A diffuse interface approach to phase transformation via virtual melting

by

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DEDICATION

I would like to dedicate this thesis to my parents and deceased brother.
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ABSTRACT

This work represents development of the first phase field models and detailed study solid-solid transformations via intermediate melting within nanometer size interface. Such phase transformations can occur in different materials, including HMX energetic crystals, PbTiO$_3$ nanowires, complex pharmaceutical substances, electronic and geological materials, as well as colloidal, and superhard materials. A thermodynamically consistent phase field model for three phases is developed using two polar order parameters. It includes the effect of energy and width of solid-solid and solid-melt interfaces, interaction between two solid-melt interfaces, temperature, mechanics, and interface stresses. The derived thermodynamic potential satisfies all the equilibrium and stability conditions for homogeneous phases. The HMX energetic crystal is used as the model material and numerical simulations are performed using COMSOL and Cystorm high performance computing facility. Depending on parameters, the intermediate melt may appear and disappear by continuous or discontinuous barrierless disordering or via critical nucleus due to thermal fluctuations. The intermediate melt may appear during heating and persist during cooling at temperatures well below what it follows from sharp-interface approach. For some parameters when intermediate melt is expected, it does not form, producing an intermediate melt free gap. Elastic energy promotes barrierless intermediate melt formation in terms of an increasing degree of disordering, interface velocity, and width of intermediate melt. Drastic reduction (by a factor of 16) of the energy of the critical nuclei of the intermediate melt within the solid-solid interface caused by mechanics is captured. Interfacial stresses surprisingly increase nucleation temperature for the intermediate melt. Interfacial stresses alter the kinetics of phase transformation, resulting in formation of new interfacial phases and drifting of a thermally activated spontaneous phase transformation to a stable phase.
CHAPTER 1. GENERAL INTRODUCTION

Phase transformations (PT) in materials is an area of interest in various disciplines of science such as mechanics, materials science, geomechanics, and physics. It has a wide range of applications including, material synthesis (such as diamond and cubic boron nitride), design and utilization of shape memory materials, melting/solidification, heat treatment of materials (e.x. heat treatment of steel), analysis of earthquake (instability caused by shear strain induced PT) (Green II and Burnley, 1989).

Phase transformations can be classified in three different categories,

• **Diffusion dependent without composition change**: As examples of these PTs, it can be referred to melting and solidification of pure materials.

• **Diffusion dependent with composition change**: Eutectic or eutectoid transformations are examples of such PTs.

• **Diffusionless phase transformation**: This PTs occur through small displacement of atoms in the structure, such as martensitic PTs.

In this study we focused on polymorphic PTs. These are PTs that the aggregate state does not change. In solid state this is related to the change in crystal lattice, while in liquids it is related to the change in density. (Levitas, 2012)

In nanosized samples, which the contribution of surface energy is comparable with the bulk energy, size of the sample is also a key parameter in determining the state of material. Difference in the surface energy of different phases may change the final solution and result in new surface phenomena such as surface premelting, (Levitas and Samani, 2011a,b) ordering and disordering, and barrierless nucleation.

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This chapter is adapted from (Levitas, 2010).
There are a number of numerical techniques for modeling and simulation of nanomaterials and capturing the size scale effect, such as \textit{ab initio} techniques, (Kresse and Hafner, 1993) molecular dynamics (MD), (Haile, 1992) Monte-Carlo simulation, (Binder and Heermann, 2010) phase field, (Moelans et al., 2008) and multi-scale simulation methods. (Nguyen et al., 2011) Among these methods, phase field approach provides a versatile tool for mesoscale modeling of microstructure evolution. One of the advantages of this approach is its ability to sincerely implement effect of different thermodynamic driving forces, such as interfacial energy, elastic and electric energy. Furthermore, due to the diffuse-interface description the position of interface during evolution of microstructure will be determined and there is no need to track the interface position using complex mathematical formulations. (Moelans et al., 2008) It also eliminates the necessity of making any presumption on the shape of interface. Diffuse interface approach can resolve the finite width and intermediate states, which provides a more detailed tool compared to sharp interface approach.

Phase field approach does not consider the behavior of individual atoms explicitly. Therefore, it is inherently a phenomenological method. The equations for evolution of the phase-field variables will be derived using law of thermodynamics and kinetics, and specific properties of the material will be introduced into the model using phenomenological parameters.

1.1 Virtual Melting: concept, governing mechanism, and proof of existence

Virtual melting (VM) is a new phenomena that governs various PTs. It was first predicted for solid-solid PT of materials with large transformation strain, $\varepsilon^t$, at temperatures much below the melting temperature. (Levitas et al., 2004) Primary theoretical calculations predict that large transformation stresses increase the driving force for melting and reduce the thermodynamic melting temperature. Immediately after melting, stresses relax and unstable melt solidifies to a crystalline phase (at $\theta > \theta_g$) and to amorphous phase (at $\theta < \theta_g$). Formation of intermediate virtual melt relaxes all the stresses and removes the interface friction, increases the mobility of atoms, and reduces the kinetic barrier. (Levitas et al., 2004) Silicon, Ge, C, BN, ice, quartz, HMX, jadeite, and albeite are some of the materials that VM plays a key role

\(\theta_g\) is the glass formation temperature.
in their PTs.

It has also been proved that VM is the governing mechanism of plastic deformation at high strain rates, which other relaxation mechanisms are not fast enough. Plastic deformation and stress relaxation through VM has been studied and confirmed using large scale MD simulations. The simulations show formation of melt at temperatures much lower than the thermodynamic melting temperature.

The main focus of this research is on the study of PT and stress relaxation in energetic crystalline HMX. To fulfill this goal a phase-field approach is pursued. A new thermodynamic potential function is developed, which captures the thermodynamic properties of different morphologies of HMX.

1.1.1 Concept of VM and governing mechanisms

Inelastic deformation of materials under the action of external load includes dislocation generation and motion, twinning, and fracture. The same mechanisms of inelastic deformation and internal stress relaxation can operate when stresses arise due to solid-solid phase transformation (PT). Internal stresses are caused by the transformation strain tensor $\varepsilon^t$, which transforms the unit cell of the parent crystalline phase 1 into the unit cell of the product phase 2. This work is based on our discovery of virtual melting (VM) as an alternative mechanism of reconstructive PT, stress relaxation, and loss of coherency at a moving solid-solid interface. (Levitas et al., 2004; Levitas, 2005; Levitas et al., 2006a, 2005) VM occurs under conditions in which classical plasticity and fracture are suppressed. If melting occurs along a nanoscale layer along the interface, the elastic energy completely relaxes. This change in elastic energy increases the driving force for melting, reduces melting temperature, and causes melting. Immediately after melting, stresses relax and unstable melt ($m$) crystallizes in a stable crystalline phase 2c (above the glass transition temperature $\theta_g$) or amorphous ($a$) phase 2a (below $\theta_g$), if it exists. Melt in each transforming material point exists for an extremely short time sufficient for stress relaxation, and it is a transitional activated state rather than real (thermodynamically stable) melt. We called this state the virtual melt.

Below we will review our work on this PT mechanism in more detail. We also will suggest
and try to justify the concept that the VM can serve as mechanisms for various structural changes: plastic flow under high strain rate and shock loading of organic energetic crystal HMX, bulk metals (Cu and Al), and metallic nanowires; fracture; nanofriction; sublimation; and grain growth and sliding. Also, we will show that in some cases, the virtual amorphization (VA) (which we will introduce) may play a similar role.

As an initial configuration, we consider a plane incoherent interface $AC$ between phases 1 and 2 with no external or internal stresses (figure 1.1). The change in Gibbs energy at zero stress $\Delta g_{1 \rightarrow 2} < 0$ at a given temperature. Let the PT occur in a thin layer $V_n$ by propagation of the coherent interface $BD$ from the position $AC$ (Figure 1.1).

The incoherent interface $AC$ is fixed and transforms to a grain boundary after PT in a layer $ABDC$. This process can be considered a nucleation at the grain boundary (or incoherent interface). Transformation strain and coherent interface generate elastic energy $g_e > 0$, which reduces the driving force for PT. Also, a moving interface between two solids experiences resistance $K$ due to the interaction with the stress field of crystal lattice defects. We also assume that there is no plasticity and fracture - i.e., elastic energy does not relax. It can be evaluated using the Eshelby solution for a penny-shape ellipsoid (Levitas et al., 2006a; Mura, 1987). After melting in the $V_n$, the interface is incoherent, and elastic energy is negligible. The
thermodynamic criterion for solid-solid PT in the $V_n$ in elastic material reads (Porter, 1981)

\[ F_{1 \rightarrow 2} = (-g^e - \Delta g_{1 \rightarrow 2} - K)V_n - V_n(\Gamma_{gb} + \Gamma_c - \Gamma_{in})/a \geq 0, \]

where $F$ is the net driving force for PT; $\Gamma_{gb}$, $\Gamma_c$ and $\Gamma_{in}$ are the grain boundary, coherent, and incoherent interface energies, respectively. The elastic energy reduces the driving force for the PT $1 \rightarrow 2$ and suppresses the PT. For the melting in the $V_n$, $F_{2 \rightarrow m} = (g^e - \Delta g_{2 \rightarrow m})V_n - V_n\Delta \Gamma_{2 \rightarrow m}/a \geq 0$, where $\Delta \Gamma_{2 \rightarrow m} = \Gamma_{2 \rightarrow m} + \Gamma_{1 \rightarrow m} - \Gamma_{gb} - \Gamma_c$ and $\Gamma_{i \rightarrow m}$ is the phase $i$-$m$ interface energy. We put $K = 0$, because liquid, as the hydrostatic medium, does not interact with the stress field of crystal defects; consequently, the athermal resistance to interface propagation is absent. The elastic energy before melting $g^e$ disappears after melting, thus increasing the driving force for melting.

For organic crystals, $\Gamma_{i \rightarrow m} = (0.15 - 0.3)\Gamma_{gb}$, for metals $\Gamma_{i \rightarrow m} = (0.3 - 0.45)\Gamma_{gb}$ (Porter, 1981), and $\Delta \Gamma_{2 \rightarrow m} \leq 0$ - i.e., there is no barrier for melt nucleation due to surface energy. To be on the safe side, we put $\Delta \Gamma_{2 \rightarrow m} = 0$, decreasing the driving force for melting. From the phase equilibrium condition $F_{2 \rightarrow m} = 0$, we can determine how the melting temperature $\theta_m$ reduces due to the elastic energy

\[ \theta_m = (\Delta h_{2 \rightarrow m} - g^e) / \Delta s_{2 \rightarrow m}, \quad (1.1) \]

where $\Delta h_{2 \rightarrow m}$ and $\Delta s_{2 \rightarrow m}$ are the heat and entropy of fusion, respectively. Using the $VM$ mechanism, interface velocity is found in the form

\[ v = v_0 \exp \left(-\frac{\Delta h_{2 \rightarrow m}}{R\theta}ight) \left[ \exp \left(-\frac{\Delta g_{1 \rightarrow 2}}{R\theta}ight) - 1 \right]. \quad (1.2) \]

### 1.1.2 Virtual melting in HMX

The $\beta$ and $\delta$ phases are in equilibrium at 432K and $\beta \rightarrow \delta$ PT starts above this temperature. This PT results in large expansion ($\sim 8\%$) due to difference in the crystalline structure and density of $\beta$ and $\delta$ phases which consequently forms a large internal stresses in the HMX structure. Such large stresses relax through formation of melt, and they may also form cracks and voids. (Levitas et al., 2007b, 2006a) The proposed solid-solid PT through virtual melt results in sixteen theoretical predictions which match experimental studies qualitatively and quantitatively. (Levitas et al., 2006a, 2005)
1.1.2.1 Crystalline structure and morphologies of HMX

Cyclotetramethylene-tetranitramine ($C_4H_8N_8O_8$), which is also called 1,3,5,7-tetranitro-octahydro 1,3,5,7-tetrazocine and known as HMX, is a high energy material. It has applications in gun and rocket propellants, as well as munitions and is an important ingredient of explosives such as RDX and polymer bounded explosives (PBX). (Boggs, 1984) The HMX has four well recognized morphologies, which in descending (ascending) order of stability (sensitivity) are $\beta$-, $\alpha$-, $\gamma$- and $\delta$-HMX. (McCrone, 1950) The $\beta$-HMX is stable form in ambient temperature and as the temperature rises, $\delta$-HMX becomes more stable. Presence of sensitive $\alpha$-, $\gamma$-, and $\delta$-HMX polymorphs in $\beta$-HMX and RDX can be the source of very dangerous accidents. These considerations motivated a number of investigations on properties of HMX, its polymorphs, and their phase transformation process. (Cady, 1986; Cady et al., 1962) Unfortunately, experimental measurement of HMX properties can be very difficult, if not impossible, as for example it decomposes upon melting. (Levitas et al., 2005) A number of experimental studies are performed to determine properties of HMX polymorphs, including its melting and transformation temperatures. (Landers and Brill, 1980; Cady et al., 1962) However, different values are reported which might be due to considering dissimilar crucial parameters such as temperature, pressure, atmospheric gas, degree of contamination, and heating rate, which current studies did not provide detailed information on. (Boggs, 1984) Some of the experimental results are presented in table 1.1.
Table 1.1: Temperature stability range of HMX polymorphs.

<table>
<thead>
<tr>
<th>β-HMX (°C)</th>
<th>α-HMX (°C)</th>
<th>γ-HMX (°C)</th>
<th>δ-HMX (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>27 to 102-104.5</td>
<td>102-104.5 to 160-164</td>
<td>metastable</td>
<td>160-164 to melting point</td>
</tr>
<tr>
<td>27 to 115</td>
<td>115 to 156</td>
<td>156</td>
<td>156 to melting point</td>
</tr>
<tr>
<td>27 to 103</td>
<td>103 to 162</td>
<td>metastable</td>
<td>162 to melting point</td>
</tr>
</tbody>
</table>

Values are obtained from (Cady et al., 1962; McCrone, 1950; Cady, 1986).

Threshold of weak initiation is one of the key properties of explosive materials which needs to be determined to avoid accidental explosion and proper handling of such materials. Hot spots play a key role in defining the threshold of weak initiation. For engineering applications, coarse grain models are used due to the size of simulation cells, which is about ten times larger than grain boundaries. In these applications, effect of hot spots is implemented in empirical burn models which are commonly based on pressure. However, hot spots represent localized spatial model fluctuations of temperature field, and hot spot models use chemical reaction rate of explosives that is highly sensitive to temperature. Furthermore, properties of hot spots depend on material inhomogeneities and dissipation mechanisms, which cannot be resolved by coarse grain models. (Menikoff and Sewell, 2002) Mesoscale modeling techniques can resolve deficiencies of coarse grained models while avoiding implementation difficulties of multiscale models.

Difficulties in performing experimental measurement of HMX thermophysical properties provide an abundant ground for theoretical studies and computational simulations. We can overcome the property measurement problems by using mesoscale and multiscale modeling techniques. (Sewell et al., 2003) These techniques are specially useful for explosive materials that experimental studies, such as threshold of weak initiation and effect of aging on their performance, are a major challenge. (Menikoff and Sewell, 2002) In the case of HMX, mesoscale modeling techniques are used to provide better understanding of phase transformation (PT) process between the polymorphs of HMX that helps us to develop protocols for handling and disposal of HMX-based explosive materials and munitions. (Levitas et al., 2007b) Crystalline structure of organic nitramines including HMX are studied using ab initio technique.
(Dzyabchenko et al., 1996; Lewis et al., 2000) Lattice parameters of HMX over $0 < P < 7.5$ GPa is studied using rigid molecule Monte Carlo simulations. (Sewell, 1998) Space group symmetry and structural parameters of HMX are calculated using molecular dynamics simulations with NPT ensemble. (Sorescu et al., 1999, 1998) A value of $\sim 15$–16 GPa is calculated for isothermal bulk modulus of HMX using molecular dynamics simulation technique. (Sewell et al., 2003) Calculation of thermal expansion coefficient, heat of sublimation, and thermal conductivity of liquid HMX using MD technique, have also been reported. (Bedrov et al., 2000, 2001)

Number of phenomenological kinetic models are reported for $\beta - \delta$ PT of HMX. (Henson et al., 2002; Burnham et al., 2004; Smilowitz et al., 2002; Wemhoff et al., 2007) However, they are limited by the range of temperature and pressure which their parameters are calibrated for. Although phenomenological models well illustrate isothermal experimental data at zero pressure, they failed to provide an acceptable match with high temperature and pressure data. (Gump and Peiris, 2005; Karpowicz and Brill, 1982) In contrast to phenomenological models, the models that are based on the physical mechanisms are much more reliable outside their calibration range. (Levitas et al., 2007b) We have used a mesoscale modeling technique and developed a Ginzburg-Landau model to study $\beta - \delta$ reconstructive PT and possible formation of virtual melt (Levitas et al., 2005, 2004, 2006b) under complex thermomechanical paths.

