[7] melting temperature for Al increased up to $1400K$, while $T_{eq} = 933.67K$. Such fast heating leads to a high temperature $T$ before melting starts and completes. Also, thermal expansion in constraint conditions generates compressive pressure, which is supposed to increase the equilibrium melting temperature according to Clausius-Clapeyron relation. We are not familiar of experimental or numerical studies of melting under laser heating for smaller $Q < 10^{11}K/s$. Here, we demonstrate that laser heating in a broad range of heating rates $Q < 10^{11}K/s$ can cause melting *36K below the equilibrium melting temperature* of Al at zero external pressure in biaxial confinement. The main reason of reducing melting temperature is that fast heating within a laser-irradiated region of a thin nanalayer generates constrained thermal expansion and *internal* elastic biaxial compression on the order of $2GPa$ without external pressure. Using continuum thermodynamics, we demonstrated analytically that such internal stresses and their energy, which completely relax after melting, produce a significant driving force for melting and reduce equilibrium melting temperature $T'_{eq}$ by 36K. The same reduction in actual melting temperature was obtained utilizing advanced PFA coupled to mechanics and the heat evolution equation. When mechanics is excluded, melting occurs at equilibrium temperature $T_{eq}$. At higher heating rates, this driving force still persists but
kinetic superheating takes over, leading to a significant increase in melting temperature with respect to $T_{\text{eq}}$.

### 4.1 Governing equations

We will generalize the phase field approach for melting coupled with mechanics developed in Ref. 35, 36, 4 by adding a thermodynamically consistent temperature evolution equation. Since these equations describe well experimental results for surface melting and melting of Al nanoparticles at slow heating[36] and melting at laser heating of the thin Al nanolayer (like here) for $Q = 0.95 \sim 1290 \text{ K/ps}$[4], we expect that they describe reality for the heating rates in the current paper.

Total strain tensor, $\varepsilon$, free energy per unit undeformed volume, $\psi$, and the stress tensor, $\sigma$, are described by Eq. (2.1), Eq. (2.4) and Eq. (2.7) respectively. Melting of layer is described by Ginzburg-Landau equation, Eq. (2.8) with $\varsigma = 0$ and $\omega = 0$. The temperature evolution equation of lattice only, Eq. (2.16), is considered since tested heating rate is not fast enough to make a delay in heat transfer between electron gas and lattice. The equation of motion, Eq. (2.15), is used to simulate elastodynamics.

### 4.2 Problem formulation, boundary and initial conditions, and material properties

A thin vertical nanolayer with thickness 25 nm (like in experiments[3] and simulations[4]) irradiated from the right side by a laser is treated. 1D approximated configuration of aluminum nanolayer is same as chapter 3 as shown by Fig. 3.1. Lateral surfaces of the nanolayer are stress-free. Since width of a nanolayer is much smaller than the radius of the irradiated spot, the material is under uniaxial strain condition within a heated region. The boundary conditions $\sigma^x = 0$ and $\varepsilon^y = \varepsilon^z = 0$ (i.e., uniaxial straining) for the principle stresses and strains along the axes within a layer (y and z) and normal to a layer (x) are applied.

The boundary condition for the order parameter $\eta$ at the surface with the unit normal $\mathbf{n}$ is same as section 3.2. Attenuation of the laser irradiated is modeled as same as section 3.2 with
\[ \zeta = 1.21 \times 10^8 \text{ m}^{-1}, \quad R = 0. \]  

The initial temperature was \( T_0 = 293.15 \text{ K} \) and \( \eta = 0.999 \) for all cases. The finite-element code \textit{COMSOL Multiphysics} was used for the simulations[51].

The same lattice heat capacities as section 3.3 are selected and the thermal conductivity of lattice is same as thermal conductivity of electron, \( \kappa_l = \kappa_e = \kappa_{eq} \). The same conductivity of electron gas as section 3.3 is used. Coefficients, constants, and properties used for the simulation are presented in Table 3.1[1].

### 4.3 Equilibrium melting temperature under uniaxial strain

Under the assumption of homogeneous stress-strain and thermal states, equilibrium melting temperature \( T_{eq}^\varepsilon \) is defined from the condition of the equality of free energy before and after melting \( \psi(\eta = 1, T_{eq}^\varepsilon) = \psi(\eta = 0, T_{eq}^\varepsilon) \). Elastic and thermal energies Eq. (2.5) contribute to \( \psi \) in this case only and \( \sigma_{st} = 0 \). Elastic strains are determined from the conditions \( \sigma^x = 0 \) and \( \varepsilon^y = \varepsilon^z = 0 \) and Hooke’s law:

\[
\varepsilon^x_e = (C - 1) \varepsilon_{in}, \quad C = \frac{9K}{3K + 4\mu}; \quad \varepsilon^y_e = \varepsilon^z_e = -\varepsilon_{in}; \quad (4.1)
\]
\[
\varepsilon^x_{0e} = (C - 3) \varepsilon_{in}; \quad \varepsilon^y_e = \frac{2}{3} C \varepsilon_{in}; \quad \varepsilon^z_e = -\frac{1}{3} C \varepsilon_{in}.
\]

Substitution of these elastic strains in the expression for elastic energy results in its explicit dependence on \( \eta \). In particular, for \( \eta = 1 \) and \( T = T_{eq}^\varepsilon \) the elastic energy is

\[
\psi_e = B \left( T_{eq}^\varepsilon - T_0 \right)^2; \quad (4.2)
\]
\[
B = \left( 0.5K_s(C - 3)^2 + \frac{2}{3} \mu_s C^2 \right) \alpha_s^2. \quad (4.3)
\]

After melting, elastic energy completely relaxes and \( \psi(\eta = 0) = 0 \). Thus, equality of the free energy before and after melting results in

\[
B \left( T_{eq}^\varepsilon - T_0 \right)^2 + H \left( T_{eq}^\varepsilon/T_{eq} - 1 \right) = 0 \quad (4.4)
\]

and the quadratic equation with respect to \( T_{eq}^\varepsilon \) with the solution

\[
T_{eq}^\varepsilon = \sqrt{\frac{H^2}{T_{eq}^2} - 4BH \left( T_0/T_{eq} - 1 \right)}/2B - \left( \frac{H}{2BT_{eq}} - T_0 \right).
\]
Figure 4.1: Free energy plot for aluminum vs. order parameter for uniaxial strain case. Elastic energy increases the total energy of a solid ($\eta = 1$) for any temperature.

Utilizing $T_0 = 293.15K$, we obtain $T_{eq}^\varphi = 898.1K$, which is $36K$ below $T_{eq}$. Fig. 4.1 presents a plot of the free energy vs. order parameter for various temperatures while allowing for elastic energy. For the case when size of the sample in y-direction is the same or smaller than the irradiated spot, one has to change stress-strain state to plane strain $\varepsilon_z = 0$ and $\sigma_x = \sigma_y = 0$. In this case

$$C = \frac{9K_s}{6K_s + 2\mu_s}; \quad B = \left(0.5K_s(2C - 3)^2 + \mu_s\frac{2}{3}C^2\right)\alpha_s^2$$

and $T_{eq}^\varphi = 920.8K$, which is still $13K$ below $T_{eq}$.

### 4.4 Phase field simulations

Reduction in equilibrium melting temperature does not necessarily mean that the actual melting temperature will be reduced, because melting may be delayed due to difficulties with nucleation or fast heating. To determine the actual melting process, phase field equations are solved numerically with the help of the finite element code COMSOL[51]. The simulation procedure is the same as in Ref. 4, and the details of properties of aluminum, boundary and initial conditions are summarized in section 3.2 and section 3.3. For 1-D simulation, heating by a short laser pulse with absorbed fluence of $100J/m^2$ and $200\mu$s pulse duration was chosen for slow heating rate, $7.43 \times 10^6K/s$, which does not cause kinetic superheating. Despite the one-side heating, the nanoscale size of the sample and the relatively slow heating rate limit the
Figure 4.2: Evolution of the temperature in the middle of a sample for $Q = 7.43 \times 10^6 K/s$. Variation of temperature along the sample by less than 0.1K. Temperature growth is almost linear until melting occurs followed by a plateau after the initiation of melting due to latent heat (Fig. 4.2). The temperature of the middle of the sample at the plateau is selected as the melting temperature. Melting temperature in a simulation is 897.5K, which is very close to $T_{eq}^{\epsilon} = 898.1K$. If mechanical problems and elastic energy are not included in simulation, melting temperature is 933.67K, i.e., $T_{eq}$ for unstressed case. A similar simulation for the plane strain case resulted in melting at 920.8K, same as $T_{eq}^{\epsilon} = 920.8K$.

Thus, for relatively slow heating rate, the actual melting temperature is very close to the thermodynamic equilibrium value at the same strains. This is explained by barrierless surface-induced nucleation (premelting) below $T_{eq}^{\epsilon}$ driven by a reduction in surface energy during melting (Fig. 4.3). Equilibrium thickness of the molten layer increases with temperature and diverges at $T_{eq}^{\epsilon}$. That is why at the chosen heating rate interfaces between solid and liquid propagate to the center of a sample at a temperature close to $T_{eq}^{\epsilon}$ and collide with each other. This collision produces a sudden increase of $|\frac{\partial \eta}{\partial t}|$, which induces a slight temperature drop in the middle of a sample at the end of melting through the term $H \frac{T}{T_{eq}} \frac{\partial \phi}{\partial \eta} \frac{\partial \eta}{\partial t}$ in Eq. (2.16). The temperature drop in Fig. 4.2 spreads over the entire sample, since thermal conduction is faster than external heating in this slow-heating case.

Compressive stress along a confined axis increases linearly in time (like temperature) before melting and reaches 2.0 GPa just before melting (Fig. 4.4). Stress relaxes at the propagating interfaces down to zero. $|\varepsilon_y^0|$ also increases linearly before melting with the strain rate of
Figure 4.3: Evolution of the order parameter within a sample for $Q = 7.43 \times 10^6 K/s$.

Figure 4.4: Evolution of stress $\sigma^y$ in the middle of a sample for $Q = 7.43 \times 10^6 K/s$. 

The same problem was solved in 2D formulation for a sample with width of 10nm and zero displacements and heat flux along axes y and z. Planar solid-melt interfaces propagate to the middle of a sample without any sign of the Grinfeld instability[66] (waveviness) (Fig. 4.5) at 895.3K, i.e., slightly below $T_{eq}$. Corresponding temperature evolution is presented in Fig. 4.2.
4.5 Competition with kinetic superheating

Since it is known from experiments[3, 7] and simulations[4, 37] that for laser heating with $Q > 10^{12} \text{K/s}$ melting temperature exceeds $T_{eq}$, at some point internal stress-induced reduction in melting temperature and kinetic superheating compete with each other. To better understand the initiation of such a competition, laser heating with higher heating rates, $1.51 \times 10^{10}$, $1.51 \times 10^{11}$, and $1.46 \times 10^{12} \text{K/s}$ have been simulated (Fig. 4.6). While below $Q = 1.51 \times 10^{10} \text{K/s}$ heating rate does not affect the melting temperature, the triggering of kinetic superheating is visible between $Q = 1.51 \times 10^{10}$ and $1.51 \times 10^{11} \text{K/s}$, both without and with mechanics effects. However, melting temperature under uniaxial straining at $Q = 1.51 \times 10^{11} \text{K/s}$ is still $31 \text{K}$ below $T_{eq}$. At $Q = 1.46 \times 10^{12} \text{K/s}$, the melting temperature at uniaxial straining becomes $T_{eq} = 936.9 \text{K}$, i.e., slightly above $T_{eq}$.

Note that in experiment the internal stress of 2 GPa (corresponding to $\varepsilon^y_e = -0.0181$) may partially relax due to plastic deformation reducing the above effect. The yield strength can be significantly increased and stress relaxation can be significantly suppressed for nanocrystalline and nanosized materials, as well as for high strain rate, which is the case in our problem. Strain rate is found as $log|\varepsilon^y_e| = 1.000 log Q - 4.520$, with $\varepsilon^y_e = -4.57 \times 10^5 \text{s}^{-1}$ at $Q = 1.51 \times 10^{10} \text{K/s}$ and $\varepsilon^y_e = -4.44 \times 10^7 \text{s}^{-1}$ at $Q = 1.46 \times 10^{12} \text{K/s}$. Recent molecular dynamics simulations exhibited...
Figure 4.6: Melting temperature vs. heating rate.

A lack of plastic deformation above 1 GPa near melting temperature for uniaxial loading at strain rate of $10^8/s$ for polycrystalline Al\cite{67} and at strain of 0.03 for surface melting of Al\cite{68}. Dislocations will be included in future work using the approach developed in Ref. 60.

4.6 Conclusion

In summary, in contrast to traditional superheating during intense laser-induced melting, we predicted thermodynamically and confirmed with phase field simulations the possibility of melting of the Al nanolayer 36K below $T_{eq}$ for the heating rate $Q \leq 1.51 \times 10^{10} K/s$. It is caused by internal stresses due to thermal strain under constrained uniaxial straining conditions, which relax during melting, producing an additional thermodynamic driving force for melting. Barrierless surface-induced nucleation below these temperatures eliminates kinetic barriers for such a melting. At higher heating rates, this driving force still persists but kinetic superheating takes over, leading to a significant increase in melting temperature with respect to $T_{eq}$. While we are unaware of similar studies for the reduction in melting temperature due to internal thermal stresses at high heating rate, there were to some extent similar studies under other conditions. Thus, internal stress-induced reduction of the melting temperature at the propagating interface between two solid phases was treated thermodynamically and confirmed experimentally\cite{69, 70, 71} and with PFA\cite{72}. Reduction in melting temperature under nonhydrostatic stresses have been treated thermodynamically\cite{73, 68, 74, 61} and using
molecular dynamics[68, 61] for Al, and the experiment[75] for pure helium-4 crystal. There are no contradictions between previous and currently reported phenomena. Our simulations allowed us to suggest an experiment for observation of the reduction in melting temperature. In particular, one subjects a thin Al film of 25nm thickness (like in Refs. 3, 7) to heating from one open side by laser irradiation, leading to $Q < 10^{11}K/s$. It can be, e.g., a combination of $100 \ J/m^2$ absorbed fluence and $100 \ ns$ pulse which can generate $Q = 1.51 \times 10^{10}K/s$. Film can be deposited on a rigid, low-conductive substrate to prevent deformation before melting.
CHAPTER 5. COUPLED PHASE FIELD, HEAT CONDUCTION, AND ELASTODYNAMIC SIMULATIONS OF KINETIC SUPERHEATING AND NANOSCALE MELTING OF ALUMINUM NANOLAYER IRRADIATED BY PICOSECOND LASER

Modified from the article published to Physical Chemistry Chemical Physics on 2015[76]

Melting of metals induced by ultra fast laser heating has been studied for the past several decades from both academic and applied points of view. In industrial applications, ultra fast heating and melting of metals are utilized for various purposes, such as the reforming of micron particles and hence producing nanoparticles[17], producing hollow nanoparticles[18], laser-induced forward transfer (LIFT)[19] and nano-structuring[20], even without a full understanding of melting mechanisms. Ultra fast heating and melting are parts of more complex phenomena like fast combustion of metallic nanoparticles[21] and LIFT of a nanolayer[19]. From basic perspectives, many theoretical, computational, and experimental studies have been dedicated to this topic, see reviews[21, 6, 16]; however, there are still remaining puzzles, especially for extreme conditions, which enable kinetic superheating. A melting mechanism under such high heating rates is not governed by thermodynamics only but rather by a combination of thermodynamics, kinetics, thermal conduction, mechanics, and several nanoscale effects, as well as their coupling. As will be shown, nanoscale effects are related to the width of a sample \(w = 25 \text{ nm}\), width of a premolten surface layer \(1 \text{ nm}\), where melt nucleates, width of a propagating solid-melt interface \(3 \text{ nm}\), within which all transformation-related processes occur, size of interface collapse region \(5 \text{ nm}\), where temperature drops drastically, and distance between moving interfaces, where a standing elastic wave is localized. Simple models[9, 10, 11, 12], which assumed that homogeneous melt nucleation is the only mechanism, have failed to repro-
duce the superheating temperature observed in the experiments\cite{5, 3, 4}. It is known that fast heating can produce elastic waves\cite{38} and these waves can interact with thermal physics by thermoelastic coupling. In the same way, phase transformation is coupled to thermal conduction, in particular through latent heat and the effect of temperature on the kinetics of melting. Coupled models for the melting of metals, irradiated by an ultrafast laser that include mechanics and the two temperature model (TTM) for heating have been suggested in Ref. 38, 40; however, they did not include kinetics of melting and were not able to resolve superheating or the coupling of phase transformation with temperature evolution. The melting models coupled to TTM for heating and interface tracking model based on melt nucleation kinetics was developed in Ref. 41, 42; however, it did not include mechanics and coupling between temperature evolution and mechanics. The model in Ref. 43 was focused on heating process without the kinetics of melting and elastic waves.

Recently\cite{4} we have suggested a phase field approach, which combined melting with the TTM for heating and mechanics. It was successfully applied to the study of kinetic superheating and melting beyond the theoretically predicted ultimate superheating limit of aluminum, for example, $1.38T_{eq}$, based on the entropy catastrophe\cite{8}. However, this model has several drawbacks: temperature evolution includes laser heating only and neglects coupling to melting (latent heat of fusion) and mechanics; also, the static equilibrium equation was used instead of the dynamic equation of motion. This could result in an overestimation of kinetic superheating temperature and in inaccuracy in melting kinetics. In Ref. 1, this model was expanded by developing a new lattice temperature evolution equation, which takes into account thermoelastic coupling, transformation heat, and the dissipation rate due to phase transformation. It was applied to a relatively slow heating rate; it was demonstrated that internal stresses can reduce the melting temperature for Al nanolayer below the bulk melting temperature, $T_{eq}$. Still, mechanical equilibrium was imposed and electron temperature and electron-phonon coupling were neglected. In the current research, in order to study higher heating rates, we further improved our model. Thus, we included advanced thermomechanical coupling, transformation heat, and the dissipation rate due to melting in the TTM and substituted the elastostatic formulation with an elastodynamic one. The melting of a free standing aluminum nanolayer irradiated by
a picosecond laser[3] is simulated and compared with experimentally observed melting times to verify validity of the model, and with the results of a simplified model[4]. The details of melting and superheating physics are analyzed and some surprising effects have been revealed. In particular, increase in heating rate leads to temperature reduction at the moving solid-melt interfaces due to fast absorption of the latent heat. Also, a sharp temperature decrease exceeding several hundred K (even below melting temperature) at the final stage of melting occurs, which is caused by a collision of two interfaces and accelerated melting. When surface melting is suppressed, barrierless bulk melting occurs in the entire sample above the instability temperature of the solid, promoted by elastodynamic effects.

5.1 Governing equations

Governing equations are comprised of the coupled Ginzburg-Landau equation for melting, equations of elastodynamics or elastostatics, and the two temperature model(TTM) which includes contributions due to heat of fusion, thermoelastic effects, and dissipation due to melting. They represent further development of equations formulated in Ref. 36, 35, 4, 1.

Total strain tensor, \( \varepsilon \), free energy per unit undeformed volume, \( \psi \), and the stress tensor, \( \sigma \), are described by Eq. (2.1), Eq. (2.4) and Eq. (2.7) respectively. Melting of layer is described by Ginzburg-Landau equation, Eq. (2.8), with \( \omega (x, t) = 0; \varsigma = 0 \) except bulk melting simulation. The equation of motion is written in a traditional form of Eq. (2.15). It allows to describe elastic waves caused by fast heating and melting. When melting occurs at a time scale much larger than that for an elastic wave, static equilibrium equation, \( \nabla \cdot \sigma = 0 \), is used instead. Heat transfer is described by TTM, Eq. (2.16) and (2.17).