1.1.2.2 Experimental validation of VM in HMX

To prove the validity of the VM, we consider the reconstructive $\beta \leftrightarrow \delta$ PTs in the organic energetic crystal HMX (Henson et al., 2002; Smilowitz et al., 2004). Eq.(1.2) was supplemented by the nucleation kinetics that follows from our new nucleation mechanism via melt mediated nano-cluster transformation (Levitas et al., 2006c), thus leading to fully physically based overall kinetics. Sixteen theoretical predictions are in qualitative and quantitative agreement with experiments (Levitas et al., 2006b,c, 2005, 2004). We found that, in particular: (1) Energy of internal stresses is sufficient to reduce melting temperature from 551 K to 430 K for the $\delta$ phase during the $\beta \rightarrow \delta$ PT and from 520 K to 400 K for the $\beta$ phase during the $\delta \rightarrow \beta$ PT. (2) Activation energies for direct and reverse PTs are equal to corresponding melting energy ($E_{1 \rightarrow 2} = \Delta g_{1 \rightarrow m}$ and $E_{2 \rightarrow 1} = \Delta g_{2 \rightarrow m}$). (3) Temperature dependence of the rate
constant is determined by the heat of fusion \( h_{2\rightarrow m} \) (Eq. (1.2)); both interface kinetics and a fully physically based overall kinetic model are in very good correspondence with our and published experiments (Figs. 2 and 3). (4) \( K \simeq g^e \simeq 0 \) for both \( \beta \leftrightarrow \delta \) PTs (in contrast to all known solid-solid PT). (5) Considerable nanocracking, homogeneously distributed in the transformed material, accompanies the PT. (6) The nanocracking does not change appreciably the PT thermodynamics and kinetics for the first and the second transformation \( \beta \leftrightarrow \delta \) cycles, as predicted by theory. (7) \( \beta \rightarrow \alpha \) and \( \alpha \rightarrow \beta \) transformations, which are thermodynamically preferable in the temperature range \( 382.4 < \theta < 430 \text{ K} \) and below \( 382.4 \text{ K} \), respectively, do not occur. (8) \( \delta \rightarrow \alpha \) transformation does not occur above \( 400 \text{ K} \). Because it is difficult to imagine any other mechanism that explains all these experimental results, we concluded that \( \beta \leftrightarrow \delta \) PT in the HMX crystal occurs through \( VM \). Most of the above experimental results were considered a major puzzles in HMX polymorphism for decades. In particular, absence of temperature hysteresis for \( \beta \leftrightarrow \delta \) PTs (despite the large volumetric strain, \( \varepsilon_0 = 0.08 \)), absence of \( \beta \leftrightarrow \alpha \) PTs, where they are thermodynamically preferable with respect to \( \beta \leftrightarrow \delta \) PTs (despite the two times smaller \( \varepsilon_0 \simeq 0.04 \)), and large hysteresis for \( \delta \leftrightarrow \alpha \) PTs (\( \varepsilon_0 \simeq 0.04 \)) were unexplained by known theories. Only \( \beta \leftrightarrow \delta \) PTs occur via the \( VM \), which removes the temperature hysteresis. Volumetric strain for other PTs is not sufficient for \( VM \), which explains large temperature hysteresis and suppression of some PTs due to elastic stresses and interface friction.

A continuum thermo-mechanochemical model of the behavior of a PBX 9501 formulation consisting of the energetic crystal HMX embedded in a polymeric binder is developed. The model includes the fully physically based kinetics of \( \beta \leftrightarrow \delta \) PTs in HMX; chemical decomposition of the HMX and binder leading to gas formation; gas leaking from the cylinder; and elastic, thermal, and transformational straining, as well as straining due to mass loss. We studied the kinetics of the \( \beta \leftrightarrow \delta \) PTs and pressure build-up in a rigid cylinder, as well as how they are affected by the heating rate, initial porosity, and pre-strain, HMX and binder decomposition, the and gas leaking rule.
Figure 1.3: A comparison between theoretical prediction (solid curves) with experimental data for $\beta \rightarrow \delta$ PT in the HMX under isothermal conditions. Reprinted with permission from (Levitas et al., 2006b). Copyright 2006, AIP Publishing LLC.

Figure 1.4: Equilibrium and nonequilibrium PT pressure-temperature diagrams. Solid lines ($1c - m, ...$) are the phase equilibrium lines. Dashed lines are metastable continuation of $1c - m$ and $2c - m$ lines. Bold Lines are calculated lines for initiation of PTs. 1c $\rightarrow$ internal stress-induced $VM \rightarrow 2c$ PT around $2c$ nuclei; $\bigtriangleup$ 1c $\rightarrow$ internal stress-induced $VM \rightarrow 2a$ PT around $2c$ nuclei; $\circ$ 1c $\rightarrow VM \rightarrow 2a$ PT. Reprinted figure with permission from (Levitas, 2005) Copyright 2005 by the American Physical Society.
1.1.3 Crystal-amorphous and crystal-crystal transformations via virtual melting

Pressure- and temperature-induced $c$-$a$ PTs were considered (e.g., for ice, quartz, high albeite, Cd$_{43}$Sb$_{57}$ and jadeite (Hemley et al., 1988; Johnson, 1986; Mishima et al., 1984; Ponyatovsky et al., 1990; Richet, 1988)) as a low-temperature analog of melting along the continuation of melting lines in the pressure $p$-temperature $\theta$ phase diagram (1.4). Alternatively, amorphization was related to the loss of mechanical stability of crystal lattice (Hemley et al., 1988; Johnson, 1986; Brazhkin et al., 1997; Mishima, 1996; Sharma and Sikka, 1996). However, some contradictions were found concerning metastable melting (Brazhkin et al., 1997; Mishima, 1996; Sharma and Sikka, 1996) and instability hypotheses, and the mechanism of amorphization is currently not clear. In (Levitas, 2005), we justified thermodynamically and kinetically a new mechanism of $c$ $\rightarrow$ $a$ and $c$ $\rightarrow$ $c$ PTs and internal stress relaxation via VM induced by internal stresses. VM removes interface friction, reduces kinetic barrier, and increases atomic mobility.

1.1.3.1 Virtual melting at low temperatures

We will consider materials with the equilibrium $p$-$\theta$ diagram shown in 1.4 and large volumetric transformation strain, $\varepsilon_0 > 0.1$. However, actual nonequilibrium PT lines are significantly shifted with respect to phase equilibrium lines due to elastic energy $g^e$, interface friction $K$, and kinetic barrier due to surface energy and diffusion (Levitas, 2005) (1.4). It follows from the definition of nonequilibrium PT diagram that if the loading (unloading)-heating (cooling) $p$-$\theta$ trajectory crosses the nonequilibrium PT line, this PT must occur. After melting $1c \rightarrow m$ in the stability region of phase 2, fast solidification will occur.

Above the glass transition temperature $\theta_g$ solidification occurs to $2c$ phase; below $\theta_g$ amorphization occurs to $2a$ phase (1.4). Usually, crystals are considered to directly vitrify into the $2a$ state (Hemley et al., 1988; Johnson, 1986; Brazhkin et al., 1997; Mishima, 1996; Ponyatovsky et al., 1990; Richet, 1988), which leads to some contradictions (Brazhkin and Lyapin, 1996; Brazhkin et al., 1997; Sharma and Sikka, 1996). Consideration of VM as a separate process followed by solidification below $\theta_g$ reduces solid-state amorphization to solidification.
of an undercooled liquid after quenching at an infinitely fast cooling rate. This resolves some of the contradictions (Brazhkin and Lyapin, 1996; Brazhkin et al., 1997; Sharma and Sikka, 1996), in particular that the sign of heat for melting and amorphization is different, because heat of amorphization includes heat of melting $1c \rightarrow VM$ and solidification $VM \rightarrow 2a$.

### 1.1.3.2 Internal stress-induced VM

When the transformation line $1c \rightarrow 2c$ is crossed first, a coherent $2c$ penny-shaped nucleus appears. For suppressed plasticity, we found (Levitas, 2005) that the elastic energy can be released by melt nucleation around the $2c$ nucleus (Fig. 5). Since $2c$ nucleus loses its coherency, its elastic energy $g^e$ releases, increasing the driving force for $1c \rightarrow m$ PT. We also found that for smaller axis $b > 6\Gamma_{1-m}/g^e$ there is the unique situation for nucleation: barrierless melting induced by release of internal stresses in enclosed $2c$ nucleus takes place. This condition is fulfilled, for example, for Ih→IX or II PT in ice. Internal stresses not only remove kinetic barrier but also can shift thermodynamic melting line toward the region of stability of solid phase (1.4). Our estimate for the melting pressure decrease after Ih→IX PT in ice, $0.4\, GPa$ (Levitas, 2005), exceeds maximum deviation between experimental PT line and calculated melting line at $\theta = 150K$ (Mishima, 1996; Tse et al., 1999).

Since $g^e$ disappears immediately as the stress in $2c$ nucleus relaxes, VM solidifies to $2c$ (above $\theta_g$) or to $2a$ (below $\theta_g$), producing incoherent $1c - 2c$ or $1c - 2a$ interfaces. After amorphization around $2c$ nucleus, high interface energy may transform $2c$ to $2a$ nucleus. The experimental fact that for some materials (e.g., for ice (Mishima, 1996)) amorphization starts...
below the melting pressure was used as one of the main contradictions of the metastable melting hypothesis (Brazhkin and Lyapin, 1996; Brazhkin et al., 1997; Mishima, 1996; Sharma and Sikka, 1996). The shift in the thermodynamic melting line resolves this seeming contradiction. Transformation lines for ice Ih (Mishima, 1996) are located like symbols in 1.4.

The above results were applied for a new interpretation of melting, $c-c$ and $c-a$ PT mechanisms in ice Ih; we expect them to be applicable for amorphization of $\alpha$-quartz and coesite (Hemley et al., 1988), polymet (Sharma and Sikka, 1996), Ge and Si (Brazhkin and Lyapin, 1996; Brazhkin et al., 1997; Mishima, 1996; Sharma and Sikka, 1996), jadeite, $Zn_{43}Sb_{57}$ and $Cd_{43}Sb_{57}$ (Ponyatovsky and Barkalov, 1992), BN (Eremets et al., 1998) and graphite (Goncharov, 1992). Note that $VM$ in Si and Ge, for example, occurs at more that 1000K below the thermodynamic melting temperature! Indeed, amorphization of Si II occurs during decompression at 100K (Brazhkin et al., 1997, 1995), while the thermodynamic melting temperature of Si exceeds 1100K in the same pressure range.

1.1.4 Virtual melting as a possible mechanism of various structural changes

1.1.4.1 Virtual Melting and Amorphization as Mechanisms of Plastic Deformation and Stress Relaxation for High-Strain-Rate Loading

A new mechanism of plastic deformation and stress relaxation under very strong shock loading via the $VM$ and the virtual amorphization ($VA$) several thousands K below the thermodynamic melting temperature but above the $\theta_g$ is predicted theoretically and confirmed by large-scale molecular dynamic (MD) simulations. The driving force for the melting and amorphization is due to the work and energy of nonhydrostatic stresses. After melting, nonhydrostatic stresses relax, leading to undercooled and unstable liquid under hydrostatic conditions that crystallizes. MD simulations for perfect Al and Cu crystal, shocked in [110] direction, combined with the analyzes of the stress-strain curves and thermodynamics of the process suggested the following mechanism. (Levitas and Ravelo, 2012)

Disordering first leads to isotropic virtual amorphous solid. Melting of amorphous phase (that represents the second-order transformation), leads to the hydrostatically loaded $VM$. 
The only difference between amorphous solid and melt is the finite shear modulus. Recrystallization of the VM is the final process. Note that hydrostatic compression increases the melting temperature $\theta_m$ for metals under study. We found, however, that nonhydrostatic compression reduces the melting temperature significantly. Also, melting due to shear instability (mechanical melting) usually occurs at a temperature significantly above the thermodynamic melting temperature. Here, in contrast, it starts much below $\theta_m$ due to nonhydrostatic stresses.

Amorphization of bulk elemental metal was not observed in experiments. Transformation of defect-free crystalline metal to unstable amorphous phase under compression above the glass-formation temperature is unusual, especially since it is accompanied by the volume increase (like melting). Melting of amorphous phase in the region of stability of crystalline phase is also counterintuitive; it should crystallize. However, for nonhydrostatically loaded amorphous phase, there is a driving force for the second-order PT to the melt due to disappearance of the shear modulus. We found that for high strain rate VM occurs faster than crystallization and represents an intermediate, unstable state toward crystallization.

A simplified thermodynamics approach for this problem is developed, and it significantly differs from those developed for $c-c$ and $c-a$ PTs. Direct observation of the VM in MD simulations for plastic straining indirectly supports the plausibility the VM in PTs as well.

1.1.4.2 Crystal Reorientation during the Nanofriction via the Virtual Melting

The MD simulation of the high-velocity sliding friction between two identical fcc Al single crystals, but along different crystallographic faces, exhibits the following phenomenon (Hammerberg et al., 2004). In a certain range of sliding velocities, one of the crystals melts and rapidly recrystallizes into the second orientation. The sliding interface thus moves downward, as one crystal orientation grows at the expense the other, via intermediate liquid layer. The thickness of the moving liquid layer is 4-5 atomic sizes. Furthermore, crystalline regions near the interfaces are full of dislocations.

A simplified nonequilibrium continuum thermodynamic model of the above phenomenon was developed by considering a melting process (rather than equilibrium) in a thin layer of stressed crystal under shear and normal force. Due to elastic anisotropy, melting temperatures,
\( \theta_{mi} \), of different crystal faces under the same traction are different. When temperature at the sliding contact reaches the melting temperature of the face with \( \theta_{m1} < \theta_{m2} \), it melts. However, since \( \theta < \theta_{m2} \), melt is unstable with respect to crystal face 2. Because the existing face 2 supplies perfect nucleation sites for solidification, melt solidifies into crystal structure of face 2. This is one more example of the VM phenomenon.

1.1.4.3 Virtual Amorphization as a Mechanism of Plasticity for High-Strain-Rate Tension of Metallic Nanowires

MD simulations in (Ikeda et al., 1999) demonstrated the following result for high-strain-rate tension of single crystal Ni and NiCu nanowires at 300 K. For 0.05\% and 0.5\% ps\(^{-1} \) the stress is relaxed by twin formation. For 5\% ps\(^{-1} \), the crystalline phase for both systems transforms continuously to an amorphous phase. This amorphization, which occurs directly from the homogeneous, elastically deformed system with no chemical or structural inhomogeneities, exhibits a new mode of amorphization. Slowing the strain rate to 1\% ps\(^{-1} \) leads to the recrystallization of the sample - i.e., it is VA. Effectively, the high strain rate has decreased the "melting" temperature from 1700 K to 300 K. Similar MD results were reported in (Branicio and Rino, 2000) for nickel and in (Koh et al., 2005) for platinum.

The thermodynamic effect of surface energy and tension may be very important for amorphization of nanowires. Since the disordered material supports tensile stress of 3 GPa, it is amorphous solid rather than melt. It is not clear why amorphous solid does not melt (similar to what we found in shock wave), because melting should further reduce the elastic energy and lead to fracture due to cavitation.

1.1.4.4 Virtual melting as a possible mechanism of fracture

In situ fracture studies on thin films of the NiTi intermetallic compound (Okamoto et al., 1999, 1998) revealed stress-induced amorphization of regions directly in front of moving crack tips in a temperature range 300-600 K. MD simulations in (Lynden-Bell, 1995) suggests that fcc crystals of the metals (platinum, gold, rhodium, and silver) under uniaxial tension at temperatures above half the melting temperature disordered before they failed by void formation.
We may hypothesize that disordering in both cases represents the VM.

1.1.4.5 Virtual melting as a possible mechanism for the grain boundary processes

Mott (Mott, 1948) suggested that the grain boundary sliding and migration occur through local melting and solidification of small groups of atoms. Kinetic analysis in (Mott, 1948) is oversimplified, which is why this theory was not supported by experiments (Holmes and Winegard, 1959). Later MD studies (Schönhelder et al., 1997), however, demonstrated that migration of high-angle grain boundary involves "melting" of small groups of atoms and collective reshuffling followed by crystallization onto the other crystal.