5.2 Problem formulation, boundary and initial conditions

Experimental observation of the melting of a free standing aluminum nanolayer with the thickness \( w = 25nm \), irradiated by picosecond laser[3], is simulated. Because the radius of the irradiated spot was much larger than \( w \), mm vs. ns, the problem could be safely considered to be a 1-D problem with zero displacements orthogonal to the laser axis; all parameters vary
along the laser axis $x$ only. Figure 3.1 shows the schematic of a computational domain.

Six different laser fluences ($7, 8, 9, 10, 11, 13 \text{ mJ/cm}^2$) are used in simulations with corresponding pulse durations ($1000, 350, 180, 115, 60, 20 \text{ ps}$) in accordance with experimental data. Cases with fluences 11 and 13 $\text{mJ/cm}^2$ only are treated in elastodynamic formulation since the time scale for heating for other cases is at least more than an order of magnitude larger than the acoustic time $t_a = \frac{w}{2c} \simeq 3 \text{ps}$, i.e., the time of propagation of an elastic wave with velocity $c = 4000 \text{ m/s}$ through half of a sample width $w/2$. The finite-element code COMSOL Multiphysics was used for the simulations.

**Boundary and initial conditions, and source terms.** Both plane boundaries are stress-free in the case of an elastodynamic problem, and one of the boundaries is fixed to prevent translation and rotation of a sample for elastostatic formulation. Since energy irradiated by the laser is included as a volumetric heat source according to Beer-Lambert law in Eq. (6.2), the heat flux was zero at both plane boundaries. Attenuation of the laser irradiated is modeled as same as section 3.2 with $\zeta = 1.21 \times 10^8 \text{ m}^{-1}$ and $R = 0$. The boundary condition for the order parameter $\eta$ at the surface with the unit normal $\mathbf{n}$ is same as section 3.2.

Two regimes will be considered:

(a) One for $\gamma_s$ and $\gamma_m$ presented in Table 3.1[1], which leads to the surface-induced melt nucleation and corresponds to experimental conditions in Ref. 3. Since for a homogeneous solid phase $\eta = 1$, the driving force $X = 0$ in the Ginzburg-Landau Eq.(2.8) and $d\gamma/d\eta = 0$ in Eq.(3.3), one needs some perturbations at the boundary to initiate melting. We use the condition that if at the boundaries $\eta > 1 - \hat{\eta}$, then $\eta = 1 - \hat{\eta}$, where perturbation $\hat{\eta} = 10^{-5}$. Without this condition, even if the initial value of $\eta < 1$, during heating below the melting temperature it can return to $\eta = 1$ and melting could not start. For surface-induced melting we set $\zeta = 0$ in the Ginzburg-Landau equation (2.8), since bulk perturbations are not required.

(b) To avoid surface-induced melting we assume $\gamma_s = \gamma_m$. In this case, melting starts in the bulk after exceeding the temperature at which solid loses its stability. To model thermal fluctuations one can introduce Langevin noise $\varsigma$ that satisfies the fluctuation-dissipation theorem[44, 45]. This, however, requires a separate study and here we will use the simplest possible method to initiate bulk melting. Thus, we assume $\varsigma = 10^{-4} \text{ ps}^{-1}$ if $\eta > 0.999999$.
Figure 5.1: Distribution of fluctuations of the order parameter introduced by perturbations for fluence of $13 \text{ mJ/cm}^2$.

and $\varsigma = 0$ otherwise. Independent of the time step in the numerical integration, piece-wise constant and homogeneous perturbation $\varsigma$ is introduced with a time step of $0.01\text{ps}$. Due to numerical errors in simulations, such a perturbation produces a random-like fluctuation of the order parameter as shown in Fig. 5.1. Without perturbation $\varsigma$, the magnitude of numerical errors is several orders of magnitude smaller. Heating rate $Q = 84.15 \text{ K/ps}$ is considered for this regime.

The initial temperature is $T_0 = 293.15 \text{ K}$, the sample is initially stress free and initial $\eta = 0.999$ for all cases.

Material properties. The same material properties for TTM as section 3.3 are used. Coefficients, constants, and properties used for the simulation are presented in Table 3.1[1].

5.3 Surface-induced melting and interface propagation

Some definitions. The melting of a 25-nm thin Al nanolayer irradiated by an ultrafast laser is simulated. Conditions and results are summarized in Table 5.1. In all simulations, the melting of a sample starts from both surfaces driven by the reduction in surface energy during melting. Melt nucleation away from the solid-melt interfaces was not observed. Fig. 5.2(a) shows the typical evolution of the order parameter $\eta$. The melting time, $t_m$, is defined
as time from the moment of laser irradiation to the instant when two solid-melt interfaces collide and merge together; position of an interface is defined by $\eta = 0.5$; point of meeting of interfaces (the melting center of the sample) is designated as $x_{mc}$. This definition is motivated by way of comparison with experiments, where melting time corresponds to the disappearance of x-ray peaks of solid phase. We define $T_{ms}$ as the maximum superheating temperature of the solid during melting, which is reached at the melting center while $\eta > 0.5$. We designate time corresponding to $T_{ms}$ as $t_{ms}$. As we will see $t_{ms}$ is slightly smaller than $t_m$, because there is a temperature drop, down to the temperature $T_{mf}$ at the end of melting (see Fig. 5.4).

The surface melting time, $t_{sm}$, is defined as the time when the order parameter reaches 0.5 for the first time at the external surface and the surface melting temperature $T_{sm}$ is defined as a temperature at the surface at $t_{sm}$. Heating rate is defined as $Q = \frac{T_{sm} - T_0}{t_{sm}}$ since for most cases temperature increases almost linearly before the initiation of melting.

Comparison with experiment in terms of melting time. For slow heating rate $Q = 0.015K/ps$ kinetic superheating is not observed and the melting temperature is as low as $T_{eq}' = 898.1K$, i.e., significantly below $T_{eq}$. $T_{eq}'$ is the equilibrium melting temperature under uniaxial strain conditions and corresponding biaxial stress, which relax during melting[1], thus producing an additional thermodynamic driving force for melting and reducing melting temperature. This driving force exists for the high heating rate as well, but it is overplayed by kinetic factors and melting temperature significantly exceeds $T_{eq}$. The results for the slow heating are included in Table 5.1 in order to quantify superheating with respect to this temperature. As shown in Table 5.1, simulation results exhibit good agreement with experimental data in terms of melting time, except the strongest fluence case. The relative error between simulation result and the experimental measurement for the highest fluence is 29.5%; aside from this point, the relative error is 4.0% on average. With the current fully coupled lattice heat conduction and melting equations, the predictive capability of the simulation is significantly enhanced in comparison with the previous simulation[4], see Table 5.1 and Fig. 5.3(a).

Kinetic superheating. Since the solid-melt interface has finite velocity, the temperature of the solid at the center of a sample can reach much higher values than $T_{sm}$ and $T_{eq}'$ during fast heating before the interface arrives. Superheating factors are defined as $\theta_{c}' = \frac{T_{ms} - T_{eq}'}{T_{eq}'}$ and
Figure 5.2: Evolution of distributions of (a) the order parameter, (b) temperature, and (c) \( \frac{\partial \phi}{\partial t} \) \( (\phi = \eta^2 (3 - 2\eta) \) is the interpolation function for variation of any material property between solid and melt) for \( Q = 0.015 K/ps \). When two interfaces collide, the magnitude of \( \frac{\partial \phi}{\partial t} \) drastically grows and temperature reduces due to absorption of the heat of fusion.
Table 5.1: Summary of simulation conditions and results of melting of Al nanolayer with coupling terms

<table>
<thead>
<tr>
<th>Fluence ($mJ/cm^2$)</th>
<th>$t_{sm}$ (ps)</th>
<th>$t_{ms}$ (ps)</th>
<th>$t_{m}^{exp}$ (ps)</th>
<th>$t_{m}$ (ps)</th>
<th>$t_{m}$ (ps)</th>
<th>$Q$ (K/ps)</th>
<th>$T_{sm}$ (K)</th>
<th>$T_{ms}$ (K)</th>
<th>$T_{mf}$ (K)</th>
<th>$\theta_c^c$ (K)</th>
<th>$x_{mc}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^6$</td>
<td>41600</td>
<td>$6 \cdot 10^4$</td>
<td>1</td>
<td>63500</td>
<td>0.015</td>
<td>894.5</td>
<td>899.0</td>
<td>863.9</td>
<td>1.00</td>
<td>12.4</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>638</td>
<td>896</td>
<td>$10^3$</td>
<td>1013</td>
<td>0.99</td>
<td>921.9</td>
<td>971.8</td>
<td>784.8</td>
<td>1.08</td>
<td>12.35</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>216</td>
<td>321</td>
<td>$350$</td>
<td>344</td>
<td>3.20</td>
<td>983.4</td>
<td>1086.1</td>
<td>837.9</td>
<td>1.21</td>
<td>12.25</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>110</td>
<td>160</td>
<td>$180$</td>
<td>169</td>
<td>6.90</td>
<td>1052.4</td>
<td>1197.0</td>
<td>925.7</td>
<td>1.33</td>
<td>12.1</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>69</td>
<td>100</td>
<td>$115$</td>
<td>104.4</td>
<td>11.88</td>
<td>1112.5</td>
<td>1304.4</td>
<td>1004.3</td>
<td>1.45</td>
<td>11.95</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>38.5</td>
<td>57</td>
<td>$60$</td>
<td>58.0</td>
<td>24.55</td>
<td>1238.3</td>
<td>1532.5</td>
<td>1210.3</td>
<td>1.71</td>
<td>11.85</td>
<td></td>
</tr>
<tr>
<td>$11^c$</td>
<td>37.5</td>
<td>60</td>
<td>$58.0$</td>
<td>25.26</td>
<td>1240.5</td>
<td>1538.6</td>
<td>1.71</td>
<td>11.85</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>15.4</td>
<td>21.2</td>
<td>$20$</td>
<td>25.7</td>
<td>27.7</td>
<td>83.04</td>
<td>1572.0</td>
<td>1963.8</td>
<td>1441.5</td>
<td>2.19</td>
<td>11.5</td>
</tr>
<tr>
<td>$13^c$</td>
<td>15.4</td>
<td>20</td>
<td>$25.0$</td>
<td>84.15</td>
<td>1589.1</td>
<td>1971.2</td>
<td>2.19</td>
<td>11.55</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Pulse duration $t_p$ in simulation is same as $t_{m}^{exp}$ in the experiment.

* Imaginary slow heating case to evaluate equilibrium melting temperature modified by biaxial stress. $t_{m}^{exp}$ for this case means the pulse duration in simulation.

* An elastodynamic formulation and waves are included.

* Simulated melting time without couplings[4].

Figure 5.3: (a) Melting time versus absorbed laser fluence obtained with the current model, model in Ref. 4, and in experiments[3], and (b) kinetic superheating and surface melting temperature versus the heating rate.
\[ \theta_c = \frac{T_{mc}}{T_{eq}}. \] It is clear that \( \theta_c / \theta_c^e = 0.96. \) Evolution of temperature at point \( x_{mc} \) is presented in Fig. 5.4. The melting center \( x_{mc} \) shifts left as laser power becomes stronger (Table 5.1) because faster heating produces a larger temperature gradient and the right interface appears earlier and propagates faster than the left one. For slow heating with \( Q = 0.015K/ps, \) a plateau appears due to absorption of the latent heat, following initiation of melting around \( T_{eq}. \) No superheating is observed, \( T_{ms} \sim T_{eq} \) and \( T_{sm} \) is slightly lower than \( T_{ms} \) because of surface premelting. With an increased heating rate, surface premelting and melting are delayed and \( T_{sm} \) increases. Temperature at \( x_{mc} \) grows during interface propagation and heat absorption, and transition to melting cannot be precisely detected by change of the temperature rate on the temperature evolution curves. Note that for all heating rates but \( Q = 83.04K/ps \) melting time \( t_m \) is shorter than or similar to the laser pulse duration \( t_{exp}^{m}, \) i.e., laser heating occurs through the entire melting process. In contrast, for \( Q = 83.04K/ps \) pulse duration is 20ps but melting time in the simulation is 25.7ps. That is why the temperature decreases after 20ps due to absorption of heat of fusion (Fig. 5.4). This also partially explains the much larger melting time in simulations in comparison with the experiment.

**Evolution of temperature distribution** for different heating rates allows us to shed additional light on the melting process. Slow heating with \( Q = 0.015K/ps \) does not cause a visible temperature gradient except at the very moment when melting ends, \( t = 63.76\,\text{ns}, \) and temperature at the melting center remains practically the same during melting (see Fig. 5.2(b) at time instants 60\,\text{ns} and 62\,\text{ns}). Surprisingly, an increase in heating rates leads to the opposite effect of superheating: temperature reduction in some regions. Heating with \( Q = 6.9 \, K/ps \) results in a moderate temperature gradient before the initiation of melting, see plot for 100\,\text{ps} in Fig. 5.5(b). Solid phase, which includes melting center, heats up continuously after melting initiates at \( t = 110\,\text{ps}. \) On the other hand, in the surface melting zone and then at the moving solid-melt interface temperature is lower than in the solid and even reduces in time. This happens due to absorbed heat of fusion. The maximum temperature difference between the interface and solid exceeds 250\,K. Fig. 5.6 helps to understand contribution of different terms in the temperature evolution equation, Eq. (2.16), to the evolution of the temperature profile at the finite-width interface. The largest contribution to the temperature reduction is
Figure 5.4: Evolution of temperature at the melting center for different heating rates. Red circle represents the end moment of laser pulse for $Q = 83.04 \, K/ps$.

because of the term $- \left[ 3p_e \Delta \alpha - \frac{H}{T_{eq}} \right] T \frac{\partial \phi}{\partial \eta} \frac{\partial \eta}{\partial t}$ (note that $\frac{\partial \phi}{\partial \eta} \frac{\partial \eta}{\partial t} < 0$) due to heat of fusion and change in the thermal expansion coefficient. The second, much smaller, negative contribution is caused by thermoelastic coupling $-3T (\alpha_m + \Delta \alpha) \frac{\partial p_e}{\partial t}$, because $\frac{\partial p_e}{\partial t} > 0$ due to the relaxation of elastic compressive pressure during melting. There is even smaller positive contribution to the temperature increase due to the dissipation rate of melting, $\left( \frac{\partial \eta}{\partial t} \right)^2 / L$. Similar patterns are common for $Q > 0.99 \, K/ps$.

Collision of two interfaces. One more surprise consists of a rapid temperature drop at the end of melting, i.e., just after $t/t_{ms} = 1.0$ (Figs. 5.2(b), 5.4, and 5.5(b)). For the smallest heating rate in Fig. 5.2(b), there is no temperature decrease at the moving interfaces and temperature is practically homogeneous except the final moment of melting. However, immediately after $t/t_{ms} = 1.0$, temperature almost homogeneously drops down to $T_{mf} = 863.9 \, K$, i.e., significantly below $T_{eq}$. The only reason for this is the overlap of interfaces, which continues until $\eta$ reaches zero everywhere. During this time the magnitude of the rate $\frac{\partial \phi}{\partial t}$ (Fig. 5.2(c)) and, consequently, the heat absorption rate $H \frac{T}{T_{eq}} \frac{\partial \phi}{\partial t}$ (see Eq. (2.16)) increases drastically, which causes temperature drop. This means that the overlapping interfaces attract each other and accelerate melting; the degree of acceleration of melting in fact characterizes attraction of interfaces. Homogeneity of the temperature even during the drop is caused by relatively slow
Figure 5.5: Evolution of the distributions of (a) the order parameter, (b) temperature, and (c) $\frac{\partial \phi}{\partial t}$ for $Q = 6.9 \text{ K/ps}$. 
Figure 5.6: Contribution of three source terms in the temperature evolution equation \((2.16)\) at 150\(\text{ps}\) for \(Q = 6.9\, \text{K/ps}\): the third term, \(-3T(\alpha_m + \Delta\alpha\phi)\frac{\partial p_e}{\partial t}\) due to thermoeelastic coupling, the fourth term, \(\left(\frac{\partial\eta}{\partial t}\right)^2/L\) due to the dissipation rate of melting, and the fifth term \(-\left[3p_e\Delta\alpha - \frac{H}{T_{eq}}\right]T\frac{\partial\phi}{\partial t}\frac{\partial\eta}{\partial t}\) due to heat of fusion and change in thermal expansion coefficient.

heating and melting. Similar phenomenon occurs, even more pronounced, for high heating rates (Fig. 5.5). It superposes on the temperature drop that takes place at the moving interfaces due to absorption of the heat of fusion. In Fig. 5.5(c), the maximum magnitude of \(\frac{\partial\phi}{\partial t}\) at the moving interface grows slightly only due to an increase in temperature before interfaces start overlapping. After overlapping, \(\frac{\partial\phi}{\partial t}\) increase significantly and causes localized temperature drop near the melting center. Localization is due to the high heating and melting rate, as well as relatively slow heat transfer. Since the same (or similar) absorption of heat causes temperature reduction in a smaller region than for \(Q = 0.015\, \text{K/ps}\), the magnitude of temperature drop is significantly larger. Integration of \(\frac{\partial\phi}{\partial t}\) over volume gives an overall rate of the heat absorption in the sample and shows a sharp peak just after reaching \(t_{ms}\) and \(T_{ms}\) (Fig. 5.7).

*Analytical approximation* of function \(T_{ms}\) and \(T_{sm}\) vs. \(\log Q\) plotted in Fig. 5.3(b) are: \(T_{ms} = 976.49 + 111.11 \log Q + 192.65(\log Q)^2 + 12.43(\log Q)^3\) \((R^2 = 0.998)\) and \(T_{sm} = 924.24 + 112.40\log Q - 1.94(\log Q)^2 + 64.57(\log Q)^3\) \((R^2 = 0.9998)\).

*Effect of elastic wave.* For very fast heating at the picosecond scale, when melting time reduces and becomes comparable with acoustic time, dynamic treatment is required. Plots of evolution of stress \(\sigma_{11}\) and elastic mean stress \(p_e\) before melting are presented in Fig. 5.8.
Figure 5.7: Evolution of the volume integral of $\partial \phi / \partial t$ for (a) $Q = 0.015 K/ps$ and (b) $Q = 6.9 K/ps$.
Since \( \sigma_{11} \) does not receive contributions from the interface stresses, \( \sigma_{11} = \sigma_{11}^e \); then \( \sigma_{22}^e = \sigma_{33}^e = (3p_e - \sigma_{11})/2 \) can be evaluated based on plots in Fig. 5.8. Due to a temperature increase under constraint of uniaxial strain conditions, compressive stresses \( \sigma_{22} = \sigma_{33} \) grow within the layer. They cause growth of the compressive stress \( \sigma_{11} \), with the maximum at the center and zero values at the surfaces, due to boundary conditions. A standing wave with nodes at the surfaces and wave length \( \lambda = 2w \) is formed, in which stress \( \sigma_{11} \) oscillates around the zero value (which is the static solution) with the magnitude of \( 1.25GPa \) (reaching maximum tensile stress at 6 ps) and stresses \( \sigma_{22} = \sigma_{33} \) oscillate around growing compressive stress. When melting starts and occurs at the surfaces, compressive stresses \( \sigma_{22} = \sigma_{33} \) and stress \( \sigma_{11} \) relax in melt down to zero. During melting, solid-melt interfaces become new nodal points so that pressure oscillates between two interfaces within the solid with reducing magnitude, which is relatively small compared to the pressure for elastostatic formulation (Fig. 5.8(c)).

As shown in Table 5.1, elastic waves do not remarkably affect characteristic melting times and temperatures. The reasons for this small effect follow from Fig. 5.8(c), where elastic pressure distribution for elastostatic and elastodynamic formulations are compared. Nodal points at both surfaces mean that the surface is not affected by elastic waves and the elastic pressure at surfaces is the same in both formulations. That is why conditions for surface-induced melt nucleation and \( T_{sm} \) in Table 5.1, which depend on pressure distribution near external surfaces, are very close. Pressure distribution within interfaces is very similar in both formulations and consequently do not affect interface velocity.

## 5.4 Bulk melting

Problem formulation based on initiation of surface-induced melting and without fluctuations in bulk led to good correspondence between calculated and experimental melting times for \( Q \leq 25.26 K/ps \), see Table 5.1. For the fastest heating rate \( Q \geq 83 K/ps \), calculated melting time is 29.5% larger than the experimental one and maximum superheating temperature is well above the temperature at which the solid loses its thermodynamic stability, in the current model \( 1.2T_{eq} = 1120K \). This means that in addition to surface melting followed by propagation of interfaces toward the sample center, barrierless melting in the bulk may occur, which
Figure 5.8: Evolution of (a) $\sigma_{11}$, (b) $p_e$ distributions before melting starts, and (c) comparison of evolution of elastic mean stress $p_e$ distribution for simulation in elastostatic (solid line) and elatodynamic (dashed line) formulations for $Q = 84.15\, K/ps$. 
will accelerate melting and reduce maximum superheating. For a thick enough sample, the
time for bulk melting may be much smaller than the time before two interfaces meet, that is
why surface melting is not important. Surface melting can also be avoided if one reduces the
difference between surface energies of a solid and melt, $\gamma_s - \gamma_m$, e.g., by placing at the surface
crystal faces which do not undergo surface melting, changing surrounding, or producing proper
surface treatment. To study bulk melting, we set $\gamma_s = \gamma_m$ in the boundary condition (Eq.
(3.3)) and specified perturbation term $\varsigma$ in Ginzburg-Landau equation (Eq. (2.8)) to initiate
the bulk melting.

Results for elastodynamic and elastostatic problem formulations are presented in Fig. 5.9
and compared with previous elastodynamic simulations for surface-induced melting. Melting
starts quasi-homogeneously within the entire sample, while melting in the right side is slightly
more advanced because of the higher temperature. Since the tracking order parameter at the
melting center is meaningless for this case, $\frac{1}{w} \int \phi dx$ is calculated in order to compare melting
time with surface-induced melting. In elastostatic formulation, melting near the right surface
progresses and completes significantly faster than near the left surface. For elastodynamic
formulation, the standing $p_e$ wave in Fig. 5.8(b) has a maximum in the central region of
the sample. Since the temperature of the sample is above the solid instability temperature,$1.2T_{eq}$, pressure oscillation promotes melting by lowering equilibrium melting temperature and
solid instability temperature in its tensile peak without essential suppressing melting in its
compression stage. Distribution of the order parameter is less heterogeneous than in elast-
static formulation. While bulk melting starts later and at a higher temperature than the
surface-induced melting, it completes faster. Thus, melting time for bulk melting is $22.6ps$ and
$21.6ps$ for elastostatic and elastodynamic formulation, respectively. It is significantly closer to
experimentally measured time, $20ps$, than $25.7ps$ for surface-induced melting (Table 5.1).

5.5 Conclusion

Here, an advanced thermodynamically consistent model for kinetic superheating and melt-
ing of an Al nanolayer irradiated by a picosecond laser is formulated. It includes the coupled
system of phase field equations for melting, two-temperature model for electron and lattice heat
Figure 5.9: Time evolution of distribution of (a) the order parameter $\eta$ and (b) the $\frac{1}{w} \int \phi dx$ for the fluence $13 \text{mJ/cm}^2$. In figure (a), solid and dashed lines represent bulk melting in elastodynamic and elastostatic formulations and dash-dot line is elastodynamic simulation of the surface-induced melting.
conduction, the equations of elastodynamics that allow for interface stresses. The Ginzburg-Landau equation for melting is fully coupled with elastodynamic and lattice thermal conduction. The lattice heat conduction equation includes electron-phonon coupling, heat of fusion, thermoelastic effects, and the dissipation rate due to melting. Usually, it included just heat of fusion. Laser irradiation is described as a distributed-in-bulk heat source according to Beer-Lambert law. Reduction in surface energy during the melting is included in the boundary conditions for the order parameter. This system of equations was solved using finite element method and code COMSOL Multiphysics. Such a sophisticated physical formulation allowed us both to describe some nontrivial experimental results and reveal new phenomena. Two main regimes were considered. In the first one, barrierless nucleation of surface premelting and melting occurs followed by the propagation of two solid-melt interfaces toward each other and their collision. For slow heating rate $Q = 0.015 \text{ K/ps}$ melting occurs at the equilibrium melting temperature under uniaxial strain conditions $T_{eq}^e = 898.1K$ (i.e., below $T_{eq} = 933.67K$) and corresponding biaxial stress, which relaxes during melting. For high heating rate $Q = 0.99 - 84 \text{ K/ps}$, significant overheating above $T_{eq}$ is observed before complete melting. Surprisingly, an increase in the heating rate leads to a temperature reduction at the moving interfaces due to fast heat of fusion absorption. A significant, rapid temperature drop (even below melting temperature) at the very end of melting is revealed, which is caused by the collision of two interfaces and accelerated melting. An analytical approximation of surface melting $T_{ms}$ and solid maximum superheating $T_{sm}$ temperatures as the third degree polynomial of $\log Q$ describes the results of simulations well. For $Q = 25 - 84 \text{ K/ps}$, standing elastic stress waves are observed in the solid with nodal points at the moving solid-melt interfaces, which however, do not have a profound effect on melting time and temperatures. Simulation results are in good correspondence with known experiments[3] in terms of time for complete melting, excluding the highest heating rate $Q = 84 \text{ K/ps}$. For the second regime and the highest heating rate of $84 \text{ K/ps}$, the surface melting was suppressed but bulk thermal fluctuations have been mimicked in a simple way. In this case, barrierless bulk melting occurs in the entire sample. Elastodynamic effects are more important than in the first regime and much better correspondence with experimental melting time is obtained. More precise study in which thermal fluctuations are included that satisfy
the fluctuation-dissipation theorem[44, 45] will be pursued in the future.

Similar approaches can be applied to study various phase transformations (martensitic, reconstructive, amorphization, etc.) in different materials (metals, ceramics, and nanocomposites) and geometries (single and multilayers, nanoparticles, nanowires, and core-shell structures) under high heating rates. In particular, instead of (or in addition to) the Ginzburg-Landau equation for melting, one can utilize equations for martensitic transformations, twinning, dislocations, and their interaction[77, 48, 78, 79]. Also, surface melting (phase transformations) can be described more precisely if one explicitly introduces finite width of the external surface[80, 81]. This can also be done by considering nucleation of melt within an interface between two phases[82].
CHAPTER 6. PHASE FIELD SIMULATION WITH THERMAL FLUCTUATION OF KINETIC SUPERHEATING AND MELTING OF ALUMINUM NANOLAYER IRRADIATED BY FEMTOSECOND LASER

In a usual condition, the melting of metal is subject to heterogeneous melting so that it starts to melt from the surface which has a penalty on energy. In some conditions, metal can melt far above its equilibrium bulk melting temperature, $T_{eq}$. Suppression of heterogeneous melting is one of the known methods to make metal superheated; coating the surface and hence forming a coherent interface between the metal and coated material is one example. After eliminating heterogeneous melting, several criteria for the limit of superheating have been researched. Entropy catastrophe\cite{[8]} suggested $1.38T_{eq}$ superheating for Al, isochoric condition\cite{[24]} predicted $1.28T_{eq}$, and homogeneous nucleation theory\cite{[25]} showed around $1.21T_{eq}$ as the limit of superheating. Mei and Lu\cite{[6]} summarized these models well. MD simulation for homogeneous nucleation showed a similar melting temperature for a cubic Al sample confined by periodic boundary conditions; for example, $1.3T_{eq}$ was simulated by Forsblom and Grimvall\cite{[26]}, and $1.22T_{eq}$ was simulated by Jin and Lu\cite{[27]} using the same potential as Forsblom and Grimvall’s; the difference may not originate from the size effect since Forsblom and Grimvall had a higher melting temperature for a smaller sample and Jin and Lu’s sample was smaller than Forsblom and Grimvall’s. However, it has been observed in experiments\cite{[3, 5, 7]} and phase field simulations\cite{[4, 1, 76]} that an aluminum layer irradiated by a ultra-fast laser can be superheated up to at least $1400K \sim 1.5T_{eq}$ \cite{[7]} for $T_{eq} = 933.67K$, which is much higher than the limit temperatures predicted with equilibrium thermodynamics.

An endeavor to find the limit temperature of superheating becomes more complicated when various physical phenomena interact in a similar scale. Especially at a fast heating rate and non-equilibrium condition, phase transformation is not governed by a single physical phenomenon,
rather several physical phenomena are interwoven by complex couplings as described by our previous research\[4, 1, 76\]. Thus, for very high heating rates \(Q \geq 10^{12} \text{K/s}\), elastic wave propagation can affect the temperature of the material through thermoelastic coupling and melting temperature through the effect of stresses\[76\]. Melting also influences the temperature of materials through thermo-phase transformation coupling, mostly due to latent heat. Melting temperature becomes a function of heating rate since slower kinetics of a solid-melt interface propagation than the heating results in the kinetic superheating while heterogeneous melting is governing process of melting\[4, 50, 76\]. Under non-hydrostatic internal stresses that relax during melting, e.g. under biaxial stresses due to constraint, melting temperature reduces. See thermodynamic\[68, 1\] and phase field\[1\] treatments for a layer. Melting temperature drastically decreases during very high strain-rate uniaxial compression in a strong shock wave, as it was predicted thermodynamically and confirmed by molecular dynamics simulations\[61\]. Thermal fluctuation has a strong effect on melting when the temperature of metal surpasses its solid instability temperature\[76\].

The melting of metal induced by irradiation of a femtosecond laser would be one of the best examples for the multiphysics-involved melting. A heating rate which exceeds several hundred \(K/\text{ps}\) can produce an elastic wave in the sample which has time scale similar to that of melting even for a sample as small as several tens of nanometers\[38\]; for example, if an aluminum nanolayer is 20 nm thick, then the time required for the elastic wave to travel from one side to the middle of a nanolayer is about \(
\frac{10\text{nm}}{4\text{nm/ps}} \sim 2.5\text{ps}
\) which is in the same order as 3.5 ps for a complete melting time with femtosecond laser irradiation\[5\]. The heating of aluminum governed by the time lag between electron gas and lattice\[9\] also has a similar time scale as a melting time scale\[4, 7\]. Kinetic superheating due to fast heating can make the temperature of the solid sample increase above the instability temperature of solid state where thermal fluctuation dominates melting through homogeneous melting, and the time scale of the thermal fluctuation, usually several hundred femtosecond\[39\], is only one order smaller than the melting time scale. Thus, a simulation of the melting of nanolayer irradiated by femto-second laser needs to take into account for several physical phenomena at the same time.

Recently, we have suggested a multiphysics phase field approach that includes the phase
field model for melting developed in Ref. 36, 35; a dynamic equation of motion; a mechanical
model for stress and strain simulations; the thermal conduction model with thermo-elastic
and thermo-phase transformation coupling, as well as with a dissipation rate due to melting[4, 1]; and a primitive form of thermal fluctuation[76]. The previous research[76] revealed that
the multiphysics model with couplings and primitive thermal fluctuation is able to simulate
kinetic superheating and melting up to several tens of picoseconds and extreme heating rate,
\( Q \leq 84 \text{K}/\text{ps} \). However, the modeling of the thermal fluctuation relied on amplification of
numerical error not rigorously supported by theory. In this study, the multiphysics phase
field approach is improved with thermal fluctuation of the order parameter described by the
fluctuation-dissipation theorem on top of the previous model which contains the phase field
model for melting, a dynamic equation of motion with mechanical model, and the advanced
Two Temperature model with coupling terms; the coupling includes thermo-elastic coupling,
thermo-phase transformation coupling, and a dissipation rate due to melting. The model is
applied to replicate experimental observations for melting and superheating of an Al nanolayer
by a femtosecond laser[7]. Approximated 1-D and 3-D geometry of an aluminum nanolayer
sample are selected to test the effect of geometric simplification on thermal fluctuation.

6.1 Governing equations

The governing equation set is comprised of the Ginzburg-Landau equation with thermal
fluctuation for melting, equation of motion for elastic wave, and TTM for temperature change
of material. The total strain tensor, \( \varepsilon \), is described by Eq. (2.1). Free energy per unit
undeformed volume is presented by Eq. (2.4)[4, 36]. The stress tensor \( \sigma \) is as Eq. (2.7).
The Ginzburg-Landau equation, Eq. (2.8), with \( \zeta = 0 \) and non-zero thermal fluctuation \( \omega \)
is employed for melting simulation. Irradiation of a femtosecond laser creates fast enough
heating to delay heat transfer between electron gas and lattice. The TTM model, Eq. (2.16)
and (2.17), describes the delay. The equation of motion to take a consideration into elastic
wave is described by Eq. 2.15.
6.2 Some guideline for thermal fluctuation of the order parameter

As described by Eq. (2.10), thermal fluctuation depends on the volume of discretized cells and time. This is essential for mean field theory described by Landau and Lifshitz[83]. Thus simulations of phase transformation with thermal fluctuation have shown a dependence on discretization[45, 84]. For the time scale of thermal fluctuation for Ginzburg-Landau equation, Ichitsubo and Tanaka[39] suggested Eq. (6.1) as an appropriate maximum time step for thermal fluctuation.

\[
\Delta t \sim \frac{1}{2L^2 \psi(\eta_{eq})},
\]

(6.1)

where \( \eta_{eq} \) means the order parameter for global equilibrium, which is 0 in the case of superheating problem. The physical meaning of the relationship is to take a time step which can resolve relaxation process of fluctuation so that magnitude of order parameter fluctuation at the equilibrium state becomes similar order to the magnitude expected by fluctuation-dissipation theorem[39]. It can provide an approximation of the discretized time since the system is not at equilibrium but at a highly non-equilibrium state when the sample is kinetically superheated.

Since there has been no research about the magnitude of order parameter fluctuation and discretization of kinetically superheated metal to our best knowledge, we consider Eq. (6.1) as a guideline for the discretized time step. In Fig. 6.1 which shows calculated discretized time for free energy of aluminum without mechanical energy, the calculated time step for \( T > T_{eq} \) has \( 10^{-13} \) s order which has a similar order to the period of maximum vibrational frequency, approximately same as Debye frequency \( 10^{13} - 10^{14} / s \) of aluminum[26].

For case such as \( T < T_i = 1.2T_{eq} \), a characteristic length of dominant physical phenomena such as a critical nucleus can be the guideline of discretized dimension. Since melting for the condition of \( T > T_i \) does not need critical nucleus but thermal fluctuation, the lattice constant is used as the discretized dimension for thermal fluctuation since it is the minimum geometry where thermal fluctuation can take place.
6.3 Problem formulation, boundary and initial conditions, and material properties

The same geometry and laser condition as the reference experiment[7] are used to simulate melting of an aluminum nanolayer irradiated by femtosecond laser; i.e. \( w = 20 \text{ nm} \), the fluence \( 70 \text{ mJ/cm}^2 \) and \( 120 \text{ fs} \) pulse duration.

Attenuation of the irradiated energy across the volume is modeled with Beer-Lambert law:

\[
I = I_0 \exp(-\zeta(w-x)); \quad I_0 = \frac{\zeta W}{1 - \exp(-\zeta w)}; \\
W = (1 - R) F_0 / t_p,
\]

where \( \zeta \) is the absorption coefficient, which is \( 1.4616 \times 10^8 \text{m}^{-1} \) for the 700 nm laser[5]; \( w \) is thickness of a sample; \( R \) is the reflectance, which is 0.87 [5]; \( t_p \) is the pulse duration; \( F_0 \) is the fluence of laser.

The boundary condition for the order parameter \( \eta \) at the surface is described by Eq. (3.3). The boundary condition explains the change of surface energy during melting.

1-D simulation. Because the radius of the irradiated spot is much larger than \( w \), mm vs. nm, the problem can be safely considered as a 1-D problem with zero displacements orthogonal to the laser axis; thus, all parameters vary only along the laser axis. Two plane boundaries are
stress-free and adiabatic. While the laser irradiates only the right plane of a sample, both plane boundaries are allowed to be melt. The energy irradiated by a femtosecond laser is included as a volumetric heat source as described by Eq. (6.2).

3-D simulation. Even though dimensional simplification is an economic way to reveal characteristics of the effect of thermal fluctuation on melting, a reduced dimension introduces an ambiguity to set a discretized volume; for example, the area for the fluctuation can be determined arbitrarily since 1-D specifies only the length of the computational element. Also, 1-D simplification can overestimate fluctuation by ignoring random fluctuation along two normal coordinates to the laser axis. Therefore, the 3-D computation is performed to be compared with the results from 1-D simulations. Fig. 6.2 shows a computational domain which has $20\text{nm} \times 6\text{nm} \times 6\text{nm}$ size. $x = 0, 20\text{nm}$ planes are stress free surfaces where Eq. (3.3) is applied for the boundary condition of the Ginzburg-Landau equation. The laser irradiates at the $x = 20\text{nm}$ plane, and the irradiated energy is treated as a volumetric heat source as described by Eq. (6.2) along x-axis. All other planes have a symmetry boundary condition for every variable. The mesh size is uniformly fixed into $0.4\text{nm}$ for all coordinates which are approximated lattice constant of aluminum, $0.40495 \text{nm}$. In order to inspect the size effect, a larger sample, $20\text{nm} \times 9\text{nm} \times 9\text{nm}$, has been tested with the same boundary conditions as a smaller 3D sample.
The initial temperature is $T_0 = 293.15 \, K$, and $\eta_0 = 1.0$ for all cases. The finite-element code \textit{COMSOL Multiphysics} is used for the simulations\cite{51}. Considering the stochastic nature of thermal fluctuation, parameters which characterize melting and superheating are determined by statistical analysis with several solutions which use randomly generated seeds. For 1-D geometry, 50 solutions are solved for a single condition and 20 solutions are solved for 3-D geometry.

\textit{Material properties.}

The same material properties for aluminum as our previous study\cite{1} are used and summarized as follows. The specific heat, thermal conductivity of aluminum lattice and electron gas, and electron-phonon coupling coefficient are the same as section 3.3. Coefficients, constants, and other properties used for simulation are included in Table 3.1.