Other MD simulations (Keblinski et al., 1999; Wolf, 2001) demonstrated the possibility of a reversible, smooth transition in high-energy grain boundary from solid crystalline structure to liquid confined structure above $\theta_g$ and below $\theta_m$. The results were obtained for silicon and fcc metals. Grain boundary diffusion involves thermally activated formation of liquid-like clusters from the disordered phase and liquid-like atom migration within clusters. As a consequence, grain-boundary diffusivity and mobility occur with activation energies related to the liquid state. When temperature falls below $\theta_g$, the melt solidifies to an amorphous state, the energy of which is 15% lower than the energy of the initial crystalline structure of the grain boundary. While $c-a$ PT via VM was not observed as a single process below $\theta_g$ (because it probably requires longer simulation time), these results support our ideas (1) that melt can appear below melting temperature, (2) that if a melt nucleus appears, activation energy for self-diffusion decreases in it, and (3) that similar melting is probable at the moving $c-c$ or $c-a$ interface.

For recrystallization, a similar mechanism of melt nucleation at the intersection of several grain boundaries followed by crystallization can be considered.

1.1.4.6 Sublimation via virtual melting

In the field of tensile stresses and hot spots within a solid (e.g., in a tensile wave (Levitas et al., 2007a), in laser ablation (Zhigilei and Garrison, 2000)), solid is unstable with respect
to gas; however, an activation barrier caused by high solid-gas surface energy suppresses sublimation. Solid-liquid interface energy is usually an order of magnitude smaller than solid-gas energy, and activation energy is proportional to the cube of surface energy. That is why it is quite probable that the VM will occur in a small volume as a first kinetically favorable step. Then, either melt vaporizes or decohesion along the solid-melt interface occurs. After decohesion, a void appears due to plastic deformation, and melt evaporates into free space, producing thermodynamically stable gas. We are not aware, however, of any publications that have pursued this idea.

1.1.5 Concluding remarks

The above examples demonstrate that there are data indicating that the VM may be a general phenomenon for various structural changes in solids. VA may represent an intermediate step in the VM of solid or final step followed by crystallization. These mechanisms represent an unifying idea for various mechano-chemical phenomena (c − c, c − a, c − g PTs, plastic flow, fracture, crystal reorientation and recrystallization) in a broad class of materials (metals, intermetalics, geological, electronic, biological, and superhard materials) and may find various applications. Our goal is to develop multiple theoretical, computational, and experimental approaches that will allow us to prove the existence, to study main features, and to explore the generality of the phenomena of VM and VA in their various applications.
Solid-solid (SS) phase transformations via nanometer size intermediate melt (IM) within the SS interface, hundreds of degrees below melting temperature, were predicted thermodynamically and are consistent with experiments for various materials. A necessary condition for the appearance of IM, using a sharp interface approach, was that the ratio of the energies of SS and solid-melt (SM) interfaces \( k_E > 2 \). Here, an advanced phase-field approach coupled with mechanics is developed that reveals various new scale and interaction effects and phenomena. Various types of IM are found: (a) continuous and reversible premelting and melting; (b) jump-like barrierless transformation to IM, which can be kept at much lower temperature even for \( k_E < 2 \); (c) unstable IM, i.e., a critical nucleus between SS interface and IM. A surprising scale effect related to the ratio of widths of SS and SM interfaces is found: it suppresses barrierless IM but allows keeping IM at much lower temperature and even for \( k_E < 2 \). Relaxation of elastic stresses strongly promotes IM, which can appear even at \( k_E < 2 \) and retained at \( k_E = 1 \). Developed theory can be adjusted for the diffusive phase transformations, formation of intergranular and interfacial phases, and surface-induced phase transformations.

2.1 Introduction

Recently, phase transformations between two solid phases through nanometer-size molten layer, hundreds of degrees below melting temperature, were predicted thermodynamically (Levitas et al., 2004, 2006a; Levitas, 2005; Levitas et al., 2012) and confirmed in experiments for \( \beta - \delta \) phase transformation in HMX energetic crystals (Levitas et al., 2004, 2006a; Levitas,

This chapter is adapted from (Levitas and Momeni, 2014).
$PbTiO_3$ nanowires (Levitas et al., 2012) (Fig. 2.1), and for amorphization in avandia (Randzio and Kutner, 2008) and materials with reducing melting temperature under pressure (e.g., ice, Si, Ge, geological, and other materials) (Levitas, 2005). While moving solid 1-melt-solid 2 ($S_1 MS_2$) interface propagates through the sample, one solid phase melts and resolidifies into another phase. The thermodynamic condition for $IM$ is (Levitas et al., 2012),

$$E^{21} - E^{10} - E^{20} - E^e > (G^0 - G^s)\delta^*, \quad (2.1)$$

where $E^{10}$, $E^{20}$, and $E^{21}$ are the energies of the $S_1 M$, $S_2 M$, and $SS$ interfaces, $E^e$ is the elastic energy of the coherent $SS$ interface, and $G^0$ and $G^s$ are the bulk thermal energies of the melt and solid phase with the smaller melting temperature $\theta^m_e$. Thus, the reasons for melting significantly below $\theta^m_e$ are the reduction in total interface energy and relaxation of the elastic energy.

For $E^{10} = E^{20} = E^{e0}$, neglected elastic energy, and close to $\theta^m_e$ (i.e., for $(G^0 \simeq G^s)$), the necessary thermodynamic condition for $IM$ reduces to $k_E = E^{21}/E^{e0} > 2$. It is clear that for hundreds of degrees below $\theta^m_e$, $k_E$ should significantly exceed 2. However, thermodynamic treatment with sharp interfaces (Grinfeld, 1991; Levitas et al., 2004, 2006a; Levitas, 2005; Levitas et al., 2012) is oversimplified and cannot be considered as a strict proof of phenomena. Melting may not be complete (i.e., premelting) during the $SS$ phase transformation and the width of the $IM$, $\delta^*$, is comparable with the widths $\delta^{21}$ and $\delta^{e0}$ of $SS$ and $SM$ interfaces. Furthermore, kinetic effects and alternative nanostructures may play a key role in $IM$. Therefore, here, a phase field approach is developed, which led to much more precise proof of existence of $IM$ and finding corresponding conditions, and revealed new phases, effects, and phenomena.

We are not aware of any previous phase field approach to the solid-solid phase transformations via $IM$. The closest phase field approaches are for premelting in grain boundaries (Lobkovsky and Warren, 2002a; Tang et al., 2006a; Bishop et al., 2005), but due to different phenomena they are quite different from what we suggest below and do not include mechanical stresses. Premelting at the external surface (Levitas and Samani, 2011a,b) and surface-induced martensitic phase transformation (Levitas and Javanbakht, 2010, 2011b) include mechanics but utilize two phases only and do not include moving $SS$ interface. Also, premelting in (Lipowsky, 1982;
Lobkovsky and Warren, 2002a; Tang et al., 2006a; Levitas and Samani, 2011a,b) occurs a few degrees below $\theta_{cm}$, while IM in experiments (Levitas et al., 2004, 2006a; Levitas, 2005; Levitas et al., 2012; Randzio and Kutner, 2008) takes places several hundreds of degrees below $\theta_{cm}$; prior to this, there was no evidence that phase field approach could reproduce these phenomena.

One of the advantages of the developed approach is that, in contrast to multiphase models (Tiaden et al., 1998; Levitas et al., 2003; Levitas and Javanbakht, 2010, 2011b), each of three phase transformations is described by a single-order parameter, without additional constraints on the order parameters. One of the nontrivial points in the theory is an introduction of gradient energy for SS interface within IM (governed by a parameter $a_0$), which describes interaction between two SM interfaces. The effect of two unexplored parameters, namely $a_0$ and the ratio $k_{\delta} = \delta_1^{21}/\delta_0^{s0}$ of widths of SS and SM interfaces, along with ratio $k_{E} = E_{s}^{21}/E_{s0}^{s0}$, temperature $\theta$, and elastic stresses, is examined in detail. Several types of IM are found: (a) continuous and reversible pre-melting and melting for small $k_{\delta}$; (b) jump-like (i.e., first-order) barrierless transformation to IM for larger $k_{\delta}$; (c) persistence of IM as a metastable phase at lower temperatures without barrierless resolidification, even for $k_{E} < 2$, i.e., when the necessary condition for thermodynamically equilibrium IM is not satisfied even for $\theta_{cm}$; and (d) unstable IM, which represents a critical nucleus between SS interface and IM and provides a thermally activated transition between them. Surprising scale effect related to $k_{\delta}$ is revealed: increasing $k_{\delta}$ suppresses barrierless IM but allows one to keep IM at much lower temperature and even for $k_{E} < 2$. For $2 < k_{E} \leq 2.5$, a nontrivial nonmonotonous effect of $k_{\delta}$ is revealed, including the IM gap (i.e., lack of IM) in some $k_{\delta}$ range. Crossover from the expected increasing dependence of the width of the IM $\delta^*$ on parameter $a_0$ to decreasing dependence at very low temperature is revealed. Velocity of SMS interface is lower than the velocity of SS interface. Elastic stresses at coherent SS interface further reduce temperature and ratio $k_{E}$ for barrierless IM nucleation (even below $k_{E} = 2$) and for its retaining (even at $k_{E} = 1$).

Developed theory can be adjusted for the description of diffusive phase transformations with evolving concentration (Luo, 2007; Luo and Chiang, 2008; Luo, 2012), premelting/disordering at grain boundaries (Lobkovsky and Warren, 2002a; Tang et al., 2006a), wetting (Cahn, 1977; Baram et al., 2011; Luo, 2007; Luo and Chiang, 2008; Luo, 2012) of the external and internal
surfaces, surface premelting and melting (Levitas and Samani, 2011a,b; Lipowsky, 1982) at moving solid-melt-gas interface, surface-induced SS phase transformation (Levitas and Javanbakht, 2010, 2011b), SS phase transformation via surface or grain-boundary-induced premelting (Levitas et al., 2012), formation of intergranular and interface amorphous or crystalline phases (complexions) (Lobkovsky and Warren, 2002a; Tang et al., 2006a; Luo, 2007; Luo and Chiang, 2008; Luo, 2012; Cahn, 1977; Baram et al., 2011; Luo and Chiang, 2000; Avishai and Kaplan, 2005; Avishai et al., 2005; Cantwell et al., 2014; Qian et al., 2008; Chung and Kang, 2003) in metallic and ceramic systems and developing corresponding interfacial phase diagrams (Luo, 2007; Luo and Chiang, 2008; Luo, 2012), amorphization via IM (Levitas, 2005), and austenite nucleation at martensite-martensite or twin interfaces (Levitas and Javanbakht, 2010, 2011b). Examples of some intergranular and interface phases are collected in Fig. 2.1.

### 2.2 Mathematical model

The relationship between strain tensor $\varepsilon = 1/3 \varepsilon_0 I + e$ (where $\varepsilon_0$ and $e$ are the volumetric and deviatoric contributions) and the displacement vector $u$, decomposition of strain into elastic
\( \varepsilon_{el} \) and transformational \( \varepsilon_t \) parts, and the equilibrium equation are:

\[
\varepsilon = (\nabla u)_s; \quad \varepsilon = \varepsilon_{el} + \varepsilon_t; \quad \nabla \cdot \sigma = 0.
\] (2.2)

Here, \( \sigma \) is the stress tensor, \( \nabla \) and \( \nabla \cdot \) are the gradient and divergence operators, \( I \) is the unit tensor, and subscript \( s \) means symmetrization. Two order parameters are introduced using polar system in the plane of the order parameters to develop the model for phase transformations between three phases: radial \( \Upsilon \) and angular \( \vartheta \), where \( \pi \vartheta/2 \) is the angle between the radius vector \( \Upsilon \) and the positive 1\textsuperscript{st} axis. Value \( \Upsilon = 0 \) for any \( \vartheta \) represents the reference phase, which in this paper will be considered as melt \( M \) (but in general it also can be solid). Solid phases correspond to \( \Upsilon = 1 \); phase \( S_1 \) is described by \( \vartheta = 0 \), and phase \( S_2 \) is described by \( \vartheta = 1 \) (Fig. 2.2). Each of the phase transformations: \( M \leftrightarrow S_1 \), corresponding to variation in \( \Upsilon \) between 0 and 1 at \( \vartheta = 0 \); \( M \leftrightarrow S_2 \), corresponding to variation in \( \Upsilon \) between 0 and 1 at \( \vartheta = 1 \), \( S_1 \leftrightarrow S_2 \), corresponding to variation in \( \vartheta = 0 \) between 0 and 1 at \( \Upsilon = 1 \), is described by potential and theory in (Tiaden et al., 1998; Levitas et al., 2003). Thus, the desired potential should be reduced to known potentials for each of the phase transformations and have some noncontradictory representation for simultaneous variation of \( \Upsilon \) and \( \vartheta \). The Helmholtz energy per unit volume consists of elastic \( \psi^e \), thermal \( \psi^\theta \), and gradient \( \psi^{\nabla} \) parts, and the term \( \tilde{\psi}^\theta \) describing double-well barriers between phases:

\[
\psi = \psi^e + \tilde{\psi}^\theta + \psi^\theta + \psi^{\nabla};
\] (2.3)

\[
\psi^\theta = \Delta G^\theta(\theta, \vartheta)q(\Upsilon, 0);
\] (2.4)

\[
\psi^e = 0.5 \left( K(\Upsilon, \vartheta)\varepsilon_{el}^2 + 2\mu(\Upsilon, \vartheta)|\varepsilon_{el}|^2 \right);
\] (2.5)

\[
\psi^{\nabla} = 0.5 \left( \beta^{s0}(\vartheta)|\nabla \Upsilon|^2 + \beta^{21}\phi(\Upsilon, a_\vartheta, a_\theta)|\nabla \vartheta|^2 \right);
\] (2.6)

\[
\tilde{\psi}^\theta = A^{s0}(\theta, \vartheta)\Upsilon^2(1 - \Upsilon)^2 + A^{21}(\theta)\vartheta^2(1 - \vartheta)^2 q(\Upsilon, 0).
\] (2.7)

Here, \( K \) and \( \mu \) are the bulk and shear moduli; \( \beta^{s0} \) and \( \beta^{21} \) are \( SM \) and \( SS \) gradient energy coefficients, respectively; \( \Delta G^\theta \) and \( A^{s0} \) are the difference in thermal energy and energy barrier between \( S \) and \( M \); \( A^{21} \) is the \( SS \) energy barrier; \( q \) and \( \phi \) are the interpolating functions, and \( a \) with various subscripts are parameters in them. The transformation strain is

\[
\varepsilon_t = [\varepsilon_{t1} + (\varepsilon_{t2} - \varepsilon_{t1}) q(\vartheta, a_{t\vartheta})] q(\Upsilon, a_{t\Upsilon}).
\] (2.8)
All functions of Υ (or ϑ) smoothly interpolate properties of solid-melt (or two solid) phases, e.g., difference between thermal energy of solids and melt,

\[ \Delta G^\theta(\vartheta) = \Delta G^\theta_{10} + (\Delta G^\theta_{20} - \Delta G^\theta_{10}) q(\vartheta, 0), \]  

(2.9)

barrier between solid and melt,

\[ A^{s0}(\theta, \vartheta) = A^{10}(\theta) + (A^{20}(\theta) - A^{10}(\theta)) q(\vartheta, a_\theta), \]  

(2.10)

gradient energy coefficient,

\[ \beta^{ms}(\vartheta) = \beta^{s1-m} + (\beta^{s2-m} - \beta^{s1-m}) q(\vartheta, a_{ms}), \]  

(2.11)

bulk modulus,

\[ K(\Upsilon, \vartheta) = K_0 + (K_s(\vartheta) - K_0) q(\Upsilon, a_K), \]  

(2.12)

\[ K_s(\vartheta) = K_{s1} + (K_{s2} - K_{s1}) q(\vartheta, a_{ks}), \]  

(2.13)

and shear modulus,

\[ \mu(\Upsilon, \vartheta) = \mu_0 + (\mu_s(\vartheta) - \mu_0) q(\Upsilon, a_\mu), \]  

(2.14)

\[ \mu_s(\vartheta) = \mu_{s1} + (\mu_{s2} - \mu_{s1}) q(\vartheta, a_{ms}). \]  

(2.15)

Interpolating function \( q(x, a) = ax^2 - 2(a - 2)x^3 + (a - 3)x^4 \) varies between 0 and 1 when \( x \) varies between 0 and 1 and has zero \( x \)--derivative at \( x = 0 \) and \( x = 1 \). Function \( \phi(\Upsilon, a_\phi, a_0) = a_\phi \Upsilon^2 - 2(a_\phi - 2(1 - a_0)) \Upsilon^3 + (a_\phi - 3(1 - a_0)) \Upsilon^4 + a_0 \) differs from \( q \) in that it is equal to \( a_0 \) (rather than 0) at \( \Upsilon = 0 \). Thus, we penalized the gradient energy for solid-solid interface even within the complete \( IM (\Upsilon = 0) \). The difference between thermal energy of \( S \) and \( M \) is

\[ \Delta G^{s0}_{s0} = -\Delta s_{s0}(\theta - \theta^{s0}_c), \quad s = 1, 2, \]  

(2.16)

where \( \theta^{s0}_c \) is the equilibrium temperature between solid phase \( S_s \) and \( M \), and \( \Delta s_{s0} \) is the jump in entropy between \( S_s \) and \( M \). Energy barriers between \( S_s \) and \( M \) are \( A^{s0}(\theta) = A^{s0}_c(\theta - \theta^{s0}_c) \) with \( \theta^{s0}_c \) for critical temperature of the loss of stability of the phase \( S_s \) toward melt; barrier between solid phases is \( A^{21}(\theta) = A^{21}_c + A^{21}_c(\theta - \theta^{21}_c) \) with \( \theta^{21}_c \) for the critical temperature of the loss of stability of the phase \( S_2 \) toward \( S_1 \) (when \( A^{21}_c(0) = 0 \)).
Figure 2.2: Plot of the local Landau potential $\psi = \psi^0 + \hat{\psi}$ with neglected elastic energy (Eqs. (1) and (4)) at different temperatures in the polar system of the order parameters $\Upsilon$ and $\vartheta$. (a) The 3D plot of the potential surface at $\theta = \theta_e^{21}$; (b) contour plot of the potential at $\theta < \theta_e^{21}$ when the $S_2$ phase is stable and two other are metastable; (c) contour plot of the potential at $\theta = \theta_e^{21}$, when both solids are at equilibrium, and (d) contour plot of the potential at $\theta > \theta_e^{21}$.