6.4 1-D homogeneous melting

The calculated $\Delta t$ using free energy with mechanical energy gives 192 $fs$ at 1400 $K$, which is utilized as the base time step for thermal fluctuation. Constant $\Delta t$ is used to manifest its effect on melting and for simplicity. The discretized order parameter fluctuation, $\Delta \eta$, is defined to demonstrate the magnitude of order parameter fluctuation at a given discretized time and facilitate analysis of the effect of order parameter fluctuation on melting. Since only one coordinate is specified in 1-D approximation, the area, $A$, should be provided in order to define discretized volume. $\Delta \eta$ and $A$ have the relationship as described by Eq. (6.3).

\[
\sigma_\eta = \frac{\Delta \eta}{\Delta t}; \quad A = \frac{2k_BLT_{ref}}{\Delta x \Delta t \sigma_\eta^2}; \quad \Delta V = \Delta x A,
\]

(6.3)

where $\Delta x = 0.4 \, nm$ is the size of mesh in 1-D computational domain, and $T_{ref}$ is the reference temperature for thermal fluctuation, 1400 K here. $\sigma_\eta$ is controlled by setting value of $\Delta \eta$ and $\Delta t$, and in turn it corresponds to $A$ and $\Delta V$ by Eq. (6.3). In a given condition, $\Delta \eta$ means the magnitude of order parameter fluctuation during $\Delta t$ at $T_{ref}$; about 68.2% of fluctuations are included in the range of $\pm \Delta \eta$ due to Gaussian distribution of random fluctuation. $\bar{\phi} = \int \phi \, dx / w$ is used for defining and comparing melting time with an experiment. Table 6.1 summarizes
simulation conditions and results. $t_{sm}$ and $t_m$ represent the time for $\bar{\eta} = 0.9$ and $\bar{\phi} = 0.1$ respectively.

It is obvious that simulated melting times are greatly reduced in comparison with the result without thermal fluctuation in Ref. 4 and become much closer to experimental observation; simulated results in Ref. 4 were $t_{sm} = 5.2$ ps and $t_m = 8.1$ ps. Note that melting started between 1.5 and 2.5 ps and ended at or after 3.5 ps in experiment[7]. $\sigma_\eta \geq 0.68$ ps$^{-1}$ satisfies the time for melting start, but it seems that $t_m$ is slower than in the experiment. However, considering the 1.0 ps temporal resolution in the experiment[7], the predicted $t_m$ shows reasonably good agreement with experimental result.

The Lindemann criterion describes the critical magnitude of atom fluctuation which leads to melting of material. Gilvarry[85] defined the critical portion as $\rho_L^2 = \langle u^2 \rangle / r_m^2$, where $u$ is displacement and $r_m$ is the distance between atoms. The reported value for aluminum was $\rho_L = 0.08$, which means that the material will melt if magnitude of displacement fluctuation reaches 8% of the atomic distance[85]. Since the order parameter represents volumetric expansion during melt which is assumed to be 6%, $\Delta \eta = 0.13$ for $\sigma_\eta = 0.68$ ps$^{-1}$ and $\Delta t = 192$ fs corresponds to 0.78 % volume fluctuation. Comparing 0.78 % volume fluctuation, which corresponds to 0.26 % displacement fluctuation for one coordinate, with 8% displacement fluctuation of Lindemann criterion, it can be deduced that a small amount of fluctuation is sufficient to melt the kinetically superheated material, but still it is not zero. Based on good agreement with

<table>
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<th>$\sigma_\eta$ (ps$^{-1}$)</th>
<th>$\Delta \eta$</th>
<th>$\Delta t$ (fs)</th>
<th>$t_{sm}$ (ps)</th>
<th>$\sigma_{sm}$ (ps)</th>
<th>$t_m$ (ps)</th>
<th>$\sigma_m$ (ps)</th>
<th>Number of cases</th>
<th>$T_{ms}$ (K)</th>
<th>$T_{1.5ps}$ (K)</th>
<th>Dimension</th>
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* The case was calculated without coupling between temperature and dissipation on Eq.(2.16).
* The largest sample, $9 \times 9 \times 20 nm$
experimental data, the Langevin fluctuation term, $\omega(x, t)$, satisfying the fluctuation-dissipation theorem with physically guided discretization can provide accurate and explicit way to control small order parameter fluctuation for homogeneous melting on numerical simulation.

Increasing $\sigma_\eta$ results in decreasing melting times as shown by Table 6.1 since increased negative fluctuation accelerates homogeneous melting. Changing the frequency of order parameter fluctuation for constant $\sigma_\eta$ does not make much of a difference in terms of melting times; compare $\Delta t = 147.7, 192$, and $221.5$ fs cases for $\sigma_\eta = 0.68$ ps$^{-1}$.

Order parameter distribution with respect to the time is shown by Fig. 6.3 (a) where one of 50 cases of $\sigma_\eta = 0.68$ ps$^{-1}$ and $\Delta t = 192$ fs is presented. The order parameter has large fluctuations on its distribution which has random negative and positive deviation around an average value. At 1.0 ps which is before the start of melting, the local order parameter has negative fluctuation at several spots, which is a key factor accelerating melting. Since the temperature at 1.0 ps is around 1300 K which is above instability temperature, the negative growth of the order parameter is barrierless once the order parameter becomes less than 1.0.

Fig. 6.3 (b) depicts temperature at the middle of sample and spatially averaged temperature, $\bar{T} = \int T dx/w$. The evolution of $\bar{T}$ before melting starts has several small increases and decreases which result from fluctuation while the material is being heated; the start of melting makes the increase disappear. Note that $t_m$ of the case displayed at Fig. 6.3 is closer to experimentally observed melting time, 3.5 ps, than other stochastic cases for the same condition.

In Fig. 6.3 (b), temperature at the middle of sample is larger than the average temperature at the beginning of heating since the middle part of sample is experiencing faster compression than the other part due to the elastic wave as shown by Fig. 6.4. $\bar{T}$ at 1.5 ps is 1580 K for the displayed case and 1581 K on average for 50 stochastic cases as shown in Table 6.1. It is notable that Siwick et al.[7] predicted 1400 K at 1.5 ps by using conventional TTM and confirmed the temperature by comparing the estimated Debye-Waller factor based on the predicted temperature with measured data; we also confirmed that 1400 K at 1.5 ps can be calculated by conventional TTM in our previous research[4]. Observing Fig. 8 of Ref. 7 which describes the comparison of measured Debye-Waller factor with predicted one, however, shows that the measured Debye Waller factor for 3 planes at 1.5 ps was actually less than
Figure 6.3: (a) Distribution of order parameter with respect to time and (b) evolution of $\bar{\phi}$, $\bar{T} = \int T \, dx / w$, and $T$ at the middle of a nanolayer for the $\sigma_\eta = 0.68 \, ps^{-1}$ and $\Delta t = 192 \, fs$ case.
the predicted data; only one plane showed the same value as predicted one. Therefore, it is possible to deduce that the actual temperature of the sample at 1.5 ps might be higher than 1400 K in the experiment and $\bar{T}_{1.5 \text{ps}}$ higher than 1400 K at Table 6.1 can be rationalized. This high temperature originates from thermoelastic coupling and dissipation coupling. An increase in thermal fluctuation, $\sigma_{\eta}$, makes $\bar{T}_{1.5 \text{ps}}$ increase as shown in Table 6.1; thus, $\bar{T}_{1.5 \text{ps}}$ increases from 1508.6 K to 1613.6 K as $\sigma_{\eta}$ increases from 0.36 to 0.78 for constant $\Delta t = 192 \text{fs}$. A decrease of $\Delta t$ with constant $\sigma_{\eta}$ leads to an increase of $\bar{T}_{1.5 \text{ps}}$ as shown by $\sigma_{\eta} = 0.68 \text{ps}^{-1}$ cases at the table. Large and frequent thermal fluctuation increases $\bar{T}_{1.5 \text{ps}}$ as a result of coupling term of $\left(\frac{\partial \eta}{\partial t}\right)^2 / L$ in Eq. (2.16). Getting rid of the coupling term from the lattice heating equation lowers $\bar{T}_{1.5 \text{ps}}$ from 1581.0 K to 1477.4 K and from 1613.6 K to 1476.6 K for $\sigma_{\eta} = 0.68$ and 0.78 $\text{ps}^{-1}$ cases respectively, and hence the melting time, $t_m$, retards from 4.02 ps to 4.73 ps and from 3.97 ps to 4.68 ps for $\sigma_{\eta} = 0.68$ and 0.78 $\text{ps}^{-1}$ cases respectively, as observed at Table 6.1. Decoupling of dissipation rate from the lattice conduction equation also makes $\bar{T}_{1.5 \text{ps}}$ practically independent on the magnitude of fluctuation so that $\bar{T}_{1.5 \text{ps}} = 1477.4 K$ for $\sigma_{\eta} = 0.68$ and 1476.7 K for $\sigma_{\eta} = 0.78$. The relative error between $t_m$ with and without the coupling term are not such small as 17.7% and 17.8% for $\sigma_{\eta} = 0.68$ and 0.78 $\text{ps}^{-1}$ respectively. It can be realized that the coupling term serves an important role on the prediction of melting and melting time by affecting temperature, and use of the terms enables predicted $t_m$ to become closer to the measured time for this simulation. $\bar{T}_{1.5 \text{ps}}$ is still higher than 1400 K, which is the predicted temperature with conventional TTM, due to thermoelastic coupling even without the coupling of dissipation rate. Thus, a larger $\bar{T}_{1.5 \text{ps}}$ than what was predicted by conventional TTM comes from the contribution of two couplings.

In Fig. 6.3 (b), the maximum average temperature, $\bar{T}_{ms}$, attained during melting is 1775 K at $t_{ms} = 2.38 \text{ps}$, and the temperature of a sample decreases after $\bar{T}_{ms}$. Since 4 ps delay of heating between lattice and electron gas is simulated as shown by Fig. 6.5, the lattice is still being heated during melting by electron gas so that $\bar{T}$ is increasing after melting starts at $t_{sm} = 2.26 \text{ps}$. After reaching to $\bar{T}_{ms}$, $\bar{T}$ decreases due to fast melting of bulk and diminishing difference between $T$ and $T_e$. There is no sudden drop of temperature at the end of melting as described in Ref. 76 since the solid-melt interface does not exist so that there is no acceleration
Figure 6.4: Distribution of mean elastic stress, $p_e$, with respect to time for $\sigma_\eta = 0.68 \text{ps}^{-1}$ and $\Delta t = 192 \text{ fs}$ case.

of melting by collision of interfaces. Rather, a slow and smooth decrease of temperature after $T_{ms}$ is observed. The complex pattern of temperature evolution at the middle of the sample during melting is the result of complex physical interactions between randomly distributed local melting, stress relaxation by melting, and their couplings with temperature.

Evolution of $p_e$ distribution shown by Fig. 6.4 has large fluctuations during melting while the initial distribution before 1 ps does not have them; the large fluctuation results from local stress relaxation by random local melting. Fast heating develops a standing wave of mean stress which has two nodal points at the surfaces. Maximum compressive mean stress is formed between 1.0 ps and 2.0 ps and reaches about 8 GPa. After the negative peak of $p_e$, the mean stress swings back, and a standing wave of elastic stress forms. In this 1-D femtosecond melting case, melting initiates and proceeds before the standing wave swings back to the expansion phase. Thus, the elastic wave can promote superheating of a nanolayer by creating high pressure at the middle of the sample when a sample starts melting.

The heating rate for the displayed case at Fig. 6.3 is not constant and shows 375 K/ps on average and 1408 K/ps. The consideration of additional heating from thermoelastic and dissipation rate couplings provides a larger heating rate than the one reported in our previous work[4].
Figure 6.5: Evolution of lattice temperature, $T$, and electron temperature, $T_e$, at the middle of nanolayer for $\sigma_\eta = 0.68\, ps^{-1}$ and $\Delta t = 192\, fs$ case.

6.5 3-D homogeneous melting

In a 3-D simulation, the volume of a finite element is fixed to $\Delta V = 0.4 \times 0.4 \times 0.4\, nm^3$ so that $\Delta t$ controls the magnitude of order parameter fluctuation. $\Delta t = 192\, fs$ and $147.7\, fs$, which result in $\sigma_\eta = 1.29\, ps^{-1}$ and $1.48\, ps^{-1}$ respectively, are tested.

$t_{sm}$ and $t_m$ of the 3D simulation are longer than those of the 1D simulation as shown by Table 6.1 even though a larger fluctuation is introduced into the 3D simulation for the same $\Delta t$. Thus, $t_m = 4.15\, ps$ for $\sigma_\eta = 1.29\, ps^{-1}$ and $\Delta t = 192\, fs$ of 3D and $t_m = 4.02\, ps$ for $\sigma_\eta = 0.68\, ps^{-1}$ and $\Delta t = 192\, fs$ of 1D. While the 1D simulation assumes the same fluctuation of order parameter for two perpendicular coordinates, the 3D simulation randomizes the fluctuation for all directions. As a result, the acceleration of melting by negative fluctuation in 1D has its influence on the entire local slab-like volume represented by a 1D linear element. In contrast, it is restricted into a local block-like element in the 3D simulation, which has more chances to have neighborhood elements in non-negative fluctuation. Accordingly, the probability that a local volume of 3D geometry can be affected by negative fluctuation is rarer than for a 1D geometry so that the melting start becomes slower. The melting end time, $t_m$, for the case of $\Delta t = 147.7\, fs$ shows better agreement with experimental observation than $\Delta t = 192\, fs$ case, and it is similar to $t_m$ for the 1D case of $\sigma_\eta = 0.78\, ps^{-1}$ and $\Delta t = 192\, fs$. 
In Fig. 6.6, the evolution of $\eta$ distribution for $\Delta t = 147.7 \, fs$ case is compared with the experimentally obtained diffraction pattern\[5\]. The random fluctuation of the order parameter is obvious even for solid state at 0.5 ps. Most of the sample is solid at 1.5 ps while several random spots at the surfaces show the decrease of order parameter, and it agrees well with the experimentally observed diffraction pattern which had distinctive rings created by crystalline structure of a sample. At 2.5 ps, heterogeneous nucleation melts most of the surface while the bulk of sample is still solid, although random spots in the bulk shows initiation of melting. In the experiment, the smearing of diffraction rings appears after this moment, which represents initiation of melting. The $\eta$ distribution at 3.5 ps shows that most of the bulk of the sample melts into liquid except some randomly distributed islands of solid. This prediction agrees well with the almost completely smeared pattern of diffraction rings. At 4.0 ps, the sample almost completely melts. It is worth noting that there are no recognizable nuclei in the bulk. Since the temperature of the bulk before melting starts is far above instability temperature, melting does not need nucleation so that the entire bulk of metal collapses into liquid in a random way.

The melting period, $\Delta t_m = t_m - t_{sm}$, for 3D simulation becomes shorter than for 1D simulation; for example, $\Delta t_m = 1.08 \, ps$ for $\Delta t = 147.7 \, fs$ of 3D is shorter than $\Delta t_m = 1.77 \, ps$ for 1D case of $\sigma_\eta = 0.78 \, ps^{-1}$ and $\Delta t = 192 \, fs$ while these two cases have a similar $t_m$. While the randomness for all coordinates retards the start of melting for the 3D case, mean elastic stress of the sample is increasing during this delayed period as shown by Fig. 6.7; in order words, the pressure of sample is decreasing. Comparing distribution of $p_e$ at 1.0 ps in Fig. 6.4 and Fig. 6.7 shows that the evolution of mean stress for 1D and 3D is similar. $p_e$ at 2.2 ps where 1D sample starts to melt is $-4 \sim 5 \, GPa$ at the middle part of sample while $p_e$ at 2.95 ps where 3D sample starts to melt is $0 \sim 1 \, GPa$. An at least 4 GPa decrease in pressure can make an approximately 240 K decrease in melting temperature by the Clausius-Clapeyron relationship so that it can accelerate melting for 3D case. $\bar{T}_{ms}$ and $\bar{T}_{1.5ps}$ for the $\Delta t = 147.7 \, fs$ case of 3D are 1800.0 K and 1603.7 K similar to those for the $\sigma_\eta = 0.78$ and $\Delta t = 192 \, fs$ case of 1D simulation. The big 3D sample with $\Delta t = 147.7 \, fs$ shows not much difference from the small 3D sample with the same $\Delta t$, thus $\bar{T}_{1.5ps}$ is 11.7K lower than that of small 3D sample, and $\bar{T}_{ms}$ is 49.9K lower. The $t_{sm}$ and $t_m$ are almost same as the small 3D sample, so the size
Figure 6.6: Comparison of simulated evolution of $\eta$ distribution for 3D case of $\Delta t = 147.7 \text{ fs}$ with experimentally observed diffraction pattern$^5$.

effect in the given simulation condition is quite limited.

It is an interesting observation that $t_m$ has strong correlation with $\bar{T}_{ms}$ and $\bar{T}_{1.5ps}$ as shown by Fig. 6.8. A linear curve fit shows their relationship with good approximation regardless of diverse computational conditions. In Table 6.1 and Fig. 6.8, removing the dissipation rate coupling for $\sigma_\eta = 0.68 \text{ ps}^{-1}$ and $0.78 \text{ ps}^{-1}$ largely decreases $\bar{T}_{ms}$ and $\bar{T}_{1.5ps}$, which consequently causes a large increase of $t_m$ in comparison with cases which have the same magnitude of fluctuation and the coupling. On the other hand, $t_m$ remains a similar value for the $\sigma_\eta = 0.78 \text{ ps}^{-1}$ and $\Delta t = 192.0 \text{ fs}$ case of 1D and the $\sigma_\eta = 1.48 \text{ ps}^{-1}$ and $\Delta t = 147.7 \text{ fs}$ case of 3D in spite of large difference of computational conditions because $\bar{T}_{ms}$ and $\bar{T}_{1.5ps}$ are a similar value for both cases. Thus, the major factor which determines the melting time, $t_m$, is the temperature of sample, and the prediction of the temperature is critical in this simulation. It can be deduced that increasing the temperature of a sample by the dissipation rate coupling provides another mechanism for thermal fluctuation to affect melting aside from negative fluctuation to accelerate homogeneous melting; thermal fluctuation of the order parameter increases $\left| \frac{\partial \eta}{\partial t} \right|$ and hence produces large $\left( \frac{\partial \eta}{\partial t} \right)^2 / L$ in Eq. 2.16, which can contribute to increase temperature and corresponding driving force to melt.
Figure 6.7: Evolution of mean elastic stress distribution for 3D case of $\Delta t = 147.7$ fs.

Figure 6.8: The correlation (a) between $\bar{T}_{ms}$ and $t_m$ and (b) between $\bar{T}_{1.5\text{ps}}$ and $t_m$. 
6.6 Conclusion

In summary, a phase field approach which combines elastrodynamics, TTM with couplings among physical phenomena, and thermal fluctuation is presented to simulate melting and kinetic superheating of an aluminum nanolayer irradiated by a femtosecond laser. Random thermal fluctuation of the order parameter formulated by the fluctuation-dissipation theorem is applied to the Ginzburg-Landau equation. The maximum discretized time step, $\Delta t$, on which the magnitude of order parameter fluctuation depends is estimated to describe characteristic time of relaxation process of thermal fluctuation. The discretized dimension is chosen to be a lattice parameter. The predicted melting start time, $t_{sm}$, and the melting end time, $t_{m}$, show good agreement with experimentally observed data. The accuracy of simulations is greatly enhanced in comparison with the previously proposed phase field approach which did not have thermal fluctuation and coupling terms on TTM. It is found that $\sigma_\eta = 0.68-0.78\%$ fluctuation of the order parameter with $\Delta t = 147.7-221.5fs$ period can predict experimentally observed melting time, which was 3.5 ps, with good accuracy in a 1D approximation. A 0.78–0.9% volume fluctuation, which corresponds to 13–15% fluctuation of the order parameter, greatly accelerates melting process since the material is far above its instability temperature; A 0.78 % volume fluctuation corresponds to 0.26 % displacement fluctuation which is quite small in comparison with the 8 % displacement fluctuation of Lindemann criteria for aluminum. Increasing the magnitude of fluctuation leads to a decrease of simulated melting times. It is revealed that negative fluctuation of order parameter makes melting faster by accelerating barrierless homogeneous melting of local bulk above its instability temperature. 1845.1 K maximum superheating is simulated in tested cases. The thermoelastic coupling and dissipation coupling on TTM result in an increase of simulated temperature of a sample over the temperature estimated with conventional TTM and hence a decrease of melting time for the same magnitude of fluctuation. A slow and smooth decrease in temperature after reaching $T_{ms}$ during melting is observed, which is the result of an absence of solid-melt interface and slower heating than melting due to a longer heating period between electron gas and lattice, which is simulated as 4 ps. Melting for a 1D sample starts while a standing wave of pressure is in compressive phase,
and an 8 GPa maximum compressive pressure is predicted between 1 ps and 2 ps. Random local melting produces random local stress relaxation, which makes complex, random patterns on the stress distribution.