Schematic of the developed thermodynamic potential is shown for three different temperatures in Fig. 2.2. Applying the first and second laws of thermodynamics to the system with a non-local free energy, and assuming linear relation between thermodynamic forces and fluxes, we obtain the elasticity rule,

$$\sigma = K(\Upsilon, \vartheta) \varepsilon_{0e} I + 2\mu(\Upsilon, \vartheta) \mathbf{e}_{el},$$

and Ginzburg-Landau equations,

$$\dot{\Upsilon} = L_\Upsilon \left( -\rho \frac{\partial \psi}{\partial \Upsilon} + \frac{\beta^{21}}{2} \frac{\partial \phi}{\partial \Upsilon} |\nabla \vartheta|^2 + \nabla \cdot \left( \beta^0 \nabla \Upsilon \right) \right);$$

$$\dot{\vartheta} = L_\vartheta \left( -\rho \frac{\partial \psi}{\partial \vartheta} + \nabla \cdot \left( \beta^{21} \phi(\Upsilon, a_\phi, a_0) \nabla \vartheta \right) \right).$$

Here $L_\Upsilon$ and $L_\vartheta$ are the kinetic coefficients and derivatives of $\psi$ are evaluated at $\varepsilon = \text{const.}$

For $S_1M S_2$ diffuse interface, $\Upsilon$ varies from 1 to 0 and again to 1, and $\vartheta$ varies from 0 to 1 (Fig. 2.3). It is logical to assume that in M ($\Upsilon = 0$), variation of $\vartheta$ is irrelevant, in particular $\psi^\nabla$ should be independent of $\nabla \vartheta$, i.e., $a_0 = 0$. In particular, a similar condition is satisfied for
melting within grain boundary (Lobkovsky and Warren, 2002a; Tang et al., 2006a). However, our simulations demonstrate that with \( a_0 = 0 \), the problem formulation is ill-posed and results in zero width of the \( SS \) interface within melt and strongly mesh-dependent solution. Indeed, solution with the sharp \( S_1S_2 \) interface at the point with \( \Upsilon = 0 \) is an energy minimizer, and with an increasing number of finite elements, numerical solution tends to it. Thus, one must introduce \( a_0 > 0 \) to penalize interaction between \( S_1M \) and \( S_2M \) interfaces via \( \nabla \vartheta \) in the melt. At elevated temperatures, when width of \( IM \) is large and \( \Upsilon = 0 \) in the melt, energy of \( IM \) can be approximated as \( E^* = (G^0 - G^*)\delta^* + \beta^{21}a_0/(2\delta^*) \). With \( \delta^* \to \infty \) the effect of \( a_0 \) disappears, which confirms that we do not introduce contradiction for homogeneous melt or when distance between \( SM \) interface is large.

### 2.3 Analytical solutions and verification

One of the advantages of the developed model is that, in contrast to multiphase models (Tiaden et al., 1998; Levitas et al., 2003; Levitas and Javanbakht, 2011b), each of three phase transformations is described by a single order parameter, without additional constraints on the order parameters. An analytical solution for each interface between \( i \) and \( j \) phases, propagating along \( y \)-direction is (Levitas, 2013c; Levitas et al., 2003)

\[
\eta_{ij} = \frac{1}{1 + e^{-p(y-v_{ij}t)/\delta_{ij}}}; \quad (2.20)
\]

\[
\delta_{ij} = p\sqrt{\beta_{ij}/\left(2\left(A_{ij}(\theta) - 3\Delta G^\theta_{ij}(\theta)\right)\right)}; \quad (2.21)
\]

\[
v_{ij} = 6L_{ij}\delta_{ij}\Delta G^\theta_{ij}(\theta)/p; \quad (2.22)
\]

\[
E_{ij} = \sqrt{2\beta_{ij}\left(A_{ij}(\theta) - 3\Delta G^\theta_{ij}(\theta)\right)/6}, \quad (2.23)
\]

where \( p = 2.415 \) (Levitas et al., 2003), \( \eta_{10} = \Upsilon \) at \( \vartheta = 0 \); \( \eta_{20} = \Upsilon \) at \( \vartheta = 1 \), and \( \eta_{21} = \vartheta \) at \( \Upsilon = 1 \); \( v_{ij} \) is the interface velocity. These equations allow us to calibrate material parameters \( \beta_{ij}, A_{ij}, \theta_{ij}, \), and \( L_{ij} \) when the temperature dependence of the interface energy, width, and velocity are known. Energy of the \( IM, E^* \), is defined as an excess energy, with respect to \( S_1 \) for points with \( \vartheta \leq 0.5 \) and with respect to \( S_2 \) for points with \( \vartheta > 0.5 \). Numerical solutions show good correspondence to the analytical solutions for interface profile and velocity. Note
that for $\Upsilon = 1$ our model reduces to the melting model in (Levitas and Samani, 2011a,b), which describes well experimental results on size dependence of melting temperature and temperature dependence of the width of surface melt for Al. For $\vartheta = 0$ or 1, our model reduces to the model for solid-solid transformation in (Levitas and Javanbakht, 2011b, 2010; Levitas et al., 2003), which was broadly used for studying martensitic transformations in bulk and at the surface and predicting various scale and mechanics effects. When phases 1 and 2 are the same but in twin relation to each other, our model reduces to that in (Levitas et al., 2013), which very well describes different nontrivial nanostructures during multivariant martensitic phase transformations and twinning. All these results verify correctness of our model for the nontrivial particular cases.

2.4 Results and discussion

The $SM$ interface is considered to be coherent with vanishing shear modulus for melt, $\mu_0 = 0$. For simplicity, all transformation strains are pure volumetric. Properties of melt, $\delta$ phase ($S_1$) and $\beta$ phase ($S_2$) of energetic material HMX ($C_4H_8N_8O_8$) will be used (Levitas et al., 2006a, 2004) (when available), for which $IM$ was considered. It is assumed that all $a = 3$; all phases have $K = 15GPa$, solid phases possess $\mu = 7GPa$ and $\beta^{0}(\vartheta) = const$; $L_\Upsilon = 2 L_\vartheta = 2596.5m^2/(Ns)$, $\Delta s_{10} = -793.79kJ/m^3K$, $\Delta s_{20} = -935.45kJ/m^3K$, melting temperatures $\theta_{e}^{10} = 550K$ and $\theta_{e}^{20} = 532.14K$; $\theta_{e}^{21} = 432K$, $\varepsilon_{0t}^{10} = -0.067$, $\varepsilon_{0t}^{20} = -0.147$ (i.e., $\varepsilon_{0t}^{21} = -0.08$); $\vec{A}_{e}^{21} = 0$, $\vec{A}_{i}^{ij} = -3\Delta s_{ij}$ (such a choice corresponds to the temperature-independent interface energies and widths (Levitas, 2013c)); $\theta_{e}^{ij} = \theta_{e}^{ij} + pE_{ij}/(\Delta s_{ij} \delta^{ij})$ and $\beta^{ij} = 6E_{ij} \delta^{ij}/p$ (Levitas et al., 2003); $E^{21} = 1J/m^2$ and $\delta^{21} = 1nm$. A $24 \times 8nm^2$ rectangular sample with a roller boundary condition on the left side and fixed lower left point is modeled. Two initial conditions are considered: (a) equilibrium $SS$ interface and (b) equilibrium $S_1M$ and $MS_2$ interfaces with quite a broad melt ($\Upsilon = 0$) region between two solids.

Stress-free $IM$ — First, we will consider the case without mechanics. In Fig. 2.3, minimum value of $\Upsilon$ is plotted for $\vartheta = \theta_{e}^{21} = 432K$ (i.e., 100 K below $\theta_{m}^{en}$), $\varphi_0 = 0$, and different $k_E$, $k_\delta$, and initial conditions. Note that the effect of temperature is similar to the effect of $k_\delta$. For small $k_\delta$, there is only a single stationary solution independent of the initial conditions, corresponding
to barrierless premelting and melting within SS interface. Degree of melting (disordering) continuously increases with increasing $k_E$ and temperature. There is not any hysteresis while increasing/decreasing temperature. While for $k_E \geq 2.7$ increase in $k_\delta$ promotes IM (reduces $\Upsilon_{\min}$), for $k_E \leq 2.5$, dependence $\Upsilon_{\min}(k_\delta)$ is surprisingly nonmonotonous, with disappearance of IM above critical $k_\delta$. In contrast, for larger $k_\delta$, different initial conditions result in two different stationary nanostructures. For SS initial condition, premelting does not start up to some quite large critical value $k_E$ (e.g., $k_E = 3.39$ for $k_\delta = 1$), above which jump-like (i.e., first-order) premelting or complete melting occurs. For SMS initial conditions, almost complete melt is stabilized at $k_E = 1.94$ (for $k_\delta = 1$), i.e., even below the critical value $k_E = 2$ for premelting at $\theta_m^e$. While for $k_E \geq 2.7$, increase in $k_\delta$ promotes IM (similar to SS initial state), for $k_E \leq 2.5$, dependence $\Upsilon_{\min}(k_\delta)$ is very nontrivial, with IM gap (i.e., lack of IM) in some range of $k_\delta$, which increases with decreasing $k_E$. Outside the IM gap, with increasing/decreasing temperature, discontinuous first-order phase transformations to and from melt occur at different temperatures, exhibiting significant hysteresis. Increase in $k_\delta$ increases value of $k_E$ for melting from SS state and reduces critical $k_E$ for keeping melt from SMS state. Thus, at $k_\delta = 1.2$, almost complete melt can be kept within SS interface for $k_E = 1.58$. Increasing $k_\delta$ increases the width of the hysteresis loop and also shifts melting to higher temperatures.

Presence of two stable stationary nanostructures indicates that there is one more unstable nanostructure between them, which represents a critical nucleus. If the difference between energy of the critical nucleus and SS (or SMS) interfaces is smaller than $(40 - 80)k_B\theta$, where $k_B$ is the Boltzmann constant, then melting (or solidification) within SS interface will occur due to thermal fluctuations. Finding critical nucleus and kinetic studies will be performed elsewhere.

Effect of temperature and the parameter $a_0$, on the minimum stationary value of $\Upsilon_{\min}$, interface energy, interface width, and velocity were studied for $k_E = 4$ and $k_\delta = 1$ (Fig. 2.4). The width of IM, $\delta^*$, is defined as the difference between locations of two SM interfaces where $\Upsilon = 0.5$. Note that almost complete melt of the width exceeding 1nm exists at $0.65\theta_m^e$, i.e., $240K$ below the melting temperature. For any $a_0$, increasing temperature promotes melting, i.e., reduces $\Upsilon_{\min}$ and the SMS interface energy, and increases $\delta^*$ and interface velocity (for
Figure 2.3: Intermediate melt formation at $\theta_{c2} = 432K$ ($\sim 100K$ below melting temperature) and $a_0 = 0$. (a) Minimum stationary value of $\Upsilon_{\text{min}}$ within SS interface as a function of $k_E$, starting from SS (black lines and triangles) and SMS (red lines and circles) initial states for several $k_\delta$. Inset shows distribution of $\Upsilon$ and $\vartheta$, when almost complete melt (black solid line) and premelt (dotted red line) are formed. (b) Minimum stationary value of $\Upsilon_{\text{min}}$ within SS interface versus $k_\delta$, starting from SS (dots) and SMS (solid lines) initial states for several $k_E$. Coincidence of solutions for different initial conditions corresponds to continuous reversible premelting and melting. When solutions do not coincide, a jump-like transformation to and from IM occurs, exhibiting significant hysteresis. Nonmonotonous $\Upsilon_{\text{min}}(k_\delta)$ and IM gap for small $k_\delta$ are remarkable.
Figure 2.4: Effect of temperature on the formation, energy, and width of IM, as well as interface velocity in presence of IM. (a) Minimum value of $\Upsilon_{\min}$ indicating formation of IM, (b) and (c) normalized SMS interface energy and width, (d) SMS interface velocity versus normalized temperature $\theta/\theta_{e}^{21}$. Solid line in (d) is a velocity for SS interface obtained both analytically, Eq. (2.22), and numerically. Simulations are performed for $k_{E} = 4$, $k_{\delta} = 1$, and different values of $a_{0}$, starting with SS interface.

When temperature approaches the melting temperature of $\beta$ phase, $\Upsilon_{\min} \simeq 0$ and the width of IM is determined by $\partial E^*/\partial \delta^* = 0$, which results in $\delta^* = \sqrt{0.5} \beta_{21} a_{0}/(G^{0} - G^*)$; $\delta^*$ diverges when $\theta \rightarrow \theta_{c}^{m}$ and $G^{0} \rightarrow G^*$. The energy of IM tends to the energy of two SM interfaces, which is $0.5E_{21}$ for our case. Velocity of SMS interface is below the velocity of SS interface (even for $L_T = 500L_\vartheta$), is zero at $\theta_{e}^{21}$, and varies linearly with deviation from $\theta_{e}^{21}$ with some acceleration close to the melting temperature. At very small $a_{0}$, interface velocity tends to zero. Since for very small $a_{0}$, SS interface width within melt tends to zero, a very large number of finite elements is required to obtain mesh-independent results.

Energy of SMS interface monotonously increases with increase in $a_{0}$, as expected. Value $\Upsilon_{\min}$ also increases monotonously with increase in $a_{0}$, excluding temperatures close to $\theta_{e}^{20}$. In
the entire temperature range, magnitude of the velocity of SMS interface in both directions increases with increase in $a_0$. The most unexpected is the dependence of the IM width on $a_0$. According to the above analytical model, close to the melting temperature, $\delta^*$ should grow when $a_0$ grows, which is in agreement with simulation results (Fig. 2.4c). The same is true down to $\theta/\theta_c^{21} \simeq 0.85$, while the effect of $a_0$ is getting weaker. At $\theta/\theta_c^{21} \simeq 0.85$, the effect of $a_0$ disappears and reverses at lower temperature. There are no simplified models or any indications on other plots ($Y_{min}$ and $E^*$ vs. $\theta/\theta_c^{21}$), which could explain such a behavior for the IM width. Thus, Fig. 2.4c serves for the development of new intuition and calls for finding the reasons for the crossover in temperature dependence of the IM width.