3D simulation shows that the entire sample collapses into melt without homogeneous nucleation since the sample is above instability temperature. Initial surface melting is taken over by bulk melting, and randomly located islands of solid resist melting until the sample completely melts. 3D simulation requires larger fluctuation than 1D to have similar $t_m$ to that of 1D due to reduced probability of negative fluctuation for the same volume. $\Delta t = 147.7\, fs$ shows good agreement with experimentally measured melting end time, and limited size effect of sample on melting time is observed. The melting period, $\Delta t_m = 1.08\, ps$, of 3D simulations becomes shorter than that of 1D with help of low pressure at the melting start time.

Strong correlation among $\bar{T}_{ms}, \bar{T}_{1.5ps}$, and melting time, $t_m$, regardless of diverse computational conditions, indicates the importance of accurate temperature prediction in simulation, and it also implies that the other route for thermal fluctuation to affect melting is by increasing temperature through the dissipation rate coupling in the lattice conduction equation, aside from negative fluctuation for homogeneous melting.
CHAPTER 7. SUPERHEATING AND MELTING WITHIN ALUMINUM CORE - OXIDE SHELL NANOPARTICLE FOR A BROAD RANGE OF HEATING RATES: MULTIPHYSICS PHASE FIELD MODELING

*Modified from the article submitted to Physical Review B on 2016*

Melting temperature of materials and melting mechanisms depend on various parameters: size, shape, condition at the surface, pressure (or, more generally, stress tensor), and heating rate, as well as on their interaction. Melting temperature depression with reduction of particle radius is well-known from experiments[31, 6], thermodynamic treatments[31, 6], molecular dynamics simulations[33, 86], and phase field studies without mechanics[87, 35] and with mechanics (but without inertia effects)[35, 36].

Reduction in surface energy during melting leads to premelting below melting temperature followed by surface melting and solid-melt interface propagation through the entire sample with increasing temperature. This was studied with phase field approach for plane surface analytically[88, 89] and numerically (including effect of mechanics) for low[35, 36] and high[4, 1] heating rates. Similar studies were performed for spherical particles without mechanics[87, 35] and with mechanics in quasi-static formulation[35, 36]. Strong effects of the width of the external surface and thermally activated nucleation were revealed within the phase field approach in Ref. 81. If the external surface of the material under study represents an interface with another solid, surface melting depends on the type of interface. The low-energy coherent interfaces increase energy during melting and, consequently, suppress surface nucleation and promote the superheating[22, 90]. On the other hand, an incoherent interface, of which energy reduces during melting, promotes the surface melting[6].
Hydrostatic pressure inside shell which can be created for materials with volume expansion during melting suppresses melting and increases equilibrium melting temperature $T_{eq}$ according to the Clausius-Clapeyron relationship. The effect of pressure appears automatically within the phase field approach if proper thermodynamic potential is implemented$[91, 35]$. Under non-hydrostatic internal stresses that relax during melting, e.g. under biaxial stresses due to constraint, melting temperature reduces. See thermodynamic$[68, 1]$ and phase field$[1]$ treatments for a layer. Melting temperature drastically decreases during very high strain-rate uniaxial compression in a strong shock wave, as it was predicted thermodynamically and confirmed by molecular dynamics simulations$[61]$. Metal can be kinetically superheated above its equilibrium melting temperature when it is subjected to an extremely fast heating rate, for example, during irradiation by an ultra-fast laser with high energy, such as picosecond (ps) and femtosecond (fs) lasers. It has been observed in experiments$[3, 5, 7]$ and phase field simulations$[4, 1]$ that an aluminum layer can be superheated up to at least 1400 K$[7]$, which is far above its equilibrium temperature, $T_{eq} = 933.67K$. The major reason for the kinetic superheating, when heterogeneous surface melting initiates the process, is the slower kinetics of a solid-melt interface propagation than the heating$[4, 50]$. For very high heating rates $Q \geq 10^{12} K/s$, elastic wave propagation can affect the temperature of the material through thermoelastic coupling and melting temperature through the effect of stresses$[76]$. Melting also influences the temperature of materials through thermo-phase transformation coupling, mostly due to latent heat.

Thus, an analysis of kinetic superheating of materials should take several physical processes and their couplings into account. Recently, there has been some research and suggested models$[41, 92, 38, 42, 40]$ to describe ultra-fast heating and melting with or without mechanics, including thermoelastic coupling or thermo-phase transformation coupling. However, those models neither describe complete set of participated physical phenomena nor include correct coupling terms rigorously derived from the thermodynamic laws. Recently, we have developed a novel phase field model, which includes all of the above physical phenomena and couplings in a single framework$[4, 1, 76]$. However, all the above modeling results have been obtained for melting of bare metallic
nanostructures. In reality, metallic (e.g., Al, Fe, Cu, and others) particles and layers have a strong passivation oxide layer at the external surface. Thus, nanoparticles form a core-shell structure. The aluminum oxide or alumina passivation layer can be formed even at room temperature\[93\] by transporting Al cations driven by the non-equilibrium electrostatic field, the so-called Cabrera-Mott mechanism\[94, 95\]. The aluminum oxide has a lower thermal expansion coefficient than the aluminum core, so the compressive pressure in the core and the tensile hoop stress in the oxide are generated due to volumetric expansion during heating before melting\[96\]. Since melting of Al is accompanied by a volumetric strain of 6%, pressure of several GPa can be obtained in the melt and hoop stress in the alumina shell is on the order of magnitude of 10 GPa. High pressure in the core results in an increase in the melting temperature according to Clausius-Clapeyron relationship. The generated pressure depends on the ultimate strength of the shell and relaxation processes in it, including phase transformations from amorphous alumina to crystalline $\gamma$ and $\delta$ phases. Thus, slow heating Al nanoparticles with an oxide layer at 20 K/min, depending on the Al core radius ($R_i$) and the oxide shell thickness ($\delta$), leads to wide spectrum of behavior from reduction of the melting temperature due to size effect to a minor superheating of up to 15 K\[97, 98, 99, 100\] due to sufficient time for stress relaxation. Stress measurement in Al nanoparticles was performed in Ref. 97, 100, 99, 101. In contrast, fast heating with the rate higher than $10^6 K/s - 10^8 K/s$ can lead to the estimated superheating by several hundred K due to the pressure increase\[102\] because there is not sufficient time for phase transformations and other stress relaxation mechanisms in the shell. For the higher heating rates of $10^{11} K/s - 10^{14} K/s$ used in experiments\[103, 104, 105\], both pressure-induced increase in melting temperature and kinetic superheating are expected.

Thus, for understanding and quantifying melting of metallic nanoparticles in a broad range of heating rates, one has to include and study the effect of oxide shell and major physical processes involved in melting, in particular, the effect of generated pressure, kinetic superheating, heterogeneity of temperature and stress fields, dynamics of elastic wave propagation, surface and interface energies and stresses, and coupling of the above processes. This is a basic outstanding multiphysic problem to be solved. Most of these processes strongly depend on the core radius $R_i$ and the oxide shell thickness $\delta$; thus, their effect should be studied in detail.
Understanding of melting of Al nanoparticles at a high heating rate is also very important for understanding and controlling mechanisms of their oxidation and combustion \[96, 102, 21\]. According to the melt-dispersion mechanism of reaction of Al particles\[96, 102, 21\], high pressure in the melt and hoop stresses in the shell, caused by volume increase during the melting, break and spall the alumina shell. Then, the pressure at the bare Al surface drops to (almost) zero, while pressure within the Al core is not initially altered. An unloading spherical wave propagating to the center of the Al core generates a tensile pressure up to 3 GPa at the center, which reaches 8 GPa in the reflected wave. The magnitude of tensile pressure significantly exceeds the cavitation strength of liquid Al and disperses the Al molten core into small bare drops. Consequently, the melt-dispersion mechanism breaks a single Al particle covered by an oxide shell into multiple smaller bare drops, which reaction is not limited by diffusion through the initial shell. This mechanism was extended for micron-scale particles\[62, 106\] and utilized for increasing reactivity of Al nano- and micron-scale particles by their prestressing\[107, 108\]. However, there has been no research for melting and kinetic superheating Al nanoparticles within an oxide shell at high heating rates to the best of our knowledge.

In this paper, we study superheating and melting of Al nanoparticles covered by an alumina shell and corresponding physical processes under high heating rates. We utilize our recent model\[4, 1, 76\] that includes the phase field model for melting developed in Ref. 36, 35, a dynamic equation of motion, a mechanical model for stress and strain simulations, and the thermal conduction model with thermo-elastic and thermo-phase transformation coupling, as well as with a dissipation rate due to melting\[4, 1\]. The effects of geometric parameters (which determine the stress-state and temperature evolution) and heating rate on characteristic melting and superheating temperatures and melting behavior, as well as on the maximum temperature corresponding to fracture of the shell, are simulated and analyzed by parametric study. Several nontrivial and unconventional phenomena are revealed. The influence of the above parameters on the initial stage of the melt-dispersion-mechanism of reaction of Al nanoparticles\[96\] is evaluated and discussed.
7.1 Governing equations

The model consists of phase field equation without thermal fluctuation, equation of motion, and heat conduction equation with couplings. Phase field equation is applied into aluminum core only since phase transformation of aluminum oxide is not taken into consideration, assuming temperature of Al NP is lower than melting temperature of aluminum oxide; melting temperature of $\alpha$-aluminum oxide is 2324 K[109].

**Aluminum core.** Total strain tensor, $\varepsilon$, free energy per unit undeformed volume, $\psi$, and the stress tensor, $\sigma$, are described by Eq. (2.1), Eq. (2.4) and Eq. (2.7) respectively.

Melting of core is described by Ginzburg-Landau equation, Eq. (2.8), with $\varsigma = 0$ and $\omega(\mathbf{x}, t) = 0$. The equation of motion is written in a traditional form of Eq. (2.15) to describe elastic waves caused by fast heating and melting. When melting occurs at a time scale much larger than that of an elastic wave, static equilibrium equation, $\nabla \cdot \sigma = 0$, is used instead.

The heating process can be described by Eq. (2.16) in which the thermal conduction is assumed to be the only mechanism for heat transfer. Time delay between electron gas and phonon[49] is ignored due to longer time scale than a few picosecond in these simulations. $J$ in Eq. (2.16) is zero since heating is described by heat flux at the boundary.

**Aluminum oxide shell.** For aluminum oxide shell, stain and stress are Eq. (2.18) and (2.19) respectively. Phase transformation of aluminum oxide is not considered. Equation of motion, Eq. (2.15), is used for dynamic case, and static equilibrium equation, $\nabla \cdot \sigma = 0$, is used when melting occurs at a time scale much larger than that for an elastic wave. Only lattice heat conduction equation with thermoelastic coupling, Eq. (2.20), is used for heat transfer.

7.1.1 Numerical model, boundary and initial conditions, and material properties

**Geometry.** 1D model in spherical coordinates is used to simulate Al superheating and melting in Al core - alumina shell structure. Fig. 7.1 shows 1D geometry, where $R_i$ is the radius of aluminum core, $\delta$ is the oxide shell thickness, and $R_s = R_i + \delta$. 
Finite element method code *COMSOL Multiphysics*[51] is used for numerical simulation.

Boundary and initial conditions.

The following boundary conditions at points C and S, as well as jump conditions at point I are applied.

At $r = 0$: \[ \frac{\partial n}{\partial r} = 0; \quad u = 0; \quad h = 0. \] (7.1)

At $r = R_i$: \[ u_1 = u_2; \quad \sigma_{r,1} - \sigma_{r,2} = -2\gamma_{cs}/R_i; \]
\[ T_1 = T_2; \quad h_1 = h_2. \] (7.2)

\[ J \frac{\partial \psi}{\partial \eta} \cdot n = \beta \nabla \eta \cdot n = \beta \frac{\partial n}{\partial r} = -\frac{\Delta \gamma_{ox}}{R_i}; \]
\[ \gamma_{cs}(\eta) = \gamma_m + (\gamma_s - \gamma_m)\phi(\eta). \] (7.3)

At $r = R_s$: \[ \sigma_{r,2} = -2\gamma_{ox}/R_s + p_y; \quad h_2 = h^*. \] (7.4)

Here $n$ is the unit normal to the interface, which coincides with the radial direction; subscript 1 is used for the Al core and subscript 2 for the alumina shell. Eq. (7.1) describes traditional conditions at the center of symmetry: zero radial displacement $u$, heat flux $h$, and gradient of $\eta$. At the internal core-shell interface, continuity of the displacement, temperature, and heat flux is imposed, as well as jump in normal stress component to the interface caused by interface stress. For both internal and external surfaces, we assume that interface stress is
Table 7.1: Properties of aluminum oxide[2]

<table>
<thead>
<tr>
<th>$\rho_{ox}$ ($K/m^3$)</th>
<th>$K_{ox}$ (GPa)</th>
<th>$\mu_{ox}$ (GPa)</th>
<th>$\alpha_{ox}$ ($K^{-1}$)</th>
<th>$\gamma_{ox}$ (J/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3000.0</td>
<td>234.8</td>
<td>149.5</td>
<td>0.778 $\times 10^{-5}$</td>
<td>1.050</td>
</tr>
</tbody>
</table>

equal to the interface energy. The boundary condition for the order parameter (7.3) is related to the change in Al-alumina interface energy $\gamma_{cs}$ during melting, when it changes from $\gamma_s$ for solid Al to $\gamma_m$ for molten Al.

For a solid phase, $\eta = 1$, the thermodynamic driving force $X = 0$ in the Ginzburg-Landau equation (2.8) and $d\gamma/d\eta = 0$ in Eq. (7.3). Thus, melting cannot start without some perturbations at the boundary. We introduce perturbation $\hat{\eta} = 10^{-6}$ and the condition that if $\eta > 1 - \hat{\eta}$ at the boundaries, then $\eta = 1 - \hat{\eta}$. This condition prevents disappearance of the initial perturbation when heating occurs below the melting temperature.

At the external surface, a jump in normal stress from the value of the gas pressure $p_g$ to the radial stress in a shell $\sigma_{r,2}$ due to surface tension is applied; we use $p_g = 0$ in simulations. External time-independent heat flux $h^*$ is prescribed and its magnitude is iteratively chosen in a way that it produces the desired heating rate at the point C.

The initial temperature is $T_0 = 293.15K$, initial stresses are zero, and initial order parameter is $\eta = 0.999$ for all cases.

**Material properties.** The same material properties for aluminum with our previous study[1] are used and summarized as follows. The specific heat, thermal conductivity of aluminum are same as section 3.3. Coefficients, constants, and other properties of aluminum used for simulation are included in Table 3.1. The specific heat of aluminum oxide is assumed to be temperature independent, $C_{ox} = 4.924 \times 10^6 J/(m^3 K)$. The thermal conductivity of aluminum oxide is $\kappa_{ox} = 7.5312 W/(mK)$ for amorphous aluminum oxide. Coefficients, constants, and other properties of aluminum oxide used for simulation are summarized in Table 7.1.

### 7.2 Some definitions

The influence of heating rate, particle radius, and oxide thickness on superheating of particle is investigated by parametric study. Six heating rates, $Q$, of $10^8, 10^9, 10^{11}, 10^{12}, 0.5 \times$
$10^{13}, 10^{13}$ K/s are selected to explore kinetic superheating. As a base case, we consider the Al core radius $R_i = 40\,nm$ and oxide thickness $\delta = 3\,nm$; the effect of oxide thickness is explored with $\delta = 0$ (bare particle), 2, and 4 nm and the effect of particle size with $R_i = 20$ and 60 nm.

Surface premelting and melting initiates barrierlessly from the Al-alumina interface I, driven by reduction in interface energy during melting, and followed by solid-melt interface propagation toward the center (Fig. 7.2). Homogeneous melt nucleation away from the solid-melt interface was not observed here even above the solid instability temperature $T_{si} = 1.2T_{eq} = 1120K$, because bulk fluctuations were not introduced and interface propagation completes melting before any homogeneous nucleation becomes visible. The same is true for a bare particle.

Figure 7.2: Propagation of solid-melt interface during melting for Al nanoparticle with $R_i = 40\,nm$ and $\delta = 3\,nm$ at $Q = 10^{11}$ K/s.

The reduced temperature, $\hat{T} = \frac{T}{T_{eq}}$, and time, $\hat{t} = \frac{t}{t_{eq}}$, are defined with normalization using bulk equilibrium temperature, $T_{eq} = 933.67\,K$, and time required to reach this temperature, $t_{eq}$. The heating rate for the core-shell structure is defined either as $Q = \frac{T_{eq} - T_0}{t_{eq}}$ at the center of particle or as $Q_i = \frac{T_{eq} - T_0}{t_{eq}^i}$, where $t_{eq}^i$ is the time to reach $T_{eq}$ at the interface I, if there is significant heterogeneity in temperature distribution. For a bare particle, the heating rate is defined as $Q = \frac{900\,K - T_0}{t_{900}}$, where $t_{900}$ is time to reach 900 K at the center, since temperature does not reach $T_{eq}$ due to Gibbs-Thomson effect. Surface melting start mark, $T_{sm}$, in all following
figures represents initiation of surface premelting when the order parameter reaches 0.5 for the first time at the interface I. The melting finish temperature, $T_{mf}$, is defined at the time when the order parameter reaches 0.5 for the first time in the center C. The bulk melting start temperature, $T_{bm}$, is defined as the temperature at which the order parameter at the interface I becomes smaller than 0.01 for the first time. In addition, two more characteristic temperatures are defined: the maximum superheating temperature, $T_{ms}$, which is the maximum temperature of center of solid core during melting, and maximum attainable temperature, $T_{ma}$, which is the maximum temperature of aluminum at the interface attained before fracture of the oxide shell. In this research, the fracture of oxide is assumed to occur once the maximum tensile hoop stress $\sigma_2$ reaches the theoretical ultimate strength of alumina, $\sigma_{th} = 11.33 \text{GPa}$[96]. Note that $T_{ma}$ is practically achievable maximum temperature of aluminum with the core-shell structure, above which it ceases to exist. Characteristic times corresponding to each characteristic temperature are designated by the same superscripts.

A summary of the main simulation results is presented in Table 7.2.