If $a_0$ is excluded from the dependences $E^*(\theta, a_0)$ and $\delta^*(\theta, a_0)$, one obtains dependence of the energy of the SMS interface vs. its equilibrium width for various temperatures, Fig. 2.5. While for high temperatures an expected increasing dependence of the SMS interface energy on its width is obtained, at $\theta = 382K$ interface energy is independent of $\delta^*$, and at lower temperature, a counterintuitive reduction in interface energy with growing $\delta^*$ is observed.

![Figure 2.5: Energy of the IM interface vs. its equilibrium width for various temperatures, obtained by excluding $a_0$ from plots in Figure 2b and 2c of the main article.](image)

Coupling with Mechanics — Elastic energy at coherent SS interface strongly promotes the formation of IM (Fig. 2.6 for $k_\delta = 1$), and this effect increases with the size of a sample.
Figure 2.6: Effect of mechanics on the formation of IM. Formation of IM with (bottom row) and without (top row) mechanics starting from SS interface for $\theta = \theta_{21}^2$, $k_\delta = 1$ and $a_0 = 0.01$ are shown. Melt appears at $k_E = 3.5$ when mechanical energy is negligible and at $k_E = 3.3$ for the case with mechanics.

Starting from SS interface, with energy (including the elastic energy) of $\sim 1.1 J/m^2$, melt forms at $k_E = 3.3$, while neglecting the elastic energy melt forms at $k_E = 3.5$. Elastic energy increases the width of IM and also drives an SMS interface at $\theta = \theta_{21}^2$ (when $v = 0$ without mechanics), because it changes with interface position in a finite sample. While, without mechanics, the IM is homogeneous along the SS interface, with mechanics it starts at the intersection of SS interface and free surface. Velocity, width, and energy of SMS interface when the elastic energy is considered are $70 m/s$, $2.4 nm$, and $0.834 J/m^2$, respectively. For the case without mechanics and $E_{21} = 1 J/m^2$, the interface is stationary and interface width and energy are $1.64 nm$ and $0.79 J/m^2$, respectively. For $k_\delta = 0.2$ with mechanics, jump-like incomplete IM forms for $k_E = 2.0$, in contrast to continuous premelting to the same $\Gamma_{min} = 0.57$ at $k_E = 3.1$ (see Fig. 2.7). For pre-existing melt, $k_\delta = 1$ and $a_0 = 0.01$, the IM remains stable even at $k_E = 1$, while for the case with neglected elastic energy, stationary melt remains at $k_E \geq 2$.

2.5 Concluding remarks

Phase field approach is developed for the description of solid-solid phase transformations via IM hundreds of degrees below melting temperature. Although quantitative comparison with experiment is currently impossible due to the lack of data on interface energies, our results demonstrate possibility of the IM formation under conditions that were not accessible within sharp interface approach.
Figure 2.7: Presence of mechanics promotes IM formation. $\Upsilon_{\min}$ is plotted for different ratios of the energies of SS and SM interfaces, $k_E$, for $k_\delta = 0.2$, $a_0 = 0.01$, and $\theta = \theta_{\text{c}}^2 = 432K$, for the case with initial SS interface (black) and pre-existing melt SMS (red). Results without mechanics (line) and with mechanics (dots) are presented. In both cases, continuous and reversible intermediate premelting and melting are observed. Promotional effect of relaxation of elastic stresses at the SS coherent interface on the formation of IM is evident.

Detailed parametric simulations revealed surprising scale effects as well effects of kinetics, elastic stresses, and interaction between SM interfaces. In particular, various types of IM and scenarios for its appearance and disappearance are found. They include continuous and reversible pre-melting and melting, and jump-like barrierless transformation to IM. The latter exhibits large hysteresis and persistence of IM at lower temperatures than what was expected, without barrierless resolidification. Surprising scale effect related to $k_\delta$ is revealed, indicating that increasing $k_\delta$ suppresses barrierless IM but allows retaining of IM at much lower temperature and even for $k_E < 2$. An unexpected nonmonotonous effect of $k_\delta$ is found, which produces the IM gap (i.e., lack of IM) in some $k_\delta$ and $k_E$ ranges. For the parameters under study, IM reduces interface velocity in comparison with that for the velocity of SS interface. Mechanics (i.e., stress generation by coherent SS interface and their relaxation due to IM) produces additional promoting effect on IM and further reduces temperature and ratio $k_E$ for barrierless IM nucleation (even below $k_E = 2$) and for its persistence (even at $k_E = 1$). Thermally activated IM via critical nucleus, which is probably happening in HMX (Levitas et al., 2004, 2006a), will be treated in future studies.
Our phase field approach can be adjusted to treat various other experimental problems related to wetting, surface-induced phenomena, and intergranular and interface phases, mentioned in the Introduction. If intermediate phase is solid, additional mechanics and size-induced morphological transitions are expected (Levitas and Javanbakht, 2010, 2011b).
CHAPTER 3. PROPAGATING PHASE INTERFACE WITH INTERMEDIATE INTERFACIAL PHASE: PHASE FIELD APPROACH

An advanced three-phase phase-field approach (PFA) is suggested for a non-equilibrium phase interface which contains an intermediate phase, in particular, a solid-solid interface with a nanometer-sized intermediate melt ($IM$). Thermodynamic potential in the polar order parameters is developed, which satisfies all thermodynamic equilibrium and stability conditions. Special form of the gradient energy allowed us to include the interaction of two solid-melt interfaces via intermediate melt and obtain a well-posed problem and mesh-independent solutions. It is proved that for stationary 1D solutions to two Ginzburg-Landau equations for three phases, the local energy at each point is equal to the gradient energy. Simulations are performed for $\beta \leftrightarrow \delta$ phase transformations (PTs) via $IM$ in HMX energetic material. Obtained energy - $IM$ width dependence is described by generalized force-balance models for short- and long-range interaction forces between interfaces but not far from the melting temperature. New force-balance model is developed, which describes phase field results even $100K$ below the melting temperature. The effects of the ratios of width and energies of solid-solid and solid-melt interfaces, temperature, and the parameter characterizing interaction of two solid-melt interfaces, on the structure, width, energy of the $IM$ and interface velocity are determined by finite element method. Depending on parameters, the $IM$ may appear by continuous or discontinuous barrierless disordering or via critical nucleus due to thermal fluctuations. The $IM$ may appear during heating and persist during cooling at temperatures well below than it follows from sharp-interface approach. On the other hand, for some parameters when $IM$ is expected, it does not form, producing an $IM$-free gap. The developed PFA represents a quite general three-phase model and can be extended to other physical phenomena, such as marten-

This chapter is adapted from (Momeni and Levitas, 2014).
sitic PTs, surface-induced premelting and PTs, premelting/disordering at grain boundaries, and developing corresponding interfacial phase diagrams.

3.1 Introduction

The PTs between two solid phases via nanoscale molten layer, more than 100K below the melting temperature, have been predicted thermodynamically (Levitas et al., 2004, 2006b,a) for $\beta - \delta$ PT in HMX organic crystal and confirmed indirectly but both qualitatively and quantitatively by sixteen experimental evidences (Henson et al., 2002; Smilowitz et al., 2002). In particular, equality of predicted activation energies and melting energies, absence of athermal friction during solid-solid PT, dependence of the rate constant on the heat of fusion, and the interface velocity and concentration of the $\delta$ phase versus time, which follow from the theory, were confirmed experimentally. While change in interface energy was neglected, the main reason for the melting below the melting temperature was related to the relaxation of the internal stresses generated by relatively large volumetric strain for $\beta - \delta$ PT. However, as soon as the material melts, the stresses relax and the stress-free melt resolidifies into the stable phase at a temperature much below the melting temperature. That is why such a melt was called the virtual melt and was considered an intermediate transitional state. Thus, during propagation of the solid 1-melt-solid 2 ($S_1MS_2$) interface through the sample, one solid phase melts and resolidifies into another phase. It was predicted that virtual melting would be expected in materials with a complex crystalline structure, and a large transformation strain tensor in which traditional stress relaxation mechanisms (dislocation nucleation and motion, and twinning) are suppressed.

In (Levitas, 2005), virtual melting was considered as a mechanism of crystal-crystal PTs and an amorphization for materials with decreasing melting temperature under pressure (for example, ice, Si, Ge, geological and others materials). It was not necessarily related to relaxation of internal stresses. Virtual melting was confirmed experimentally for amorphization in avandia (an important pharmaceutical substance used as an insulin enhancer) in (Randzio and Kutner, 2008) during a scanning transitionmeter study at heating.

A mechanism for crystal-crystal PTs via *surface-induced virtual pre-melting and melting*
was justified thermodynamically and confirmed experimentally in (Levitas et al., 2012) for the PT from metastable pre-perovskite to cubic perovskite in PbTiO$_3$ nanofibers, an important ferroelectric material. A theory in (Levitas et al., 2012) also introduced the IM, which in contrast to virtual melt, can be in thermodynamic equilibrium with an internally nonhydrostatically stressed solid below melting temperature. Reduction in the interface energy and relaxation of elastic energy provide driving forces for such a melting. Also, during the product crystal growth stage, a quenched melt was experimentally found within the solid-solid interface, which is the first direct experimental confirmation of the crystal-crystal PT via virtual melting or IM.

Virtual melting, as a mechanism of plastic flow and stress relaxation under high strain rate loading of copper and aluminum, was predicted thermodynamically and confirmed by molecular dynamics simulations in (Levitas and Ravelo, 2012). The thermodynamic conditions for the formation of virtual melting or IM were formulated in (Levitas et al., 2004; Levitas, 2005; Levitas et al., 2006a, 2012) using the sharp interface approach. When size-dependence of the interface energy was taken into account in (Levitas et al., 2012), it allowed us to determine the width of IM, $\delta^*$. This is similar to force-balance models (Dash et al., 1995; Luo, 2007; Dash et al., 2006; Cantwell et al., 2014; Luo and Chiang, 2008) applied for other purposes, which takes into account an additional interaction energy between two interfaces when they get close to each other. Since the width of the IM is on the order of nanometers, i.e., comparable with the width of solid-solid and solid-melt interfaces, and also because melting (disordering) may not be complete, the sharp interface approaches (Grinfeld, 1991; Levitas et al., 2004; Levitas, 2005; Levitas et al., 2006a, 2012) are oversimplified and do not represent a strict proof of phenomena.

In order to avoid the problems inherent to the sharp interface approach, we have developed a phase field approach (PFA) that resolves finite width interfaces. It represents a justification and a generalization of our PFA presented in (Levitas and Momeni, 2014). Thus, in comparison with (Levitas and Momeni, 2014), the following significant and novel results are obtained. All thermodynamic equilibrium and instability conditions are explicitly analyzed; generalization of the force-balance models for short range and long range interaction between interfaces, as well
as a new model for these interactions are suggested; phase field modeling of interaction between
two $SM$ interfaces was studied in detail and connected to force-balance models; solutions for
critical $IM$ nuclei are found and kinetic conditions for their appearance are determined. An
energy integral was found for stationary 1D solutions to two Ginzburg-Landau equations for
three phases, i.e., for plane interface with $IM$ or for all critical nuclei. Point-wise equality of
the local and the gradient energy was proved. In addition to the above new topics, which were
not considered in (Levitas and Momeni, 2014), the parametric study here is much broader than
in (Levitas and Momeni, 2014), which revealed some new effects. In particular, the $S_1MS_2$
interface velocity for some parameters is larger than the $S_1S_2$ interface velocity and $IM$ width
does not diverge when the first melting temperature is reached. We neglect mechanics here
and $IM$ is driven by the reduction in interface energy during $IM$; effects of internal stresses
and interface tension will be studied in the next paper.

The paper is arranged as follows. The thermodynamics potential for three-phase system
with polar order parameters, one of which describes melting and another one solid-solid PT is
developed in Section 3.2. It satisfies all desired thermodynamic equilibrium and instability con-
ditions. The necessity of introducing gradient energy for the $S_1S_2$ interface within $IM$ (which
sounds counterintuitive) is demonstrated from the point of view of obtaining a well-posed prob-
lem formulation and an objective (i.e., mesh-independent) solution, as well as description of
the interaction between two $SM$ interfaces. Corresponding Ginzburg-Landau (GL) equations
have been formulated. In Section 3.3, analytical solutions for dry solid-solid and $SM$
interfaces and for the determination of energy, width, and velocity of these interfaces are obtained. An
energy integral was found for stationary 1D solutions to two GL equations for three phases,
i.e., for plane interface with $IM$ or for all $IM$ critical nuclei. It results in the statement that
the excess of the local energy at each point is equal to the gradient energy. In Section 3.4,
material parameters of the model are calibrated utilizing data for HMX energetic material.
Some comparison of numerical and analytical solutions is presented. Section 3.5 is devoted to
the generalization of some known force-balance models. The best force-balance model describes
PFA results even $100K$ below the melting temperature. The effects of four parameters, namely
ratios of width, $k_\delta$, and energies, $k_E$, of $S_1S_2$ and $SM$ interfaces, temperature, and parame-
characterizing interaction of two solid-melt interfaces, on the structure, width, energy of the IM and interface velocity are determined numerically. Depending on parameters, the IM may appear by continuous reversible (without hysteresis) or discontinuous (with hysteresis) disordering. The partial and complete IM may nucleate during heating and is retained during cooling at temperatures significantly below what would be expected from the sharp-interface approach. For some parameters when IM is expected, it does not form, producing IM-free gap. In Section 3.7, the procedure to find the critical nucleus is described and its size structure is studied in detail using a kinetic criterion. Comparison with other close approaches to different phenomena and the possibility of applying the current approach to other phenomena are discussed in Section 3.8.

3.2 Thermodynamic theory

Our objective is to develop the simplest local thermodynamic (Landau) potential to describe PTs between three phases, which reduces to the potential presented in (Levitas and Preston, 2002a,b; Levitas et al., 2003) for PTs between each of the two phases. Some requirements of the thermodynamic potential in (Levitas and Preston, 2002a,b; Levitas et al., 2003) are related to the effect of stresses on PTs. Since we will include the effect of stresses in the next paper it is important to include the same requirements even in the stress-free formulation.

3.2.1 Thermodynamic potential

In order to develop a thermodynamic potential for PTs between three phases, the polar order parameters are introduced in a plane with the radial $\Upsilon$ and the angular $\vartheta$ order parameters (Fig. 3.1). In this formulation $\pi \vartheta/2$ is the angle between the radius vector $\Upsilon$ and the positive first-axis. The origin of the polar coordinate system in the plane of the order parameters, which is described by $\Upsilon = 0$ for any $\vartheta$, is considered as the reference phase 0. Here phase 0 is a melt $M$, but in general it can be any phase, e.g., austenite for multivariant martensitic transformations (Levitas and Preston, 2002b; Levitas et al., 2003, 2013). Phases 1 and 2 correspond to ($\Upsilon = 1$ and $\vartheta = 0$) and ($\Upsilon = 1$ and $\vartheta = 1$), respectively. In this paper, they will be considered as solid phases $S_1$ and $S_2$. However, if phase 0 is austenite, phases 1 and 2 can be treated as two
Figure 3.1: Contour plot of the local Landau potential $\psi_l = \psi^\theta + \tilde{\psi}$ in the polar system of the order parameters $\Upsilon$ and $\vartheta$ at thermodynamic equilibrium temperature between solid phases $\theta = \theta_1$ for different instability temperatures of solid phases $\theta_1$ and $\theta_2$ and corresponding parameters $k_E$ and $k_\delta = 1$. The 3D plot of the potential surface is shown in (e) along with its contour plot, for the same parameters as plotted in (a).

martensitic variants. Contour plots of the local part of the Helmholtz energy $\psi$ and each of the three phases are shown in Fig. 3.1 for HMX energetic crystals (see Section 3.4 for details of material properties). Each of the $S \leftrightarrow M$ PTs correspond to the variation of $\Upsilon$ between 0 and 1 at a specific $\vartheta = 0$ or 1, while the $S_1 \leftrightarrow S_2$ PTs correspond to variation of $\vartheta$ between 0 and 1 for $\Upsilon = 1$.