### 7.3 Superheating and melting of bare Al nanoparticle

For comparison and interpretation, phase equilibrium temperature, $T_{eq}^r$, corresponding to the interface radius $r_i$ and defined from the thermodynamic equilibrium condition for the stress-free case, $H(T_{eq}^r/T_{eq} - 1) = -2\gamma_{sm}/r_i$, is introduced. Thus, $T_{eq}^r$ reduces from $T_{eq}$ for the plane interface ($r_i \to \infty$) to zero for $r_i = 2\gamma_{sm}/H = 0.279\text{nm}$, and for smaller $r_i$ the interface cannot be equilibrium. We also introduce phase equilibrium temperature under the Laplace pressure $p$, $T_{eq}^{p} = T_{eq}^r + \Delta T_p$, where the Laplace pressure $p = 2\gamma_{m}/R_i = 0.046 \text{Gpa}$ is produced by the melt-vapor spherical particle surface with $R_i = 40\text{nm}$ and $\Delta T_p$ is the Clausius-Clapeyron increase in the equilibrium temperature due to this pressure, $\Delta T_p = 0.046 \text{Gpa} \times 60\text{K/GPa} = 2.76\text{K}$. Fig. 7.3 (a) shows the variation of these two phase equilibrium temperatures versus the radius of the propagating solid-melt interface.
Figure 7.3: (a) The variation of phase equilibrium temperature for solid-melt interface under stress-free conditions $T_{eq}^r$ and under Laplace pressure $T_{eq}^{rp}$ versus the interface radius $r_i$ and (b) evolution of temperature at the center of Al particle during heating with two heating rates $Q$ and melting in comparison with $T_{eq}^r$ and $T_{eq}^{rp}$ for 40 nm bare particle.

Fig. 7.3 (b) shows the evolution of temperature at the center of bare particle for $Q = 10^8$ and $10^9$ K/s and a comparison with equilibrium melting temperatures, $T_{eq}^r$ and $T_{eq}^{rp}$. The simulated curves for $Q = 10^8$ and $10^9$ K/s are almost overlapped, which means there is no effect of kinetic superheating except at the very end of melting (which will be discussed below). Temperature reduces in time and slightly (by 1 K) exceeds the equilibrium curve $T_{eq}^{rp}(r)$. Thus, temperature reduction is due to the thermodynamic effect of the interface radius on phase equilibrium temperature. Small deviation cannot be considered a nonequilibrium effect because it is independent of the heating rate. It can be explained by the difference in the sharp interface model for $T_{eq}^{rp}(r)$ and finite-width solid-melt interface in simulations. Note that for the plane solid-melt interface within a nanolayer, for such heating rates melting occurs at a constant temperature equal to the equilibrium temperature under corresponding stress[76].

The strong decrease of $T_{eq}^{rp}$ as $r_i$ approaches zero leads to dependence of temperature evolution on heating rate at the very end of melting (see Fig. 7.3 (b) and insert in Fig. 7.4 (a)). Since curves $\hat{T}(\hat{t})$ for $Q = 10^8$ K/s and $Q = 10^9$ K/s (i.e., for different rates of heat supply) coincide and the rate of heat absorption is determined by the interface velocity, the interface
velocity for these heating rates is determined by equality of heat supply and absorption.

Fig. 7.4 (a) shows the evolution of temperature at the center and the surface during heating and melting for 40 nm radius bare Al nanoparticle. The bulk melting temperature for $Q = 10^8$ and $10^9 \, K/s$, $T_{bm} = 930.4 K$ ($\hat{T} = 0.996$), is slightly below $T_{eq}$ due to radius-dependence of the melting temperature, i.e., Gibbs-Thomson effect. For higher heating rates, $Q \geq 10^{11} K/s$, kinetic superheating is observable, i.e., the evolution of temperature starts to deviate from that of $Q = 10^8 K/s$ and $Q = 10^9 K/s$ cases. Characteristic melting temperatures, also, deviate from equilibrium melting temperatures and increase according to increasing heating rates as shown in Table 7.2. The temperature drop at the final moment of melting disappears due to prevailing kinetic superheating over a relatively small heat sink by accelerated melting in the small volume of the final core. For $Q \geq 10^{12} K/s$, the heterogeneity of temperature becomes noticeable from the beginning of heating by inspecting the difference of temperature between center and surface (Fig. 7.4 (b)); it becomes about 37 K during heating with $Q = 10^{13} K/s$. The difference decreases at the beginning of surface melting due to heat absorption at the surface; starting with bulk melting it grows since the interface travels to the center absorbing heat while the surface is heated. After completion of melting and disappearance of the interface, the difference decreases again. Wavy temperature evolution in Fig. 7.4 is caused by thermo-elastic interaction and become significant for $Q \geq 10^{12} K/s$. 
Figure 7.4: Evolution of (a) normalized temperature, \( \frac{T}{T_{900K}} \), at the center (solid line) and the surface (dashed line) and (b) the temperature difference between the center and the surface of bare Al nanoparticle with \( R_i = 40 \text{nm} \).

### 7.4 Superheating and melting of Al core with radius of 40nm confined by alumina shell with thickness of 3nm

#### 7.4.1 Effect of confinement pressure on melting of Al nanoparticle

The melting temperature of an Al nanoparticle with oxide shell is neither \( T_{eq} \) nor constant, as shown in insert of Fig. 7.5 (a), if a shell can sustain high pressure inside a core. Growing pressure within a core due to a less thermally expanded shell and due to transformation volumetric expansion of 0.06 in the melt leads to increasing melting temperature, rationalized by Clausius-Clapeyron relationship, \( \frac{dT}{dp} = \varepsilon_0 \frac{T_{eq}}{H} = 60 K/GPa \).
Figure 7.5: Evolution of temperature and characteristic melting temperatures for an Al nanoparticle with $R_i = 40 \text{ nm}$ and $\delta = 3 \text{ nm}$. (a) Evolution of temperature at the center of the Al core for different heating rates. Insert is for $Q = 10^8 \text{ K/s}$. (b) The surface melting start temperature, $T_{sm}$, the bulk melting start temperature, $T_{bm}$, the maximum attainable temperature, $T_{ma}$, and the maximum superheating temperature, $T_{ms}$, as functions of the heating rate.

The evolution of core pressure at the interface I is shown in Fig. 7.6 (a). The compressive pressure at $\hat{t} = 1.13$ (corresponding to $T_{bm}$) for cases without kinetic superheating is 1.03 GPa, which should result in increase of the bulk melting temperature by $61.8K$ in comparison with $T_{bm} = 930.4K$ for a bare particle, i.e., in 992.2. This shows a good agreement with the simulated $T_{bm} = 986.1K$ (insert of Fig. 7.5 (a)). Note the surface melting start temperature is 915.6 K (Fig. 7.5 (a) and Table 7.2), and $\hat{T} = 0.981$, which is larger than $T_{sm}$ of bare particle because of pressure. After the start of surface and then bulk melting, the temperature increases (in contrast to that for a bare particle) since an increasing fraction of melt in a core increases pressure (Fig. 7.6 (a)). The effect of pressure will be further elaborated for other $R_i$ and $M$.

### 7.4.2 Effect of heating rate

Our previous phase field studies[4, 1] have demonstrated that ultrafast heating over $10^{11} \text{ K/s}$ of an aluminum nanolayer can kinetically superheat material above the melting temperature.
Figure 7.6: Evolution of pressure in the Al core at the interface I for an Al nanoparticle with $R_i = 40 \text{ nm}$. (a) For various heating rates and shell width $\delta = 3 \text{ nm}$. (b) Comparison for static and dynamic formulations, as well as for dynamic formulation with infinite thermal conductivity for $Q = 10^{13} \text{ K/s}$ and $\delta = 3 \text{ nm}$. (c) Effect of $M = \frac{R_i}{\delta}$ for $Q = 10^{13} \text{ K/s}$ and $Q = 10^8 \text{ K/s}$.
While two interfaces propagate from both surfaces of the layer until they meet in the central region of the layer, temperature increases due to fast heating. The aluminum core-shell structure is subjected to the kinetic superheating due to a similar mechanism, if heating rate is fast enough. Since an elastic wave traveling within $ps$ time scale can possibly affect the temperature, and hence melting, of the particle by thermoelastic coupling, dynamic equation of motion is incorporated into the model for $Q \geq 10^{12}$ $K/s$. Fig. 7.5 (a) displays the evolution of temperature at the center for various heating rates. While curves for $10^8$ $K/s$ and $10^9$ $K/s$ are overlapped (i.e., there is no kinetic superheating), the curve for $Q = 10^{11}$ $K/s$ shows a small deviation from them. This deviation becomes obvious as the heating rate increases. For $Q > 10^{12}$ $K/s$, temperature is affected by elastic waves, so that small oscillations appear on the temperature evolution curve. The magnitude and normalized period of oscillations grow as heating rate increases. While for $Q \leq 10^{12}$ $K/s$ temperatures of initiation and end of the bulk melting are clearly detectable by inspecting change of a slope in the temperature evolution curves, it is not the case for higher heating rates.

Kinetic superheating for $Q \geq 10^{11}$ $K/s$ retards the beginning of melting in terms of $\hat{t}$ and extends the normalized time period for melting, $\hat{t}_{mf} - \hat{t}_{sm}$. For lower heating rates without kinetic superheating, the interface propagation is completely governed by the equality of supplied and latent heats since the heating is slower than the propagation. Thus, heating becomes the limiting process, the time period for melting is inversely proportional to $Q$, and the normalized time period for completing melting becomes independent of $Q$. For heating rates with kinetic superheating, solid-melt interface propagation turns to be slower than heating and the interface kinetics becomes the limiting process, which leads to the increase in the normalized time period for melting (refer to Fig. 7.10 (d)).

Fig. 7.5 (b) shows the change of four characteristic temperatures versus the heating rate (the data are also summarized in Table 7.2). All four temperatures are practically independent on the heating rate for $Q \leq 10^9$ $K/s$, i.e., kinetic superheating is absent in any sense. Surface melting start temperature, $T_{sm}$, is as low as 915.6 K due to surface premelting, which is lower than the equilibrium temperature ($T_{eq}^p = T_{eq} + p\varepsilon_{0l}\frac{T_{eq}}{\rho_f}$), 995.5K, predicted by Clausius-Clapeyron relationship. The equilibrium temperature is quite close to $T_{bm}$, 986.1K, and the difference is
mostly due to the size effect. The maximum superheating temperature, $T_{ms}$, is 1011.6 K and is higher than the equilibrium temperature. The maximum attainable temperature before shell fracture, $T_{ma}$, is 1063.5 K and higher than $T_{ms}$, i.e., the oxide shell can withstand complete aluminum melting. Elevation of the characteristic temperatures for $Q = 10^{11} K/s$ above those for lower heating rates indicates kinetic superheating. This threshold heating rate for kinetic superheating is similar to that for Al nanolayer, see Ref. 1. The difference, $T_{bm} - T_{sm}$, increases for $Q = 10^{11}K/s$ and $10^{12}K/s$ but then reduces for $Q > 10^{12}K/s$. $T_{ms}$ is largely affected by the kinetic superheating and increases drastically. $T_{ms}$ is rapidly increased for $Q > 10^{11} K/s$, but it may not be realized in experiments for the given geometric parameters because oxide shell fractures for $Q > 10^{11} K/s$ before completing the melting. Including fracture in the model and studying melting during and after fracture will be pursued in the future work.

Temperature $T_{ma}$ is independent of the heating rate for $Q \leq 10^{11} K/s$ because the oxide shell can withstand pressure for complete melting and stress is the same after complete melting for any heating rate in this range (Fig. 7.10 (a)). For higher heating rates, the tensile stress in oxide, $\sigma_2$, reaches the ultimate stress during melting and $T_{ma}$ increases with increasing $Q$.

### 7.4.3 Effects of elastic wave and heterogeneous temperature distribution

For $Q \leq 10^{11} K/s$, temperature within the Al core is practically homogeneous (Fig. 7.7 a). For $Q = 10^{11} K/s$, the first temperature heterogeneity is observed in the oxide shell (because of lower heat conductivity of aluminum oxide than aluminum), but the temperature difference is only 2 K. For $Q = 10^{12} K/s$, the temperature heterogeneity in a core also becomes visible and it reaches 17.2 K in a shell. For $Q = 10^{13} K/s$, temperature difference in the core reaches 38.4 K and the total temperature difference between center C and external oxide surface S is almost 225 K.
Figure 7.7: (a) Temperature distribution along the radial direction for different heating rates at a moment slightly before the surface melting starts for an Al nanoparticle with $R_i = 40\, nm$ and $\delta = 3\, nm$. (b) The effect of $M = R_s/\delta$ on the evolution of the temperature difference $\Delta T$ across oxide shell between interface I and surface S for Al nanoparticle with $R_i = 40\, nm$ at $Q = 10^{13}\, K/s$.

An increasing heating rate and consequent strain rate enable dynamic processes and elastic waves to influence temperature. In geometries considered in this research, the order of magnitude of an acoustic time for the elastic wave to travel a particle is $10\, ps$ ($40\, nm/(4\, nm/ps) = 10\, ps$, where $R_i = 40nm$ and $4\, km/s = 4\, nm/ps$ is an estimated acoustic speed in aluminum). The thermoelastic coupling produces a visible effect on the temperature evolution with small oscillating pattern in Fig. 7.5 (a) for $Q > 10^{12}\, K/s$. This correlates with the appearance of similar trends in the pressure evolution in Fig. 7.6 (a): the initial reduction in pressure and pressure oscillations become obvious for $Q > 10^{12}\, K/s$. While pressure oscillations due to multiple wave propagations and reflections are not surprising, pressure reduction in a core is counterintuitive and intriguing, and the reasons for pressure reduction with increasing heating rates are not evident.

Elastic wave (inertia effect) and temperature gradient in a shell may be considered as the possible causes for the pressure reduction in core. In order to clarify this issue, melting of the particle with artificially large thermal conductivity in dynamic and quasi-static formulations
has been simulated for $Q = 10^{13} \text{K/s}$ and compared with the base case. Thermal conductivity of both liquid and solid Al was increased by a factor of $10^3$, and of alumina by a factor of $10^5$. The same heat flux provided for $Q = 10^{13} \text{K/s}$ for the base case was applied at the surface $S$.

Fig. 7.6 (b) shows the evolution of pressure for four cases, and it is clear that the large thermal conductivity eliminates pressure drop. For the actual thermal conductivity, both quasi-static and dynamic solutions exhibit a pressure drop by 0.085 GPa in a core, and the dynamic solution oscillates around the quasi-static one with relatively small amplitude. Therefore, the pressure drop is not a result of inertia but of relatively slow heat conduction. Slow heat conduction initially delays heating of a core in comparison with the infinite conductivity case. The delayed thermal expansion of a core retards pressure growth in the core and the difference of pressures for two cases is constant due to the same heat flux. Thus, the initial temperature drop in Fig. 7.5 (a) and the corresponding initial pressure drop in Fig. 7.6 (a) and (c) are originated from an initially colder core than for slower heating. The pressure drop due to heterogeneous temperature affects superheating temperature so that the $T_{sm} = 1116.9K$ for finite $k$ and $T_{sm} = 1127.7K$ for infinite $k$, both with dynamics; a lower core pressure results in lower superheating. Also, the heterogeneity of temperature slightly reduces heating rate for the same heat flux: $Q_i = 1.10 \times 10^{13}\text{K/s}$ for finite $k$ and $Q_i = 1.13 \times 10^{13}\text{K/s}$ for infinite $k$. Therefore, the drop in temperature $T_{sm}$ is the combined result of both physical phenomena: a 0.085 GPa pressure drop corresponds to 5.1 K according to the Clausius-Clapeyron relationship, and lowering the heating rate corresponds to the remaining 5.7 K. However, the effect is smaller than the melting temperature change due to kinetic superheating. Coincidence of pressure and temperature curves at $\hat{t} = 1.0$ in Fig. 7.5 (a) and Fig. 7.6 (a) and (c) for different $Q$ but the same particles is not surprising: by definition, $T = T_{eq}$ at $\hat{t} = 1.0$ for all cases, and the pressure is also almost the same since pressure depends on the core temperature.

### 7.5 Effect of the parameter $M = \frac{R_i}{\delta}$

Here, we keep the fixed Al core radius $R_i = 40 \text{nm}$ while varying the shell thickness $\delta = 2$, 3 and $4 \text{nm}$. As it follows from the static analytical solution for stresses in Ref. 96, reduction in $M$ (thicker shell) leads to higher pressure in the core and lower tensile hoop stress in the
shell for the same temperature, which should lead to higher melting temperatures and higher maximum attainable temperature, $T_{ma}$, before oxide fracture. Results in Fig. 7.6 (c), Fig. 7.9 (a) and (b), and Table 7.2 confirm this qualitative prediction for all melting temperatures and heating rates. For all $M$ kinetic superheating becomes observable when $Q$ reaches $10^{12}$ K/s, and all melting temperatures strongly grow for larger heating rates.

The different thicknesses of oxide produce different levels of heterogeneity of temperature across the oxide shell as shown in Fig. 7.7 (b). However, its effect on $T_{sm}$ appears quite limited for the same heating rate in Fig. 7.9 (a) since the difference of $T_{sm}$ among cases for $Q \geq 10^{12}$ remains almost same as for $Q < 10^{12}$. Note that we prescribed heating rate at the center of the core by adjusting heat flux. A particle with $M = 10$ has a higher heat flux than with $M = 20$ ($5.7 \times 10^{11}$ J/m$^2$/s versus $4.85 \times 10^{11}$ J/m$^2$/s) in order to have the same heating rate at the core. Such an adjustment of the heating rate diminishes lowering of the heating rate due to heterogeneous temperature as described in the previous section, and this is one of the reasons of the weak effect of $M$ on $T_{sm}$. Also, note that the shell of the particle with $M = 10$ has not only a larger temperature difference, but also a higher average temperature (see Fig. 7.8).

Fig. 7.6 (c) shows the pressure evolution in the Al core at the interface I for $Q = 10^8$ K/s and $Q = 10^{13}$ K/s. There is an initial deviation between the slowest and the fastest heating rate for all three $M$. This deviation obviously originates from heterogeneous temperature and it becomes significant as $M$ decreases due to greater temperature heterogeneity. It almost disappears at $\hat{t} = 1.0$ because the temperature of core is the same as $T_{eq}$ for all cases due to normalization. The volumetric transformation strain due to melting of core raises the pressure so that the slope of pressure evolution becomes steeper after surface melting start mark. The kinetic superheating delays the rise in pressure.

Temperature $T_{ms}$ (Fig. 7.9 (b)) demonstrates a similar behavior with respect to heating rate as $T_{sm}$ in Fig. 7.9 (a). The thicker shell (smaller $M$) results in higher $T_{ms}$ because of higher pressure inside core.

A thicker shell (smaller $M$) results not only in increase of $T_{ma}$ due to reduced tensile hoop stress within oxide, but also a slower increase of $T_{ma}$ due to growth in the heating rate in Fig. 7.9 (b). Stress $\frac{\sigma}{\sigma_{th}}$ in Fig. 7.10 (b) reaches the fracture stress (horizontal dashed line)
around the melting finish mark for $Q = 10^{12} \text{ K/s}$ for a nanoparticle with $M = 10$, while for a nanoparticle with $M = 13.3$ this happens around the melting finish mark for $Q = 10^{11} \text{ K/s}$ in Fig. 7.10 (a). That is why the effect of the heating rate on the fracture starts at $Q = 10^{12} \text{ K/s}$ in Fig. 7.10 (a) for $M = 13.3$ and at $Q = 0.5 \times 10^{13} \text{ K/s}$ in Fig. 7.10 (b) for $M = 10$, which is in agreement with Fig. 7.9 (b). As a result, the difference of $T_{ma}$ between cases in Fig. 7.9 (b) for $Q \leq 10^{12} \text{ K/s}$ is larger than for $Q > 10^{12} \text{ K/s}$.

![Figure 7.8: Evolution of temperature at the core-shell interface I and surface of alumina shell for two values of $M = \frac{R_i}{\delta}$ for $R_i = 40 \text{ nm}$ and $Q = 10^{13} \text{ K/s}$.

7.6 Effect of the radius of an aluminum core

Particles with three Al core radii, $R_i = 20 \text{ nm}$, $40 \text{ nm}$, and $60 \text{ nm}$ with $M = 13.3$ (i.e., with the thickness of the oxide shell $\delta = 1.5 \text{ nm}$, $3 \text{ nm}$, and $4.5 \text{ nm}$, respectively) are studied. Fig. 7.9 (c) demonstrates the effect of Al core radius $R_i$ on the heating-rate dependence of the surface melting temperature, $T_{sm}$. For relatively small heating rate $Q \leq 10^{11} \text{ K/s}$, $T_{sm}$ for $R_i = 20 \text{ nm}$ is $2.4 \text{ K}$ and $3.2 \text{ K}$ lower than for $R_i = 40 \text{ nm}$ and $60 \text{ nm}$ respectively. This is typical size-dependence of the melting temperature, which is observed without oxide shell[35, 36]. Kinetic superheating does not change the size-dependence, thus the smaller particle has smaller $T_{sm}$. Larger $R_i$ results in a larger temperature difference along the radius and a larger heating rate for
Figure 7.9: Effect of geometric parameters of a nanoparticle on characteristic melting temperatures versus heating rate. (a) Effect of $M = \frac{R_i}{\delta}$ on surface melting start temperature, $T_{sm}$, (b) maximum attainable temperature, $T_{ma}$, and maximum superheating temperature, $T_{ms}$, for $R_i = 40$ nm. (c) Effect of radius of core on surface melting start temperature, $T_{sm}$, (d) maximum attainable temperature, $T_{ma}$, and maximum superheating temperature, $T_{ms}$, for $M = 13.3$. 

(a) $M=10.0$, $R_i=40$ nm  
(b) $T_{ma}$, $M=10.0$  
(c) $R_i=60$ nm, $M=13.3$  
(d) $T_{ma}$, $R_i=60$ nm
the interface $Q_i$ for the same $Q$ at the center: for $Q = 10^{13} K/s$, we obtained $Q_i = 1.19 \times 10^{13} K/s$ for $R_i = 60 nm$ and $Q_i = 1.01 \times 10^{13} K/s$ for $R_i = 20 nm$. Thus, the difference in $T_{sm}$ with increasing $R_i$ for $Q = 10^{13} K/s$ increases mostly due to increased $Q_i$.

A larger particle shows larger maximum superheating temperature, $T_{ms}$, and kinetic superheating is observed at smaller $Q$ (Fig. 7.9 (d)). Thus, $T_{ms}$ for $R_i = 40$ and 60nm starts to increase below $Q = 10^{11} K/s$, while for $R_i = 20 nm$ it remains almost same until $Q = 10^{12} K/s$. This size effect on kinetic superheating is governed by heterogeneous melting: a larger dimension provides more time for interface propagation and energy for superheating during melting. Unlike the minor effect of $M$ on kinetic superheating in Fig. 7.9 (b), $R_i$ has a significant influence on $T_{ms}$. The increase in melting time shown in Fig. 7.10 (d) also has a significant effect on $T_{ma}$, which will be explored in the following section.

### 7.7 Tensile hoop stress in and fracture of the oxide shell

The maximum hoop stress in the shell is located at the interface I so that the $\sigma_2$ at the interface and $\sigma_{th}$ determine $T_{ma}$. Elastic waves produce some contributions to change of the maximum tensile hoop stress in an oxide shell for high heating rate (Fig. 7.10 (a)–(c)). However, the major contribution to the maximum tensile hoop stress in an oxide shell for high $Q$ comes from the kinetic superheating and increase in melting time due to superheating, as it will be shown below.

The heating-rate dependence of $T_{ma}$ and maximum superheating temperature at the center of particle before melting, $T_{ms}$, for three values of $M$ are shown in Fig. 7.9 (b). For $M = 20$, temperatures $T_{ma}$ and $T_{ms}$ almost coincide for $Q \leq 10^9 K/s$, which means that the hoop stress in the shell reaches its ultimate strength almost at the end of complete melting of a core. Temperature $T_{ma}$ is higher than $T_{ms}$ for $Q \leq 10^{11} K/s$ of $M = 13.3$ and $Q \leq 10^{11} K/s$ for $M = 10$, i.e., fracture occurs after complete melting of core. For all other cases, $T_{ma} < T_{ms}$ and fracture of the shell occurs before complete melting of the core, followed by propagation of the pressure reduction wave, which can result in high tensile pressure[96]. This process strongly depends on the fracture time and will be studied elsewhere. Also, since it is highly probable that the ultimate strength of the few nm thick alumina shell has significant scatter, the part
Figure 7.10: Evolution of normalized maximum tensile hoop stress in the oxide shell at the interface I versus the temperature at the interface I, $T_i$, for different heating rates and core radii: (a) for $R_i = 40 \text{ nm}$, $\delta = 3 \text{ nm}$, and $M = 13.3$, (b) for $R_i = 40 \text{ nm}$, $\delta = 4 \text{ nm}$, and $M = 10$, and (c) for three $R_i$ with $M = 13.3$. (d) Normalized time for complete melting, $t_{mf} - t_{sm}$, versus heating rate for different core radii and $M = 13.3$. 
of curves for $T_{ms}$ that are above the curves for $T_{ma}$ still may have physical sense for higher ultimate strength. If a shell is strong enough to contain complete melt for all heating rates or weak enough to break down before melting starts, $T_{ma}$ will be independent of the heating rate.

For all heating rates, $T_{ma}$ and $T_{ms}$ increase with decreasing $M$ because of increasing pressure in the core and reducing tensile stresses due to thicker shell. For $Q < 10^{11} K/s$, the heating-rate dependence of both characteristic temperatures is weak. $T_{ms}$ increases with increasing heating rate for $Q \geq 10^{11} K/s$ and $T_{ma}$ increases with increasing heating rate for $Q \geq 10^{12} K/s$ for all $M$.

The wavy oscillation of $\sigma_2$, which originates from elastic waves traveling in the core, appears for $Q > 10^{12} K/s$. Note that the dynamic equation is used from $Q = 10^{12} K/s$ and no oscillation is observed for this heating rate. The wave characteristics depend on the particle radius: oscillations of $R = 20 nm$ for $Q = 10^{13} K/s$ in Fig. 7.10 (c) have the shortest period in terms of $T$ and it increases as R increases. However, the magnitude of the wave is small for all tested cases, hence the effect of elastic waves on $T_{ma}$ is quite limited.

While the maximum superheating temperature is larger for larger particles and increases with increase in heating rate (Fig. 7.9 (d)), the maximum attainable temperature, $T_{ma}$, for $Q \leq 10^{11} K/s$ has an opposite trend, i.e., it increases with the reduction in the core radius (Fig. 7.9 (d)). This happens due to surface tension at the surface S and interface I, which produce compressive hoop stress in oxide shell which increases with reduction in $R_i$. For example, the hoop stress at the interface I for $R_i = 20 nm$ at $T_0$ is $-0.38 GPa$ in comparison with $-0.13 GPa$ for $R_i = 60 nm$, which delays the fracture of oxide shell. This is to some extent similar to pre-stressing of the Al core-shell structures by relaxing internal stresses by annealing at a higher temperature and quenching to ambient temperature in order to suppress fracture and enhance the melt-dispersion mechanism[107, 110]. The trend of $T_{ma}$ in the size effect, however, has a crossover for higher heating rates at $10^{11} K/s \leq Q \leq 10^{12} K/s$ in Fig. 7.9 (d). The reason for the crossover can be deduced from the evolution of the maximum hoop stress in the shell during heating in Fig. 7.10 (c) just by analyzing the position of the intersection point of the stress $\sigma_2/\sigma_{th}$ with horizontal line $\sigma_2/\sigma_{th} = 1.0$. For $Q = 10^9 K/s$, melting completes before fracture for all $R_i$, and temperature at the intersection (which is $T_{ma}$) is higher for smaller $R_i$ (as we
discussed, due to interface stresses). For $Q = 10^{12} K/s$, melting almost completes at fracture points for $R_i = 20nm$ and does not complete for $R_i = 40nm$ and $R_i = 60nm$; temperature at the intersection point is lower as the radius is smaller, which results in crossover. For $Q > 10^{12} K/s$, fracture occurs during melting, and again, temperature at the intersection point reduces with reducing radius $R_i$. The increase in normalized melting time in Fig. 7.10 (d) has an important role in the increase of $T_{ma}$ since volumetric transformation strain for the same temperature becomes smaller and so does hoop stress in a shell. That is why the slope of the curves in Fig. 7.10 (c) increases with reduction in core radius $R_i$.

7.8 Relationship to the melt-dispersion mechanism of reaction of aluminum nanoparticles

Understanding of melting of Al nanoparticles at high heating rates is very important for understanding and controlling mechanisms of their combustion[102, 21]. According to the melt-dispersion mechanism of reaction of aluminum nanoparticles described in Ref. 96, 102, 21 and Introduction, high pressure in the melt and hoop stress in the shell, caused by volume increase during the thermal expansion and melting, break and spall the protective alumina shell, which traditionally suppresses the Al reaction with an oxidizer. Following dispersion of the molten core further promotes contact of Al with the oxidizer and drastically increases the reaction rate and flame speed. The main desirable condition in optimizing this mechanism is that fracture of the shell occurs after complete melting of the Al core because only molten Al disperses and participates in the fast reaction. Thus, it is desired that $T_{ma} \geq T_{ms}$ (or $t_{ma} \geq t_{ms}$) and that $T_{ma}$ (or $t_{ma}$) should not be sensitive to some scatter in geometric parameters of the core shell system and strength of the shell. In Ref. 96, fracture of the shell occurred after complete melting for $M \leq 19$ and this result weakly depends on $\delta$ and $R$ separately since a simplified method of analysis for fracture of the shell in the previous research was independent of the heating rate. Based on our much more precise results in Fig. 7.9 (b) and Table 7.2, we can conclude the following.

Temperatures $T_{ma}$ and $T_{ms}$ (or times $t_{ma}$ and $t_{ms}$) are independent of $Q$ for $Q = 10^8 K/s$
and \( Q = 10^9 \text{K/s} \), and, consequently, at least for \( Q \leq 10^9 \text{K/s} \). This is important for the analysis of the melt-dispersion mechanism, because the estimated heating rate at the reaction front was \( 10^8 \text{K/s} \) in Ref. [96]. For \( Q \leq 10^9 \text{K/s} \) and \( M = 20 \), the condition for complete melting before oxide fracture is almost met, i.e. \( T_{ma} \sim T_{ms} \), which is consistent with Ref. 96, 63. However, for \( M = 20 \) and \( Q \geq 10^{11} \text{K/s} \), fracture occurs well before completing melting. Since all other cases in Table 7.2 have smaller \( M \) than 19, melting completes before fracture for \( Q \leq 10^{11} \text{K/s} \), excluding particles with \( R_i = 60\text{nm} \) and \( M = 13.3 \) for \( Q = 10^{11} \text{K/s} \). Note that \( Q = 10^{11} \text{K/s} \) is estimated heating rate in experiments in Ref. 104, 105. For \( Q \geq 10^{12} \text{K/s} \) (which is typical for experiments in Ref. 103), fracture occurs before completion of melting for all cases, which is far from optimal for melt dispersion. Consequently, there is an upper bound of \( Q \leq (10^{11} - 10^{12}) \text{K/s} \) for optimal melt dispersion, in contrast to the previous wisdom that the larger \( Q \) is the better.

Thus, while predictions for \( Q \leq 10^9 \text{K/s} \) from the simplified theory in Ref. 96 are confirmed by the current and more precise simulations, results for \( Q \geq 10^{11} \text{K/s} \) differ quantitatively and qualitatively.

Also, Table 7.2 contains data on the maximum rate of the hoop strain in the shell at the interface I, \( \dot{\varepsilon}_{oxm,2} \). For \( Q = 10^8 \text{K/s} \), it is in the range of \( 4 - 5 \times 10^3 \text{s}^{-1} \), which may be high enough for avoiding relaxation processes. It was roughly estimated in Ref. 96 as \( 3.3 \times 10^4 \). The almost order of magnitude reduction in \( \dot{\varepsilon}_{oxm,2} \) here is attributed to the more precise approach and insignificant growth of temperature during melting with resultant reduction of effective \( Q \). Generally, \( \dot{\varepsilon}_{oxm,2} \) is scaled proportionally to \( Q \). Thus, for \( Q = 10^7 \text{K/s} \) and even for \( Q = 10^6 \text{K/s} \), for which melt-dispersion is still expected in Ref. 96, 21, \( \dot{\varepsilon}_{oxm,2} \) is \( 4 - 5 \times 10^2 \text{s}^{-1} \) and \( 40 - 50 \text{s}^{-1} \), respectively.

### 7.9 Temperature drop at the completion of melting

An abrupt decrease in temperature by several degrees is observed at the end of melting for \( Q = 10^8 \text{K/s} \) and \( Q = 10^9 \text{K/s} \), with and without oxide shell, and for all geometric parameters, as it follows from Table 7.2. The maximum temperature drop of \( T_{mf} - T_{ms} = 14.6 \text{K} \) is for \( Q = 10^9 \text{K/s} \), \( R_i = 20\text{nm} \), and \( \delta = 1.5\text{nm} \). This temperature drop comes from acceleration
of melting when the interface reaches the center of a particle, $T_{eq}^r$ drastically reduces, and interfaces become incomplete (i.e., maximum $\eta$ reduces to smaller than 1). Fig. 7.11 (a) shows a large negative magnitude of the local $\frac{\partial \phi}{\partial t}$ near the particle center. Volume integration of the local $\frac{\partial \phi}{\partial t}$ presented in Fig. 7.11 (b) takes into account that melting occurs within a smaller volume when the interface propagates toward the center. They show how the melting at the center of a sample is drastically accelerated, which eventually results in the temperature drop of the particle through Eq. (2.16). For higher heating rates, the temperature drop is absent and $T_{ms} = T_{mf}$ (Table 7.2). A similar but much larger temperature drop was observed at completion of melting of a plane nanolayer, when two solid-melt interfaces collided, for all heating rates (from $1.5 \times 10^{10} \text{K/s}$ to $8.4 \times 10^{13} \text{K/s}$) studied in Ref. 76 since the volume of colliding region for a plane structure is much larger than that for a spherical structure.

Figure 7.11: Evolution of (a) $\frac{\partial \phi}{\partial t}$ distribution and (b) volume integral of $\frac{\partial \phi}{\partial t}$ for Al nanoparticle with $R_i = 40 \text{nm}$ and $\delta = 3 \text{nm}$ for $Q = 10^9 \text{K/s}$.

### 7.10 Physical phenomena involved in melting and superheating of Al nanoparticles

In this section, we summarize the effect of different parameters on characteristic melting temperatures (Fig. 7.12) and maximum attainable temperature, $T_{ma}$, which is determined by fracture of the oxide shell (Fig. 7.13). The maps are presented for two ranges of the heating...
rates: (a) for $Q \leq 10^{9} \text{K/s}$, when the effect of $Q$ is absent and melting is quasi-equilibrium, and (b) for $Q \geq 10^{12} \text{K/s}$, when effects of the heating rates are pronounced. For the intermediate heating rate, $Q = 10^{11} \text{K/s}$, the effect of $Q$ appears but is weak.

In all maps:

(a) Reduction of the radius of a core $R_i$ and solid-melt interface radius $r_i$ leads to reduction in melting temperatures according to the Gibbs-Thomson effect. The reduction of the radius of a core $R_i$ in turn causes reduction of $T_{ma}$ due to shifting volumetric expansion and corresponding stress increase in a shell to lower temperature if $\sigma_2$ reaches $\sigma_{th}$ during melting.

(b) For small particles ($R_i = 20nm$), surface tension at core-shell interface and external shell surface produce pressure in a core, which increases all melting temperatures and, consequently, $T_{ma}$, if $\sigma_2$ reaches $\sigma_{th}$ during melting.

(c) A decrease in $M$ (an increase of thickness of oxide) causes pressure growth in a core and increase of all melting temperatures and, consequently, $T_{ma}$, if $\sigma_2$ reaches $\sigma_{th}$ during melting.

For low heating rates of $Q \leq 10^{9} \text{K/s}$, in addition to the above effects:

(a) Surface tensions at core-shell interface and external shell, and decrease in $M$ also decrease tensile stresses in a shell and, consequently, increase $T_{ma}$. The same is true for high heating rates.

(b) There is a small reduction in temperature and, consequently, melt finish temperature $T_{mf}$ at the end of melting at the core center. This reduction does not practically affect $T_{ma}$; it is not visible for high heating rates because of kinetic superheating.

For high heating rates, in addition to the above effects:

(a) Kinetic superheating leads to an increase of all melting temperatures and $T_{ma}$ if the oxide shell fractures during melting. Heterogeneity in temperature in a shell reduces pressure and heating rate in a core but this effect is small in comparison with kinetic superheating.

(b) An increase in core radius significantly increases kinetic superheating and normalized time for complete melting, and hence it raises $T_{ms}$ and $T_{ma}$ if the oxide shell fractures during melting.

For bare particles, the effects of $M$, $\delta$, and surface tension at $S$, as well as temperature $T_{ma}$ are irrelevant. Elastic waves have a much smaller magnitude than for particles with the
shell and practically do not affect melting temperatures. The main effects are a reduction in melting temperatures due to reduction in $R_i$ (Gibbs-Thomson effect), kinetic superheating for high $Q$, and a small increase in melting temperatures for small particles due to pressure caused by surface tension at $R_i$.

![Map of competing physical phenomena affecting melting temperatures for $Q \leq 10^9$](a)

![Map of competing physical phenomena affecting melting temperatures for $Q \geq 10^{12}$](b)

Figure 7.12: The map of physical phenomena affecting melting temperatures (a) for $Q \leq 10^9 \, K/s$ and (b) for $Q \geq 10^{12} \, K/s$.

7.11 Conclusion

In the paper, we utilize our model[4, 1, 76] that includes the phase field model for surface and bulk melting, dynamic equation of motion, mechanical model for stress and strain simulations, interfacial and surface stresses, and the thermal conduction model with thermo-elastic, thermo-
Figure 7.13: The map of physical phenomena affecting maximum attainable temperature, $T_{ma}$, (a) for $Q \leq 10^9$ K/s and (b) for $Q \geq 10^{12}$ K/s.
Table 7.2: Summary of simulation conditions and results of melting of Al nanoparticle for wide range of heating rates

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*a $t_{eq}$ for bare particle is defined as the time for $T = 900 K$.\[1cm\]
phase transformation coupling and transformation dissipation rate, to study the effects of geometric parameters and heating rate on characteristic melting and superheating temperatures and melting behavior. Several unconventional phenomena are revealed. The main results are enumerated below.

1. In contrast to the plane interface, spherical interface exhibits strong decrease of equilibrium temperature at the interface, $T_{eq}$, as $r_i$ approaches zero. This leads to temperature drop for $Q = 10^8 \text{ K/s}$ and $Q = 10^9 \text{ K/s}$, which is slightly different for $Q = 10^8 \text{ K/s}$ and $Q = 10^9 \text{ K/s}$ at the end of the melting. Excluding the end of melting, curves $\hat{T}(\hat{t})$ for $Q = 10^8 \text{ K/s}$ and $Q = 10^9 \text{ K/s}$ coincide.