One of the requirements in (Levitas and Preston, 2002a,b; Levitas et al., 2003) is that each phase corresponds to the extrema of the thermodynamic potential for any temperature $\theta$. In other words, for any temperature $\theta$, equations $\frac{\partial \psi}{\partial \Upsilon} = \frac{\partial \psi}{\partial \vartheta} = 0$ have roots at $M \equiv (\Upsilon = 0$ and any $\vartheta), S_1 \equiv (\Upsilon = 1$ and $\vartheta = 0)$ and $S_2 \equiv (\Upsilon = 1$ and $\vartheta = 1)$. This condition allows one to easily approximate variation of all properties of phases during phase transformation. In particular, it allows one to prescribe a transformation strain tensor independent of temperature (Levitas and Preston, 2002a,b; Levitas et al., 2003). The other requirement is related to the condition for instability of equilibrium for each phase. The thermodynamic condition for instability
is traditionally expressed in terms of the second derivatives of the thermodynamic potential. Thus, if the matrix of the second derivatives of $\psi$ with respect to $\Upsilon$ and $\vartheta$ ceases to be positive definite for the given phase, this phase loses its stability and transforms to an alternative phase. In general, this condition results in very complex equations which do not introduce the desired instability condition. Therefore, an additional requirement was formulated in (Levitas and Preston, 2002a,b; Levitas et al., 2003), which significantly simplifies the instability conditions, which is the cross derivative $\partial^2 \psi(\theta, \Upsilon, \vartheta)/\partial \Upsilon \partial \vartheta = 0$ for $M$, $S_1$, and $S_2$ at any temperature (see below). Then the desired conditions for $M \to S$ PT (Eq. (3.23)) and $S_1 \to S_2$ PT (Eq. (3.25)) can be easily satisfied.

It is assumed that the material properties including potential barriers, thermal parts of free energy, and the critical temperatures for the loss of stability of each phase are known from either experimental measurements or molecular simulations. The simplest expression for the Helmholtz free energy within a fourth-degree polynomial that satisfies all the desired conditions has the following form:

Helmholtz Energy

$$
\psi = \psi^\theta + \tilde{\psi}^\theta + \psi^\nabla = \psi^I + \tilde{\psi}^\theta; \quad \psi^I = \psi^\theta + \tilde{\psi}^\theta. \quad (3.1)
$$

Thermal Energy

$$
\psi^\theta = G^\theta_{10}(\theta) + \Delta G^\theta_{10}(\theta, \vartheta)q(\Upsilon, 0). \quad (3.2)
$$

Energy Barrier

$$
\tilde{\psi}^\theta = A^{S_0}(\theta, \vartheta)\Upsilon^2(1 - \Upsilon)^2 + A^{21}(\theta)\vartheta^2(1 - \vartheta)^2q(\Upsilon, a_A). \quad (3.3)
$$

Gradient Energy

$$
\psi^\nabla = 0.5 \left[ \beta^{S_0}(\vartheta)|\nabla \Upsilon|^2 + \beta^{21}(\Upsilon, a_\vartheta, a_0)|\nabla \vartheta|^2 \right]. \quad (3.4)
$$

Change in Thermal Energy of Phases

$$
\Delta G^\theta(\theta, \vartheta) = \Delta G^\theta_{10} + \Delta G^\theta_{21}q(\vartheta, 0). \quad (3.5)
$$
Solid-Melt Energy Barrier Coefficient

\[ A^{S0}(\theta, \vartheta) = A^{10}(\theta) + [A^{20}(\theta) - A^{10}(\theta)] q(\vartheta, a_\vartheta). \] (3.6)

Solid-Melt Gradient Energy Coefficient

\[ \beta^{S0}(\vartheta) = \beta^{10} + (\beta^{20} - \beta^{10}) q(\vartheta, a_\vartheta). \] (3.7)

Interpolating Functions

\[
q(y, a) = ay^2 - 2(a - 2)y^3 + (a - 3)y^4; \quad (3.8) \\
\phi(\Upsilon, a_\phi, a_0) = a_\phi \Upsilon^2 - 2[a_\phi - 2(1 - a_0)] \Upsilon^3 + [a_\phi - 3(1 - a_0)] \Upsilon^4 + a_0. \quad (3.9)
\]

In Eqs. (3.1)-(3.9), \( G_0^\theta(\theta) \) is the thermal energy of the melt, \( \Delta G_0^\theta(\theta, \vartheta) \) is the difference in thermal energy between \( S \) and \( M \), \( \Delta G_{s0}^\theta \) \((s = 1, 2)\) is the difference in thermal energy between a specific solid phase \( S_s \) and \( M \), and \( \Delta G_{21}^\theta \) is the difference in thermal energy between solid \( S_2 \) and \( S_1 \); \( \beta^{S0} \) and \( \beta^{21} \) are \( SM \) and \( S_1S_2 \) gradient energy coefficients, respectively; thus, while capital \( S \) in super- and subscripts means solid and usually designates some function of \( \vartheta \), small \( s \), \( s = 1, 2 \), designates specific solid \( S_s \); \( A^{S0} \) and \( A^{21} \) are \( SM \) and \( S_1S_2 \) energy barrier coefficients, respectively. The interpolation function \( q(y, a) \), with \( y = \vartheta \) or \( \Upsilon \) and different values of \( a \) \((a_\vartheta, a_\beta, ...)\) monotonously connects properties of phases and satisfies the following conditions

\[ q(0, a) = 0; \quad q(1, a) = 1; \quad \partial q(0, a)/\partial y = \partial q(0, a)/\partial y = 0; \quad 0 \leq a \leq 6. \] (3.10)

The first two equations of (3.10) provide proper change in values of the chosen property; the second two equations allow one to satisfy conditions \( \partial \psi/\partial \Upsilon = \partial \psi/\partial \vartheta = 0 \) for each phase \((M \ or \ S_s)\) at any temperature \( \theta \) and provide smooth transition for the property of each phase. The last condition provides monotonous behavior of the function \( q \).

The interpolation function \( \phi(\Upsilon, a_\phi, a_0) \) satisfies the following conditions:

\[
\phi(0, a_\phi, a_0) = a_0; \quad \phi(1, a_\phi, a_0) = 1; \quad \partial \phi(0, a_\phi, a_0)/\partial \Upsilon = \partial \phi(1, a_\phi, a_0)/\partial \Upsilon = 0. \] (3.11)

where \( 0 \leq a_\phi \leq 6 \) and \( q(y, a) = \phi(y, a, 0) \). They are the same as conditions for \( q(y, a) \) except that \( \phi(\Upsilon, a_\phi, a_0) \) has a finite value \( a_0 \) (rather than 0) at \( \Upsilon = 0 \). The parameter \( a_0 \)
Figure 3.2: Interpolating functions \( q(y, a) \) (a) and \( \phi(y, a_\phi, a_0) \) (b) used in the thermodynamic potential functions are shown for \( 0 \leq a \leq 6 \). They have zero derivative at \( y = 0 \) and \( y = 1 \) and vary monotonously for \( 0 \leq y \leq 1 \). The horizontal dotted line indicates \( \phi(0, a_\phi, a_0) = a_0 \).

scales the dependence of \( S_1S_2 \) gradient energy within melt (\( \Upsilon = 0 \))—i.e., \( \psi(\Upsilon = \nabla\Upsilon = 0) = 0.5\beta^{21}a_0|\nabla\vartheta|^2 \), which seems irrelevant at first glance. However, it will be shown in the following sections that \( a_0 \) determines the interaction between two \( SM \) interfaces and plays a key role in determining the width of the \( IM \). Plots of the interpolating functions \( q(y, a) \) and \( \phi(\Upsilon, a_\phi, a_0) \) are shown in Fig. 3.2 for different parameter values. For PT between two phases the developed thermodynamic potential reduces to the following expressions. By setting \( \vartheta = 0 \) or 1, the potential simplifies to

\[
\psi = \Delta G_{s0}^\theta(\vartheta)q(\Upsilon, 0) + A^{s0}(\vartheta)\Upsilon^2(1 - \Upsilon)^2 + 0.5\beta^{s0}|\nabla\Upsilon|^2 \tag{3.12}
\]

for \( M-S_1 \) PT and by setting \( \Upsilon = 1 \), it reduces to

\[
\psi = \Delta G_{10}^\theta + \Delta G_{21}^\vartheta q(\vartheta, 0) + A^{21}(\vartheta)\vartheta^2(1 - \vartheta)^2 + 0.5\beta^{21}|\nabla\vartheta|^2. \tag{3.13}
\]

for \( S_1S_2 \) PT. Equations (3.12) and (3.13) are equivalent to within designations and the unimportant constant term \( \Delta G_{10}^\theta \). They are also equivalent to two-phase potential for austenite-martensite PT (Levitas and Preston, 2002a) and melting (Levitas and Samani, 2011b).

### 3.2.2 Ginzburg-Landau equations

Applying the first and second laws of thermodynamics to the system with a non-local free energy, and assuming a linear relation between thermodynamic forces and fluxes, we obtain the
GL equations:

\[
\frac{1}{L_T} \frac{\partial \Upsilon}{\partial t} = -\frac{\partial \psi}{\partial \Upsilon} - \frac{\beta^{21}}{2} \frac{\partial \phi(\Upsilon, a, a_0)}{\partial \Upsilon} |\nabla \vartheta|^2 + \nabla \cdot \left[ \beta^{S0}(\vartheta) \nabla \Upsilon \right];
\]

(3.14)

\[
\frac{1}{L_\vartheta} \frac{\partial \vartheta}{\partial t} = -\frac{\partial \psi}{\partial \vartheta} - \frac{\partial \beta^{S0}(\vartheta)}{\partial \vartheta} |\nabla \Upsilon|^2 + \nabla \cdot \left[ \beta^{21} \phi(\Upsilon, a, a_0) \nabla \vartheta \right],
\]

(3.15)

where \( L_T(\Upsilon, \vartheta, \theta) \) and \( L_\vartheta(\Upsilon, \vartheta, \theta) \) are the kinetic coefficients. The only requirements for the kinetic coefficients are

\[
L_T(\Upsilon, 0, \theta) = L_{10}(\Upsilon, \theta); \quad L_T(\Upsilon, 1, \theta) = L_{20}(\Upsilon, \theta); \quad L_\vartheta(1, \vartheta, \theta) = L_{21}(\vartheta, \theta),
\]

(3.16)

where \( L_{s0} \) are the kinetic coefficients for melting of the solid phase \( s \) and \( L_{21} \) are the kinetic coefficients for solid-solid PT. \( L_\vartheta(\Upsilon, \vartheta, \theta) \) should be a non-decreasing function of \( \Upsilon \) in order to avoid promotion of transition between incomplete solid phases (i.e., for \( \Upsilon < 1 \)). In the simplest case, \( \Upsilon \)- and \( \vartheta \)-dependence of the kinetic coefficients can be omitted. Elaborating the GL equations using the developed potential function results in

\[
\frac{1}{L_T} \frac{\partial \Upsilon}{\partial t} = \nabla \cdot \left[ \beta^{S0}(\vartheta) \nabla \Upsilon \right] - 2 \Upsilon (1 - \Upsilon) \left\{ 6 \Delta G^S(\theta, \vartheta) \Upsilon + A_{21}^{S0}(\theta, \vartheta) (1 - 2 \Upsilon) + \right. \\
A_{21}(\theta) \vartheta^2 (1 - \vartheta)^2 [a_{A} - 2 (a_{A} - 3) \Upsilon] + 0.5 \beta^{21} \left\{ a_{\phi} - 2 [a_{\phi} - 3 (1 - a_{0})] \Upsilon \right\} |\nabla \vartheta|^2 \right\};
\]

(3.17)

\[
\frac{1}{L_\vartheta} \frac{\partial \vartheta}{\partial t} = \nabla \cdot \left[ \beta^{21} \phi(\Upsilon, a, a_0) \nabla \vartheta \right] - 2 \vartheta (1 - \vartheta) \Upsilon^2 \left\{ 6 \Delta G_{21}^S \vartheta \Upsilon (4 - 3 \Upsilon) + \right. \\
A_{21}(\theta) (1 - 2 \vartheta) [a_{A} - 2 (a_{A} - 2) \Upsilon + (a_{A} - 3) \Upsilon^2] + \left[ A_{20}(\theta) - A_{10}(\theta) \right] (1 - \Upsilon)^2 \\
[a_{\beta} - 2 (a_{\beta} - 3) \vartheta] + 0.5 \left( \beta^{20} - \beta^{10} \right) [a_{\beta} - 2 (a_{\beta} - 3) \vartheta] (|\nabla \Upsilon|/\Upsilon)^2 \right\}.
\]

(3.18)

Eqs. (3.17)-(3.18) in combination with boundary conditions \( \mathbf{n} \cdot \nabla \Upsilon = 0 \) and \( \mathbf{n} \cdot \nabla \vartheta = 0 \) form the complete system of equations for the description of the PT process. Chosen boundary conditions imply conservation of energy of the external surface during PT.

### 3.2.3 Thermodynamic equilibrium and stability conditions for homogeneous states

For homogeneous states the gradient terms disappear and right-hand-side of Eqs. (3.17)-(3.18) reduces to \( \partial \psi^l/\partial \Upsilon \) and \( \partial \psi^l/\partial \vartheta \), respectively. It is clear that both derivatives are zero at any temperature for each of the phases—i.e., for \( M \equiv \{ \Upsilon = 0 \) and any \( \vartheta \} \), \( S_1 \equiv \{ \Upsilon = 1 \) and \( \vartheta \} \),
\( \vartheta = 0 \} \) and \( S_2 \equiv \{ \Upsilon = 1 \text{ and } \vartheta = 1 \} \). Therefore, each phase corresponds to thermodynamic equilibrium conditions at any temperature, as we required. The solutions of the equilibrium equations (extremum points of the free energy) along the paths between two solid phases (\( \Upsilon = 1 \)) are

\[ \vartheta^I = 0; \quad \vartheta^{II} = 1; \quad \vartheta^{III} = 0.5A^{21}/(A^{21} - 3\Delta G^{\theta}_{21}), \tag{3.19} \]

and for solid-melt interface (\( \vartheta = 0 \) or 1) they are

\[ \Upsilon^I = 0; \quad \Upsilon^{II} = 1; \quad \Upsilon^{III} = 0.5A^{s0}/(A^{s0} - 3\Delta G^{\theta}_{s0}). \tag{3.20} \]

If all three phases are stable or metastable (i.e., represents the local minima of the free energy), the roots \( \vartheta^{III} \) and \( \Upsilon^{III} \) correspond to the local energy maximum or minimax and represent energy barrier between phases. The barrier height for \( S_1 \rightarrow S_2 \) PT is

\[ \psi(\vartheta^{III}) - \psi(\vartheta^I) = (A^{21} - 4\Delta G^{21})(\vartheta^{III})^3/2, \tag{3.21} \]

and for \( M \rightarrow S \) PT is

\[ \psi(\Upsilon^{III}) - \psi(\Upsilon^I) = (A^{s0} - 4\Delta G^{s0})(\Upsilon^{III})^3/2, \tag{3.22} \]

The mixed derivative is also zero for each of the phases. In this case, the conditions for the loss of stability of each phase—i.e., PT criteria, simplify to:

\[ M \rightarrow S_s : \quad \frac{\partial^2 \psi^I(\theta, \Upsilon = 0, \vartheta = s - 1)}{\partial \Upsilon^2} \leq 0 \rightarrow A^{s0}(\theta) \leq 0; \tag{3.23} \]

\[ S_s \rightarrow M : \quad \frac{\partial^2 \psi^I(\theta, \Upsilon = 0, \vartheta = s - 1)}{\partial \Upsilon^2} \leq 0 \rightarrow A^{s0}(\theta) - 6\Delta G^{\theta}_{s0} \leq 0; \tag{3.24} \]

\[ S_1 \rightarrow S_2 : \quad \frac{\partial^2 \psi^I(\theta, \Upsilon = 1, \vartheta = 0)}{\partial \vartheta^2} \leq 0 \rightarrow A^{21}(\theta) \leq 0; \tag{3.25} \]

\[ S_2 \rightarrow S_1 : \quad \frac{\partial^2 \psi^I(\theta, \Upsilon = 1, \vartheta = 1)}{\partial \vartheta^2} \leq 0 \rightarrow A^{21}(\theta) + 6\Delta G^{\theta}_{21} \leq 0. \tag{3.26} \]

Eqs. (3.23) and Eq. (3.25) are desired PT conditions; other two conditions just follow from the potential and are non-contradictory.
Let us consider some specifications. Thus, let $\Delta G_{s0} = -\Delta s_{s0}(\theta - \theta_{e0}^{s0})$, where $\Delta s_{s0} < 0$ is the jump in entropy between solid phase $S_s$ and melt $M$ and $\theta_{e0}^{s0}$ is the thermodynamic equilibrium melting temperature of $S_s$. The linear temperature dependence of $\Delta G^\theta$ is due to neglecting the difference between specific heats of phases; it can be taken into account in a standard way. Then $\Delta G_{21} = \Delta G_{20} - \Delta G_{10} = -\Delta s_{20}(\theta - \theta_{e0}^{20}) + \Delta s_{10}(\theta - \theta_{e0}^{10}) = -\Delta s_{21}(\theta - \theta_{e0}^{21})$, where $\Delta s_{21} = \Delta s_{20} - \Delta s_{10}$ and $\theta_{e0}^{21} = (\Delta s_{20}\theta_{e0}^{20} - \Delta s_{10}\theta_{e0}^{10})/\Delta s_{21}$.