2. Increasing pressure within a Al core due to a less thermally expanded oxide shell and, after initiation of melting, due to transformation volumetric expansion of 0.06 leads to growing melting temperatures, rationalized by the Clausius-Clapeyron relationship, $\frac{dT}{dp} = \varepsilon_0 \frac{T_{eq}}{H} = 60 \text{K/GPa}$. Increasing the fraction of melt during heating increases pressure and, consequently, the melting temperature of the particle even without kinetic superheating. This is confirmed by coincidence of the $\hat{T}(\hat{t})$ curves for $Q = 10^8 \text{ K/s}$ and $Q = 10^9 \text{ K/s}$. In contrast, for a bare particle, temperature slightly decreases for $Q = 10^8 \text{ K/s}$ and $Q = 10^9 \text{ K/s}$ due to reduction in $r_i$. For small particles, there is a small temperature increase due to pressure caused by surface tension at the core external surface.

3. Heating rates $Q \geq 10^{11} \text{ K/s}$ trigger kinetic superheating (i.e., increase in melting temperatures $T_{sm}$, $T_{bm}$, $T_{mf}$, and $T_{ms}$ with increasing $Q$), and the effect becomes obvious for $Q \geq 10^{12} \text{ K/s}$.

4. The heating rates $Q \geq 10^{12} \text{ K/s}$ produce heterogeneity in temperature distribution; thus, for $Q = 10^{13} \text{ K/s}$, the temperature difference is 38.4 K across the 40 nm core and 225 K across 3 nm oxide layer. The heterogeneity in temperature creates colder core and corresponding pressure drop in a core, which leads to lowering superheating temperatures. It can change of heating rate across core radius so that $Q_i > Q$. However, the effect of heterogeneity is minor relatively to kinetic superheating.

5. The heating rates $Q \geq 10^{12} \text{ K/s}$ also result in wave propagation within the core, which causes oscillation in pressure and temperature (due to thermoelastic coupling), but the effect
of the wave on melting temperatures and $T_{ma}$ is relatively small for tested heating rates.

6. A reduction in $M = R_i/\delta$ increases the pressure growth in the core and leads to the increase of melting temperatures for all tested $Q$.

7. For $Q \leq 10^{11} \, K/s$, the oxide shell fractures after complete melting and the heating-rate dependence of $T_{ma}$ is very weak. Temperature $T_{ma}$ increases with reduction of $M$ which decreases tensile hoop stress in the shell. $T_{ma}$ increases with the reduction in the core radius due to surface tension at the surface $S$ and interface $I$ which produce compressive hoop stress in oxide shell. If oxide fractures before completing melting (for $Q > 10^{11} - 10^{12} \, K/s$), the maximum attainable temperature, $T_{ma}$, depends on the heating rate. It increases with an increase in the heating rate if melting temperatures increase, which delays the stress growth due to transformation expansion. A thicker shell increases the $Q$ for which heat-rate dependence of $T_{ma}$ starts, and a larger $R_i$ strengthens this dependence due to augmented kinetic superheating and increased melting time.

8. A parametric study of high-heating rate melting allows us to shed light on the melt-dispersion mechanism of combustion of an Al nanoparticle[96]. It is desired for the promotion of Al reactivity that oxide breaks after complete melting of the particle, i.e., $T_{ma} \geq T_{ms}$. $T_{ma}$ and $T_{ms}$ are independent of $Q$ for $Q \leq 10^9 \, K/s$, and for $M = 20$, the condition for complete melting before oxide fracture is met or almost met. However, for $M = 20$ and $Q \geq 10^{11} \, K/s$, fracture occurs well before completing melting. For $M \leq 13.3$, melting completes before fracture for $Q \leq 10^{11} \, K/s$, excluding particles with $R_i = 60 \, nm$ and $M = 13.3$ for $Q = 10^{11} \, K/s$. For $Q \geq 10^{12} \, K/s$, fracture occurs before completing melting for all cases under study. An interaction with an elastic wave shows the oscillating evolution of $\sigma_2$ but its effect on $T_{ma}$ is minor for all tested $Q$. Consequently, there is an upper bound of $Q \leq 10^{11} - 10^{12} \, K/s$ for optimal melt dispersion, in contrast to previous wisdom that the larger $Q$ is better. While for $Q \leq 10^9 \, K/s$ predictions of the simplified theory in Ref. 96 are confirmed by the current more precise simulations, for $Q \geq 10^{11} \, K/s$ results are quantitatively and qualitatively different. The maximum rate of the hoop strain in the shell, which characterizes the possibility to avoid stress relaxation before fracture, is determined.

9. Various physical phenomena that promote or suppress melting and affect melting tem-
peratures and $T_{ma}$ for different heating rate ranges are summarized in the schemes in Fig. 7.12 and 7.13.

The developed multiphysics phase field model is applicable for other core and shell materials. As the next step, we plan to include the phase field simulation of the fracture of shell and its effect on melting. A sharp drop in pressure causes large tensile pressure in the reflected wave and corresponding large drop of melting temperature, which can lead to additional significant overheating and "homogeneous" melting in the entire particle due to thermal fluctuations. It also can lead to cavitation which has been studied in Ref. 111. A coherent core-shell interface, which excludes surface melting, will be treated as well. Due to broad distributions of core and shell sizes and shell strengths in a manufactured powder sample, it will be desirable to find connection of these distributions in a representative number of particles with a distribution of melting temperatures.
CHAPTER 8. CONCLUSION

The multiphysics phase field model which includes elastodynamics, fast heating of metal considering delayed heat transfer between electron gas and lattice phonon and couplings among physics, and phase transformation with thermal fluctuation. Ginzburg-Landau phase transformation equation is augmented by Newton equation to describe elastic wave and two temperature model which can explain picosecond time delay of heat transfer between electron gas and lattice phonon in metal. Lattice heat transfer equation is reinforced with coupling terms which can incorporate thermo-elastic coupling, coupling between temperature and phase transformation, and coupling with dissipation of phase transformation. Random fluctuation as white noise is added to conventional Ginzburg-Landau equation so as to explain thermal fluctuation of the order parameter. The magnitude of fluctuation is formulated by fluctuation-dissipation theorem which is based on a random force of Langevin equation. Discretized time step is selected to resolve relaxation process of fluctuation, which provides a physical guideline to select the magnitude of order parameter which depends on discretization. The continuum based model is applied to simulate nanoscale melting and kinetic superheating of aluminum nanostructures; i.e. melting and kinetic superheating of aluminum nanolayer in high heating rate created by irradiation of picosecond laser and femtosecond laser, and melting and kinetic superheating of aluminum nanoparticle which has an oxide shell. Several new physics in spatially nanoscale and temporally pico- and femtoscale revealed by simulation are summarized;

Phase field simulation of kinetic superheating and melting of aluminum nanolayer irradiated by pico- and femtosecond laser

1. Melting and kinetic superheating of free standing aluminum nanolayer irradiated by pico- and femtosecond laser is simulated with the phase field approach which includes Ginzburg-Landau equation without thermal fluctuation, conventional two temperature model without
couplings, and elastostatics.

2. A fair correspondence between the simulated and experimental melting time is obtained for laser heating of the Al nanolayer for the heating rates from 1 to 1290 K/ps. This does not require modification of the PFA in comparison with the slow-heating regimes. We reproduce and quantify the two main mechanisms found in MD simulation[50], namely (a) heterogeneous melting initiated from surface melting at both surfaces and propagation of two interfaces until they meet, and (b) homogeneous melting without interfaces above $T_i$.

3. These mechanisms substitutes the traditional homogeneous nucleation mechanism, which is not applicable here because $T > T_i$. The same approach can be applied, e.g., for laser ignition of nano- and micron scale Al particle[62, 63] and nano structuring of thin metal film[64, 65].

*Internal stress-induced melting below melting temperature at high-rate laser heating*

1. Under a plane stress condition, internal stresses due to thermal strain under constrained uniaxial strain, which relax during melting, produces an additional thermodynamic driving force for melting. As a result, it is possible that the Al nanolayer melts at 36 K below $T_{eq}$ for the heating rate $Q \leq 1.51 \times 10^{10}$ K/s. The reduced melting temperature, $T_{eq}$, is predicted analytically and confirmed with phase field simulations which has elastodynamics, phase field model without thermal fluctuation, and TTM with couplings; under a plane strain condition, it is 13 K below $T_{eq}$. Nanolayer is favorable to observe the phenomena since it is less probable to relax the stress by defects.

2. At higher heating rates than $1.51 \times 10^{10}$ K/s, this driving force still persists but kinetic superheating takes over, leading to a significant increase in melting temperature with respect to $T_{eq}$.

3. The experiment for confirming $T_{eq}$ is suggested that one open end of thin Al film of 25 nm thickness is subjected to laser which has 100 J/m² absorbed fluence and 100 ns to generate $Q = 1.51 \times 10^{10}$ K/s; film can be deposited on a rigid, low-conductive substrate to prevent deformation before melting.

*Coupled phase field, heat conduction, and elastodynamic simulations of kinetic superheating and nanoscale melting of aluminum nanolayer irradiated by picosecond laser*
1. Simulated melting time of 25 nm thick and free standing aluminum nanolayer irradiated by picosecond laser shows good agreement with experimental data in 4.0% average relative error up to 60 ps melting time, which is higher accuracy than simulation result without couplings on lattice heat transfer equation. For faster heating, imitated thermal fluctuation which can initiate barrierless homogeneous melting enables to replicate melting time with 8% relative error for 20 ps observed melting time.

2. Barrierless nucleation of surface premelting and melting occurs followed by the propagation of two solid-melt interfaces toward each other and their collision. For slow heating rate $Q = 0.015 K/ps$ melting occurs at the equilibrium melting temperature under uniaxial strain conditions $T_{eq}^* = 898.1 K$ (i.e., below $T_{eq} = 933.67 K$) and corresponding biaxial stress, which relaxes during melting. For high heating rate $Q = 0.99 - 84 K/ps$, significant kinetic superheating over 1400K is observed before complete melting.

3. An increase in the heating rate leads to a reduction of temperature at the 3 nm thick solid-melt interfaces due to fast local heat absorption of fusion. A significant, rapid temperature drop over several hundred Kelvin (even below melting temperature) at the very end of melting is revealed, which is caused by the collision of two interfaces and accelerated melting.

4. An analytical approximation of surface melting $T_{ms}$ and solid maximum superheating $T_{sm}$ temperatures as the third degree polynomial of $\log Q$ describes the results of simulations well.

5. For $Q = 25 - 84 K/ps$, standing elastic stress waves are observed in the solid with nodal points at the moving solid-melt interfaces, which however, do not have a profound effect on melting time and temperatures.

Phase field simulation with thermal fluctuation of kinetic superheating and melting of aluminum nanolayer irradiated by femtosecond laser

1. Phase field approach which combines elasto-dynamics, two temperature model with couplings among physics, and thermal fluctuation is presented to simulate melting and kinetic superheating of aluminum nanolayer irradiated by femtosecond laser. Random thermal fluctuation of the order parameter of which magnitude is formulated by fluctuation-dissipation
Theorem is applied into the Ginzburg Landau equation.

2. Discretized time step, $\Delta t$, which a magnitude of order parameter depends on is calculated as it can describe characteristic time of relaxation process of thermal fluctuation. The predicted starting time, $t_{sm}$, and ending time, $t_m$, of melting show good agreement with experimentally observed data. The accuracy of simulation is greatly enhanced in comparison with the previously proposed phase field approach which did not have thermal fluctuation and couplings on two temperature model.

3. It is found that $\sigma_\eta = 0.68\text{–}0.78\%$ fluctuation of the order parameter with $\Delta t = 147.7\text{–}221.5fs$ period can predict experimentally observed melting time, which was 3.5 ps, with good accuracy in 1D approximation. 0.78–0.9% volume fluctuation which corresponds 13–15% fluctuation of the order parameter greatly accelerates melting process since the material is far above its instability temperature; 0.78 % volume fluctuation corresponds to 0.26% displacement fluctuation which is quite small in comparison with 8 % displacement fluctuation of Lindemann criteria for aluminum. Increasing of fluctuation and decreasing of $\Delta t$ lead decreasing of simulated melting times.

4. It is revealed that negative fluctuation of order parameter makes melting faster by accelerating barrierless homogeneous melting of local bulk which is at the above its instability temperature. 1845.1 $K$ maximum superheating is simulated. Slow and smooth decrease of temperature after reaching maximum superheating temperature, $T_{ms}$, is observed, which is the result of absence of solid-melt interfaces and slower heating than melting due to time delay of heat transfer between electron gas and lattice which is simulated as 4 ps.

5. Melting starts while standing wave of pressure is in compression, and 8 GPa maximum compressive pressure is predicted between 1 ps and 2 ps. Random local melting produces random local stress relaxation which makes complex random pattern on stress distribution. Fast evolution of compressive mean elastic stress produces additional heat source by thermo-elastic coupling and hence faster heating rate is predicted than the result with two temperature model without couplings and elastostatic equation.

6. 3D simulation shows that entire sample collapses into melt without nucleation since the sample is above instability temperature. Initial surface melting is taken over by homogeneous
melting and randomly located islands of solid resist melting and disappear eventually. 3D simulation shows longer melting time than 1D simulation does even for the stronger fluctuation since it has smaller probability to have negative fluctuation in the same volume than 1D. \( \Delta t = 147.7 \text{ fs} \) shows good agreement with experimentally measured melting end time. And limited size effect of sample on melting time is observed.

7. Strong correlation among \( T_{ms}, T_{1.5ps} \) and melting time, \( t_m \), regardless of diverse computational conditions indicates importance of accurate temperature prediction in simulation, and also it implies the other route for thermal fluctuation to affect melting by increasing temperature through the dissipation rate coupling to the lattice conduction equation aside from negative fluctuation for homogeneous melting.

Superheating and melting within aluminum core - oxide shell nanoparticle for a broad range of heating rates: Multiphysics phase field modeling

1. In contrast to the plane interface, spherical interface exhibits strong decrease of equilibrium temperature at the interface, \( T_{eq} \), as \( r_i \) approaches zero. This leads to temperature drop for \( Q = 10^8 \text{ K/s} \) and \( Q = 10^9 \text{ K/s} \), which is slightly different for \( Q = 10^8 \text{ K/s} \) and \( Q = 10^9 \text{ K/s} \) at the end of the melting. Excluding the end of melting, curves \( \hat{T}(\hat{t}) \) for \( Q = 10^8 \text{ K/s} \) and \( Q = 10^9 \text{ K/s} \) coincide.

2. Increasing pressure within a Al core due to a less thermally expanded oxide shell and, after initiation of melting, due to transformation volumetric expansion of 0.06 leads to growing melting temperatures, rationalized by the Clausius-Clapeyron relationship, \( \frac{dT}{dp} = \varepsilon_0 T_{eq} ^{\frac{1}{2}} = 60K/GPa \). Increasing the fraction of melt during heating increases pressure and, consequently, the melting temperature of the particle even without kinetic superheating. This is confirmed by coincidence of the \( \hat{T}(\hat{t}) \) curves for \( Q = 10^8 \text{ K/s} \) and \( Q = 10^9 \text{ K/s} \). In contrast, for a bare particle, temperature slightly decreases for \( Q = 10^8 \text{ K/s} \) and \( Q = 10^9 \text{ K/s} \) due to reduction in \( r_i \). For small particles, there is a small temperature increase due to pressure caused by surface tension at the core external surface.

3. Heating rates \( Q \geq 10^{11} \text{ K/s} \) trigger kinetic superheating (i.e., increase in melting temperatures \( T_{sm}, T_{bm}, T_{mf}, \) and \( T_{ms} \) with increasing \( Q \)), and the effect becomes obvious for
$Q \geq 10^{12} K/s$.

4. The heating rates $Q \geq 10^{12} K/s$ produce heterogeneity in temperature distribution; thus, for $Q = 10^{13} K/s$, the temperature difference is 38.4 K across the 40 nm core and 225 K across 3 nm oxide layer. The heterogeneity in temperature creates colder core and corresponding pressure drop in a core, which leads to lowering superheating temperatures. It can change of heating rate across core radius so that $Q_i > Q$. However, the effect of heterogeneity is minor relatively to kinetic superheating.

5. The heating rates $Q \geq 10^{12} K/s$ also result in wave propagation within the core, which causes oscillation in pressure and temperature (due to thermoelastic coupling), but the effect of the wave on melting temperatures and $T_{ma}$ is relatively small for tested heating rates.

6. A reduction in $M = R_i/\delta$ increases the pressure growth in the core and leads to the increase of melting temperatures for all tested $Q$.

7. For $Q \leq 10^{11} K/s$, the oxide shell fractures after complete melting and the heating-rate dependence of $T_{ma}$ is very weak. Temperature $T_{ma}$ increases with reduction of $M$ which decreases tensile hoop stress in the shell. $T_{ma}$ increases with the reduction in the core radius due to surface tension at the surface S and interface I which produce compressive hoop stress in oxide shell. If oxide fractures before completing melting (for $Q > 10^{11–10^{12}} K/s$), the maximum attainable temperature, $T_{ma}$, depends on the heating rate. It increases with an increase in the heating rate if melting temperatures increase, which delays the stress growth due to transformation expansion. A thicker shell increases the $Q$ for which heat-rate dependence of $T_{ma}$ starts, and a larger $R_i$ strengthens this dependence due to augmented kinetic superheating and increased melting time.

8. A parametric study of high-heating rate melting allows us to shed light on the melt-dispersion mechanism of combustion of an Al nanoparticle[96]. It is desired for the promotion of Al reactivity that oxide breaks after complete melting of the particle, i.e., $T_{ma} \geq T_{ms}$. $T_{ma}$ and $T_{ms}$ are independent of $Q$ for $Q \leq 10^9 K/s$, and for $M = 20$, the condition for complete melting before oxide fracture is met or almost met. However, for $M = 20$ and $Q \geq 10^{11} K/s$, fracture occurs well before completing melting. For $M \leq 13.3$, melting completes before fracture for $Q \leq 10^{11} K/s$, excluding particles with $R_i = 60nm$ and $M = 13.3$ for $Q = 10^{11} K/s$. 

For $Q \geq 10^{12} \text{K/s}$, fracture occurs before completing melting for all cases under study. An interaction with an elastic wave shows the oscillating evolution of $\sigma_2$ but its effect on $T_{ma}$ is minor for all tested $Q$. Consequently, there is an upper bound of $Q \leq 10^{11} - 10^{12} \text{K/s}$ for optimal melt dispersion, in contrast to previous wisdom that the larger $Q$ is better. While for $Q \leq 10^9 \text{K/s}$ predictions of the simplified theory in Ref. 96 are confirmed by the current more precise simulations, for $Q \geq 10^{11} \text{K/s}$ results are quantitatively and qualitatively different. The maximum rate of the hoop strain in the shell, which characterizes the possibility to avoid stress relaxation before fracture, is determined.

9. Various physical phenomena that promote or suppress melting and affect melting temperatures and $T_{ma}$ for different heating rate ranges are summarized in the schemes in Fig. 7.12 and 7.13.

The developed multiphysics phase field model is applicable for several nanostructures under the high heating rate. The reaction or combustion of aluminum nanoparticles can be the best example suited to the developed model. As the next step, we plan to include the reaction of aluminum and oxygen through an oxide shell, the phase field simulation of the fracture of shell, and their effect on melting. The reaction of aluminum and oxygen is exothermic and creates a heat source to heat and melt the aluminum core. Also, a sharp drop in pressure after fracture of the shell causes large tensile pressure in the reflected wave and a corresponding large drop of melting temperature, which can lead to additional significant overheating and "homogeneous" melting in the entire particle due to thermal fluctuations. It also can lead to cavitation which has been studied in Ref. 111. A coherent core-shell interface, which excludes surface melting, will be treated as well. The simulation and analysis of such a nanostructure under extreme conditions with a multiphysics phase field model will shed new light into the deeper understanding of nano-physics.
Bibliography