The coefficients that determine loss of stability of melt toward $S_s$ are $A_{s0}^{s0}(\theta) = A_{c}^{s0}(\theta - \theta_{e0}^{s0})$, where $\theta_{e0}^{s0}$ is the critical temperature at which melt loses its stability toward $S_s$. A similar coefficient between two solid phases is accepted in a more general form $A_{21}^{s0}(\theta) = \tilde{A}_{c}^{21}(\theta) + A_{c}^{21}(\theta - \theta_{c}^{21})$ with $\theta_{c}^{21}$ designating the critical temperature of the loss of stability of the phase $S_1$ toward $S_2$. If such a critical temperature exists, e.g., for solid phases with different thermal properties, then the instability condition (3.25) requires $\tilde{A}_{c}^{21} = 0$. If critical temperature does not exist, e.g., for two martensitic variants that have the same thermal properties, one has to accept $A_{21}^{s0}(\theta) = A_{c}^{21}(\theta)$. In this case instability can be caused by stresses, which are neglected in the current study. Here, we will focus on the case with $\tilde{A}_{c}^{21} = 0$. Then, instability conditions (3.23)-(3.26) simplify to the critical temperatures for the loss of stability of each phase,

\begin{align*}
M \rightarrow S_s & : \theta \leq \theta_{c}^{s0}; \\
S_s \rightarrow M & : \theta \leq \theta_{c}^{s0} = \frac{A_{c}^{s0}\theta_{e0}^{s0} + 6\Delta s_{s0}\theta_{e0}^{s0}}{A_{c}^{s0} + 6\Delta s_{s0}}; \\
S_1 \rightarrow S_2 & : \theta \leq \theta_{c}^{21}; \\
S_2 \rightarrow S_1 & : \theta \leq \theta_{c}^{12} = \frac{A_{c}^{21}\theta_{e0}^{21} + 6\Delta s_{21}\theta_{e0}^{21}}{A_{c}^{21} + 6\Delta s_{21}}.
\end{align*}

It should be noted that obvious inequality $\theta_{c}^{s0} < \theta_{e0}^{s0} < \theta_{c}^{s0}$ results in $A_{c}^{s0} < -6\Delta s_{s0}$. If we assume that the equilibrium temperature is the average of critical temperatures, then we obtain $A_{c}^{s0} = -3\Delta s_{s0}$ and $A_{c}^{21} = -3\Delta s_{21}$. In the next section, it will be shown that this choice of parameters makes the interface energy and width to be temperature independent.

It is worth noting that for the fourth degree polynomial potential for each of the PTs, the next higher order term in local potential energy satisfying all the above requirements to the thermodynamic potentials (i.e., which does not change thermodynamic equilibrium and
instability conditions) is a ninth-degree term

\[ G_9(\Upsilon, \vartheta) = A_9 \Upsilon^3 (1 - \Upsilon)^2 \vartheta^2 (1 - \vartheta)^2. \]  

(3.31)

This term does not change the solution for an interface (and consequently, its width, energy, and velocity) between any two phases. It contributes only where all three phases are present, in particular, at \( S_1MS_2 \) interface, and can be used to adjust its energy and width by choosing a proper parameter \( A_9 \), if such data will be available.

While we cannot prove that the above potential does not possess any other minima than corresponding to \( M, S_1, \) and \( S_2 \) (which will result in unwanted spurious phases), numerous calculations at different parameters demonstrate that this is the case. If some exception will be found, an additional term \( G_9 \) can be used to eliminate it.

3.2.4 Well-posedness of problem formulation

In the developed model the \( S_1MS_2 \) diffuse interface corresponds to \( \Upsilon \) varying from 1 to 0 and again back to 1, and \( \vartheta \) varies from 0 to 1 (Fig. 3.3). Variation of \( \vartheta \) in the completely molten region—i.e., at \( \Upsilon = 0 \), from the first glance does not have any physical meaning as melt does not have memory of its previous solid phase. This implies that \( \psi \nabla \) should be independent of \( \nabla \vartheta \) when \( \Upsilon = 0 \), i.e., \( a_0 = 0 \). However, for \( a_0 = 0 \) energy-minimizing solution corresponds to the sharp solid-solid interface, i.e., \( \vartheta \) is the step function and \( \Upsilon = 0 \) at one point only corresponds to the jump in \( \vartheta \) (Fig. 3.3). Indeed, for such a solution the contribution of \( \nabla \vartheta \) to the total energy is zero and the size of the region of high energy complete melt (where \( \Upsilon = 0 \)) is minimized. Such a solution was found for intergranular premelting in (Tang et al., 2006a), in which \( a_0 = 0 \). It is convenient for analytical study as the limit simplified case, but the lack of characteristic size for the \( IM \) region means that the problem is ill-posed and will lead to catastrophic mesh-dependence of the solution for any discretization method. Indeed, finite element solutions to the GL equations demonstrated that the width of the region with sharp change in \( \vartheta \) is approximately equal to the size of a single finite element (Fig. 3.3) and it tends to zero (and \( \nabla \vartheta \to \infty \)) when element size tends to zero. Interface velocity \( v \) also strongly depends on the mesh size (see Fig. 3.4), leading also to interface trapping, i.e., to a
Figure 3.3: Mesh dependence of solutions to the GL equations at $a_0 = 0$. Effect of the mesh size on the distribution of the order parameters, $\vartheta$ and $\Upsilon$, at $\theta = 492K$, for $k_\delta = 1.0$ and $k_E = 4.0$, using perturbed $S_1S_2$ initial conditions. Solutions are shown for the entire width of $IM$ (a) and for the zoomed region close to the $S_1S_2$ interface within melt (b). Subscripts on the order parameters indicate the number of elements per equilibrium $S_1S_2$ interface width $\delta^{21}$ without melt.

A non-zero interface velocity for a non-zero driving force. This trapping reduces with the reduction of the finite element size. Therefore, $a_0$ must be chosen to be greater than zero (and greater than the numerical error, see below) to obtain well-posed formulation. As it will be shown in Section 3.5, parameter $a_0$ allows us to describe the interaction between two solid-melt interfaces.

Note that the interface velocity also strongly depends on the mesh size even for very small but non-zero $a_0$ (see Fig. 3.4), when $a_0$ is comparable to the error of calculation. Thus, for $a_0 = 10^{-6}$, $v = 0$ for the number of finite elements per width of the equilibrium $S_1S_2$ interface $\delta^{21}$ (without melt), $N$, smaller than or equal to 25, which, however, means interface trapping rather than mesh-independence of the interface velocity. Indeed, interface velocity is getting non-zero for $N > 200$. For $a_0 = 10^{-5}$, mesh-dependence of $v$ can be neglected for $N > 20$ and trapping occurs at $N \leq 10$, and numerical simulations are still quite costly. For $a_0 = 10^{-4}$, mesh-dependence of $v$ can be neglected for $N \geq 5$, which is typical for any interface, and trapping occurs at $N \leq 3$. For $a_0 = 0.1$ the $IM$ is broad enough and $N = 1$ is sufficient for a mesh-independent solution.
Figure 3.4: Mesh dependence of the interface velocity in presence of IM for $\theta = 492K$, $k_s = 1.0$, $k_E = 4.0$ and different $a_0$. Significant mesh dependence is captured for small $a_0$ values, especially for $a_0 = 10^{-6}$ and $a_0 = 10^{-5}$ that are smaller than relative numerical error $10^{-4}$. With increasing $a_0$, the number of elements needed for a mesh-independent solution reduces.

### 3.3 Analytical treatment of the Ginzburg-Landau equations

#### 3.3.1 Analytical solution for two phases

In contrast to the reported multiphase models (Tiaden et al., 1998; Levitas et al., 2003; Levitas and Javanbakht, 2010, 2011b), in the developed model each of the PTs can be described by a single order parameter without constraints. It allows us to utilize analytical solutions (Levitas et al., 2010) for the interface between two phases propagating in the $x$– direction, including its profile, energy $E$, width $\delta$, and velocity $v$. For the $S_1S_2$ interface solutions are

$$\vartheta = 1/\left[1 + e^{-p(x-v_1t)/\delta_1} \right] ; \quad v_{21} = 6L_{21}\delta_{21}^{21} \Delta G_{21}^\theta (\theta)/p; \quad (3.32)$$

$$E^{21} = \sqrt{2}\beta_{21} \left[A^{21}(\theta) - 3\Delta G_{21}^\theta (\theta) \right]/6; \quad \delta_{21} = p\sqrt{\beta_{21} / \left\{2 \left[A^{21}(\theta) - 3\Delta G_{21}^\theta (\theta) \right] \right\}} \quad (3.33)$$

and for $SM$ they are presented below

$$\Upsilon = 1/\left[1 + e^{-p(x-v_0t)/\delta_0} \right] ; \quad v_{s0} = 6L_{s0}\delta_{s0}^{s0} \Delta G_{s0}^\theta (\theta)/p; \quad (3.34)$$

$$E^{s0} = \sqrt{2}\beta_{s0} \left[A^{s0}(\theta) - 3\Delta G_{s0}^\theta (\theta) \right]/6; \quad \delta_{s0} = p\sqrt{\beta_{s0} / \left\{2 \left[A^{s0}(\theta) - 3\Delta G_{s0}^\theta (\theta) \right] \right\}} \quad (3.35)$$

where $p = 2.415$. The interface width is defined as

$$\delta_0 = \left\{dq[\Upsilon(x),3]/dx\right\}_{max}^{-1} ; \quad \delta_{21} = \left\{dq[\vartheta(x),3]/dx\right\}_{max}^{-1}. \quad (3.36)$$
The choice of the interpolation function \( q(y, 3) \) in Eq. (3.36) instead of the traditional choice of the order parameter profile is related to the fact that the order parameter itself does not have a specific physical meaning, while variation of all properties does. Choice \( a = 3 \) is a usual mean-value choice when the specific value of \( a \) is unknown. Change in the definition of the interface width will change the value of \( p \), while \( \delta/p \) remains invariant. Energy of the nonequilibrium interfaces is defined as an excess energy, with respect to bulk phases, assuming that the Gibbs dividing surface is located where the corresponding order parameter is equal to 0.5 (see justification in (Levitas, 2014b)). Thus,

\[
E^{21} = \int_{-\infty}^{x_\theta=0.5} (\psi - \psi_1)dx + \int_{x_\theta=0.5}^{\infty} (\psi - \psi_2)dx; \quad E^{s0} = \int_{-\infty}^{x_\theta=0.5} (\psi - \psi_0)dx + \int_{x_\theta=0.5}^{\infty} (\psi - \psi_s)dx.
\]

(3.37)

Here, \( x_\theta=0.5 \) and \( x_\theta=0.5 \) define the locations where \( \theta = 0.5 \) and \( \Upsilon = 0.5 \), respectively. For the particular case \( A^{ij}_c = -3\Delta s_{ij} \), the interface energies and width became temperature-independent:

\[
E^{21} = \sqrt{\beta^{21}} \left[ \Delta s_{21}(\theta^{21}_c - \theta^{21}_e) \right] / 6; \quad \delta^{21} = p\sqrt{\beta^{21}} / \left\{ 6 \left[ \Delta s_{21}(\theta^{21}_c - \theta^{21}_e) \right] \right\};
\]

\[
E^{s0} = \sqrt{\beta^{s0}} \left[ \Delta s_{s0}(\theta^{s0}_c - \theta^{s0}_e) \right] / 6; \quad \delta^{s0} = p\sqrt{\beta^{s0}} / \left\{ 6 \left[ \Delta s_{s0}(\theta^{s0}_c - \theta^{s0}_e) \right] \right\}.
\]

(3.38)

(3.39)

Equations (3.32)-(3.33) and (3.34)-(3.35) allow us to calibrate material parameters \( \beta^{21}, \beta^{s0}, A^{21}, A^{s0}, \theta^{21}_c, \theta^{s0}_c, L_\theta \), and \( L_\Upsilon \) when the temperature dependence of the interface energy, width, and velocity are known, along with the thermodynamic parameters \( \Delta s_{ij} \) and \( \theta^{ij}_c \). The ratios of \( S_1 S_2 \) to \( S M \) interface energies and widths, \( k_E \) and \( k_\delta \), play the key role in determining the material response. Using the equations (3.33) and (3.35), \( k_E \) and \( k_\delta \) are:

\[
k_E = \frac{E^{21}}{E^{s0}} = \sqrt{\beta^{21}} \frac{A^{21}(\theta - \theta^{21}_c) + 3\Delta s_{21}(\theta - \theta^{21}_e)}{A^{s0}_c(\theta - \theta^{s0}_c) + 3\Delta s_{s0}(\theta - \theta^{s0}_e)};
\]

\[
k_\delta = \frac{\delta^{21}}{\delta^{s0}} = \sqrt{\beta^{21}} \frac{A^{s0}_c(\theta - \theta^{s0}_c) + 3\Delta s_{s0}(\theta - \theta^{s0}_e)}{A^{21}(\theta - \theta^{21}_c) + 3\Delta s_{21}(\theta - \theta^{21}_e)}.
\]

(3.40)

(3.41)

For \( A^{ij}_c = -3\Delta s_{ij} \), the equations (3.40) and (3.41) reduce to

\[
k_E = \sqrt{\beta^{21}} \frac{\Delta s_{21}(\theta^{21}_c - \theta^{21}_e)}{\Delta s_{s0}(\theta^{s0}_c - \theta^{s0}_e)}; \quad k_\delta = \frac{\delta^{12}}{\delta^{s0}} = \sqrt{\beta^{21}} \frac{\Delta s_{s0}(\theta^{s0}_c - \theta^{s0}_e)}{\Delta s_{21}(\theta^{21}_c - \theta^{21}_e)}.
\]

(3.42)
which are temperature independent. Energy of the $S_1MS_2$ interface containing $IM$, $E^*$, is defined as excess energy with respect to $S_1$ for points with $\vartheta \leq 0.5$ and with respect to $S_2$ for points with $\vartheta > 0.5$—i.e.,

$$E^* = \int_{-\infty}^{x_{\vartheta=0.5}} (\psi - \psi_{s1}) \, dx + \int_{x_{\vartheta=0.5}}^{\infty} (\psi - \psi_{s2}) \, dx. \quad (3.43)$$

### 3.3.2 Energy integral for stationary solutions for three phases

It is known that for stationary 1D solutions of the GL equation for two phases, i.e., for plane stationary interface or critical nucleus, an energy integral can be found. It results in the statement that the excess of the local energy at each point is equal to the gradient energy. We will derive an energy integral and prove a similar statement for two GL equations (3.14) and (3.15) and taking into account dependence of $\beta_S(\vartheta)$ and $\beta^{21}(\Upsilon)$. Thus, Eqs. (3.14) and (3.15) for the stationary case and the 1D case simplify to

$$\frac{\partial \psi^l}{\partial \Upsilon} = -\frac{\beta^{21}}{2} \frac{d\phi(\Upsilon)}{d\Upsilon} \vartheta_x^2 + \frac{d(\beta_S(\vartheta)\Upsilon_x)}{dx}; \quad (3.44)$$

$$\frac{\partial \psi^l}{\partial \vartheta} = -\frac{1}{2} \frac{d\beta_S(\vartheta)}{d\vartheta} \Upsilon_x^2 + \frac{d(\beta^{21}\phi(\Upsilon)\vartheta_x)}{dx}, \quad (3.45)$$

where subscript $x$ designates the derivative with respect to $x$. It is proven in Eq. (A.7) in Appendix that $d\psi^l(\theta, \Upsilon, \vartheta) = d\psi^\nabla$. Integrating $d\psi^l$ at constant temperature, we obtain

$$\psi^l(\theta, \Upsilon, \vartheta) - \psi_0 = \psi^\nabla, \quad (3.46)$$

where $\psi_0$ is the integration constant. Consequently, for any stationary solution, the excess of the local energy at each point is equal to the gradient energy.

*Stationary interface.*—Let us consider a stationary plane interface, when one has solid phase $S_1$ (i.e., $\vartheta = 0$ and $\Upsilon = 1$) as $x \to -\infty$ and $S_2$ (i.e., $\vartheta = 1$ and $\Upsilon = 1$) as $x \to \infty$. Then both gradients and $\psi^\nabla = 0$ for $x \to \pm\infty$, and both sides of Eq. (3.46) are zero, i.e.,

$$\psi_0 = \psi^l(\theta, \Upsilon = 1, \vartheta = 0) = G_1(\theta) = \psi^l(\theta, \Upsilon = 1, \vartheta = 1) = G_2(\theta). \quad (3.47)$$

The equality of free energies of phases $S_1$ and $S_2$ means that temperature is equal to the phase equilibrium temperature $\theta^{21}_e$, —i.e., $\psi_0 = G_1(\theta^{21}_e) = G_2(\theta^{21}_e)$. Since energy is known to within a constant, one can chose $G_1(\theta^{21}_e) = G_2(\theta^{21}_e) = 0$ and obtain $\psi_0 = 0$. Similar treatment is valid
if we consider the appearance of any third phase at the stationary interface between two other phases, at their thermodynamic equilibrium temperature.

**Critical nuclei.**—Let us consider critical nucleus of one of the phase or two combined phases within another homogeneous phase or at the interface between two other phases. For all cases, assume that both gradients and $\psi\nabla = 0$ for $x \to \pm\infty$, and both sides of Eq. (3.46) are again zero—i.e., $\psi_0 = \psi^d(\theta, x = \pm\infty)$. If we consider the appearance of the third phase at the stationary interface between two other phases, in particular, the critical nucleus of $IM$ at stationary $S_1S_2$ interface, then it is possible at the thermodynamic equilibrium temperature of these phases. Another nontrivial case is nucleation of a compound critical nucleus consisting of two phases within the homogenous matrix of the third phase, see for example Ref (Tóth et al., 2011). In this case temperature should not be equal to the phase equilibrium temperature. The last case, nucleation of one phase within another, is well known from two-phase studies and again temperature should not be equal to the phase equilibrium temperature.

For all these solutions, namely, the equilibrium interface with the third phase and all critical nuclei, excess energy of the system with respect to the energy of the ground phase or equilibrium phases at $x = \pm\infty$, according to Eqs. (3.43) and (3.47) one has

$$E^* = \int_{-\infty}^{\infty} (\psi - \psi^d(\theta, x = \pm\infty))dx = \int_{-\infty}^{\infty} 2\psi\nabla dx. \quad (3.48)$$

Thus, the total excess energy is equal to double the total gradient energy. Note that the equality of gradient and local excess energies for three-phase solutions for different $S_1MS_2$ interfaces and critical $IM$ nuclei was confirmed in our numerous finite element simulations below. This is one of the nontrivial confirmations of correctness and precision of our numerical procedure.

### 3.4 Numerical implementation

*Material properties.* As a model material, we consider cyclotetramethylene-tetranitramine $(C_4H_8N_8O_8)$ (which is also called 1,3,5,7-tetranitro-octahydro 1,3,5,7-tetrazocine) also known as HMX. The HMX is an energetic material with applications in ammunitions and propellants. It has four phases, which in ascending order of sensitivity to ignition are: $\beta-$, $\alpha-$, $\gamma-$, and $\delta-$
HMX (McCrone, 1950). The $\beta$-HMX is the stable form at ambient temperature and as the temperature rises, $\delta$-HMX becomes more stable. The presence of more sensitive $\alpha$-, $\gamma$-, and $\delta$-HMX polymorphs in $\beta$-HMX can be the source of dangerous accidents. These considerations motivated a number of investigations on properties of HMX, its polymorphs, and their phase transformation process (Cady, 1986; Cady et al., 1962). In fact, the necessity to explain various experimental data for kinetics of $\beta - \delta$ phase transformations in HMX leads to introducing the concept of the solid-solid transformation via the virtual melting (Levitas et al., 2004, 2006a,b).

Thermodynamic properties of HMX are determined in (Cady, 1986; Cady et al., 1962; Teetsov and McCrone, 1965; Menikoff and Sewell, 2002; Henson et al., 2002; Smilowitz et al., 2002) and collected in (Levitas et al., 2006a, 2007c). They are presented in Table 3.1. In addition, the molar mass of HMX is considered to be $M \simeq 0.296 \, \text{kg/mol}$ and its density at $\theta = \theta^c_{21}$ is $1848.78 \, \text{kg/m}^3$ (Menikoff and Sewell, 2002). It is also assumed that all $a = 3$. As mentioned above, we have assumed $A^c_{s0} = -3\Delta s_{s0}$, $A^c_{21} = -3\Delta s_{21}$, and $\bar{A}^c_{21} = 0$, which results in temperature-independent interface energy and width—i.e., equation (3.42). Interface widths and energies are unknown. We have assumed the same energy and width for both SM interfaces. Therefore, $\beta^{20} = \beta^{10}$ and $\beta^{20}$ will be independent of $\vartheta$—i.e., $\beta^{20}(\vartheta) = \beta^{s0}$. Choosing $\theta^c_{21} = -16616 \, \text{K}$, the $S_1S_2$ interface energy and width are $1 \, \text{J/m}$ and $1 \, \text{nm}$, respectively. The properties of $SM$ interface and consequently, $\beta^{s0}$ and $\theta^c_{s0}$ will be determined by specifying values of $k_E$ and $k_\delta$. Negative instability temperature does not contradict $\theta > 0$. It just means that such an instability cannot occur in reality. Negative instability temperature was also obtained for martensitic PT in NiAl (Levitas and Preston, 2002b).

In all simulations, width of a sample was at least an order of magnitude larger than the largest interface width. In most cases with propagating interface, sample width was 50 times larger than the largest interface width in order to have space to obtain steady interface profile and velocity. Sample width was varied to prove that solution is size-independent. In all simulations excluding critical nuclei, 1D formulation was used and sample size was up to $500 \, \text{nm}$. Since width of solid-solid interface was fixed at 1 nm, the key parameter for determining the sample size is the size scale parameter $k_\delta$. Smaller $k_\delta$ values require larger sample sizes as they result in larger $SM$ interface widths. A uniformly distributed fine finite element of Lagrange
Table 3.1: Thermodynamic and kinetic properties of phase transformations in HMX.

<table>
<thead>
<tr>
<th></th>
<th>(\Delta s) (kJ/m(^3)·K)</th>
<th>(\theta_e) (K)</th>
<th>(L) (m·s/kg)</th>
<th>(\theta_c) (K)</th>
<th>(\beta) (nJ/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\delta - \beta)</td>
<td>-141.66</td>
<td>432</td>
<td>1298.3</td>
<td>-16616</td>
<td>2.4845</td>
</tr>
<tr>
<td>(m - \delta)</td>
<td>-793.79</td>
<td>550</td>
<td>2596.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(m - \beta)</td>
<td>-935.45</td>
<td>532.14</td>
<td>2596.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Values are obtained from (Levitas et al., 2007c,c,c).

elements mesh with quadratic approximation was utilized. By varying size of the mesh, it was proven that solutions are mesh-independent, see for example Fig. 3.4. To find 2D critical IM nucleus within stationary \(S_1S_2\) interface, an axisymmetric sample with a size of \(60 \times 40\) nm was utilized and size- and mesh-independence of solutions was verified. The model is implemented in the commercial finite element software package COMSOL. The characteristic time in the simulations \(1/(A^{21}L_\theta)\) is on the order of 0.1 ps. We have used the automatic time stepping method with a relative tolerance of \(10^{-4}\) and an initial time step on the order of 0.01 fs. Typical time to simulate 1D systems as large as 0.5\(\mu\) up to 10\(\mu\)s was about an hour using conventional desktop computers.

**Initial conditions.**—As we will discuss below, for a fixed temperature there are generally two steady propagating solutions for the order parameters for which profiles of \(\vartheta\) and \(\Upsilon\) propagate with some velocity without changing their shape. That why two types of initial conditions have been used. To study barrierless IM at the solid-solid interface, an analytical solution for dry \(S_1S_2\) interface (3.32) was utilized with small perturbation for \(\Upsilon\):

\[
\vartheta(x, x_0) = \left\{1 + \exp \left[-p(x-x_0)/\delta^{21}\right]\right\}^{-1} ; \quad \Upsilon = 0.99 .
\]

(3.49)

To study disappearance of the IM (i.e., its resolidification), two equilibrium \(S_1M\) and \(MS_2\) interfaces with a broad melt (\(\Upsilon = 0\)) region between two solid phases have been applied using Eq. (3.34):

\[
\Upsilon(x) = 1 - \left\{1 + \exp \left[-p(x-W/4)\right]\right\}^{-1} + \left\{1 + \exp[-p(\delta^{s0}(x-3W/4))\right\}^{-1} ,
\]

(3.50)

where \(W\) is the width of the sample and it needs to be at least an order of magnitude larger than the \(\delta^{s0}\) to assure formation of a wide IM and avoid sample size effects. The \(\vartheta\) varies
according to Eq. (3.49).

Note that the steady solutions are quite sensitive to wrong initial conditions. Thus, if initial conditions possess artificially high energy (e.g., a sharp solid-solid or solid-melt interface, or an analytical solution (3.49) with much smaller interface width), one can obtain a wrong steady solution among two existing ones. In particular, the IM would appear under conditions when its barrierless nucleation is energetically impossible, promoted by high initial energy. Initial conditions (3.49) and (3.50) are physically correct and allowed us to obtain the correct parameters for nucleation and resolidification of the IM.

To test the implemented numerical model, simulations are performed for a wide temperature range and different $k_E$ values. The simulation results show good correspondence with an analytical solution for the interface profile, energy, width, and velocity—i.e., Eqs. (3.32)-(3.35). Fig. 3.5 shows comparison between the numerical results (dots) and analytical solutions (lines) for the $S_1S_2$ and $SM$ interface velocity. Calculations are performed for two $k_E$ values: (i) $k_E = 1.933$ that is the maximum $k_E$ for disappearing of the IM during the resolidification process (open dots); (ii) $k_E = 3.39$ that is the minimum $k_E$ for the barrierless formation of IM at $S_1S_2$ interface (filled dots). While for three-phase configurations analytical solutions are unavailable, the equality of gradient and local excess energies (Eq. (3.46)) at each point for different $S_1MS_2$ interfaces and critical IM nuclei was confirmed in our numerous simulations. This is a nontrivial confirmation of correctness and precision of our numerical procedure.

### 3.5 Interface Interactions: force-balance models and phase field simulations

In general, there are three main forces between two interfaces that play a key role in the determination of interfacial or surfacial phase thickness and stability, which are related to volumetric free-energy, short-range steric forces, and long-range dispersion forces (Luo, 2007). The volumetric free energy is presented in our local potential. Short-range forces are originating from non-uniform structural and chemical composition within thickness of an interfacial phase (intermediate melt). They are often repulsive forces and stabilize finite thickness of the interfacial phase. Long-range dispersion forces are weak attractive forces caused by electromagnetic interaction of dipole moments that are formed due to instantaneous polarization of molecules.
Figure 3.5: Simulation results for $S_1S_2$ and $S_1M$ interface velocity as a function of temperature for $k_E = 3.39$ (solid dots; melt forms at $k_E > 3.39$ for $S_1S_2$ initial condition) and $k_E = 1.933$ (open dots; melt disappears for $k_E < 1.933$ for $S_1MS_2$ initial condition). Numerical simulations (point plot) match the analytical solutions (line plot).

Within sharp interface approach, interaction between interfaces are described by force balance models, i.e., by formulating energy of the system versus distance between two interfaces, in our case, $S_1M$ and $S_2M$ interfaces. In PFA, we will describe such an interaction by the term $0.5\beta^{21}\phi(0,a_\phi,a_0)|\nabla \vartheta|^2 = 0.5a_0\beta^{21}|\nabla \vartheta|^2$ within melt $\Upsilon = 0$ scaled with the material parameter $a_0$. The aim of this Section is as follows. First we will show that our PFA is able to capture the relation between energy-IM width described by force balance models for short-range (Ackler and Chiang, 1999) and long-range (French, 2000) interaction forces. For this purpose, we first slightly generalize force balance equations to make them more consistent for the case when interacting interfaces have finite width, like in PFA. We also develop a force balance model, which for a relatively large IM width obtained directly from our PFA and combining it with short-range interaction model (the same can be done for a long-range interaction). After demonstrating that our PFA can reproduce interfacial interaction and the IM width obtained by force-balance models, we expect that it realistically describes interfacial interactions and IM width for the cases when sharp interface models do not work, namely for small IM width when melt is not complete, i.e., $\Upsilon > 0$. 
3.5.1 Force-balance models of interface interactions

In the force-balance method (Dash et al., 2006, 1995) adapted for our problem, an energy of the system is given versus the width of the \( IM \) \( \delta^* \), i.e., \( G(\delta^*) \). This function satisfies the requirements that \( G(0) = E^{21} \) and for \( \delta^* \to \infty \) one has \( G(\delta^*) = \Delta G \delta^* \), where \( \Delta G \) is the bulk excess energy, i.e., the difference between the energy of melt and initial state with two solid phases in the region where \( IM \) appeared. The \( IM \) can appear if \( G(\delta^*) - G(0) < 0 \). The equilibrium thickness of the \( IM \), \( \delta^*_e \), can be found by minimizing the energy function \( G(\delta^*) \)–i.e. \( \frac{\partial G}{\partial \delta^*} = 0 \).

**Long-range interface interaction model.**—Long-range London dispersion force is a weak intermolecular force due to instantaneous polarization of molecules and interaction of fluctuation dipoles (French, 2000). These forces play a key role in the interfacial behavior of materials such as ice and molecular substances. The energy for this case is

\[
G_{lr}(\delta^*) = 2E^{s0} + \Delta G \delta^* - \Delta \gamma / \left[ 1 + \left( \frac{\delta^*}{\delta_a} \right)^2 \right], 
\]

(3.51)

where \( \delta_a \) is a characteristic length and \( \Delta \gamma = 2E^{s0} - E^{21} \) is the difference between energy of two \( SM \) interfaces and \( S1S2 \) interface. While this expression satisfies all the above limit cases and is formally noncontradictory for sharp interface approach, it requires modifications when the finite width of \( SM \) interface is taken into account. Let us introduce the width of a disordered (non-solid) phase, \( \delta \), which is calculated as the width where \( \Upsilon \leq 0.99 \), and \( \delta_{int} \) is the width of two \( SM \) interfaces. The problem in the application of Eq. (3.51) for the case with finite width of \( SM \) interface is related to the definition of \( \delta^* \). If \( \delta^* = \delta \) then the condition \( G_{lr}(0) = E^{21} \) is satisfied but \( \Delta G \) contributes when there is no complete melt, which is contradictory. If \( \delta^* = \delta - \delta_{int} \), then there is no nonphysical contribution due to \( \Delta G \) when there is no complete melt (\( \delta = \delta_{int} \)) but \( G_{lr}(0) = E^{21} \) while we have two \( SM \) interfaces. Also, the condition for the \( S1S2 \) interface \( \delta = 0 \) is not satisfied, i.e., \( G_{lr}(-\delta_{int}) \neq E^{21} \). We suggest the simplest generalization

\[
\tilde{G}_{lr} = 2E^{s0} + \Delta G (\delta - \delta_{int}) - \Delta \gamma / \left[ 1 + \left( \delta / \delta_a \right)^2 \right]. 
\]

(3.52)
The bulk term $\Delta G$ is multiplied by the width of the complete melt and it disappears when the region with complete melt disappears. Condition $\partial \tilde{G}_{lr} / \partial \delta = 0$ results in

$$\Delta G + 2\Delta \gamma \delta_a^2 \delta / (\delta^2 + \delta_a^2)^2 = 0,$$

(3.53)

which is independent of $\delta_{int}$. Thus, $\delta_{int}$ just changes the values of energy by the same amount for any $\delta$. Note that $\delta_{int}$ will be determined below from the best fit of energy to PFA simulations rather than from geometric definitions (e.g., as the width where $0.01 \leq \Upsilon \leq 0.99$ for each interface or any other range), because different geometric definitions may give quite different widths. We do not expect that $\tilde{G}_{lr}$ has some specific value for $\delta = \delta_{int}$, because it follows from the phase field solution that it is equal to $2E^{s0}$ plus the contribution due to $0.5\beta^2 \phi(\Upsilon, a_\phi, a_0)|\nabla \vartheta|^2$, which is not easy to estimate. We also do not expect that Eq. (3.51) would work for small $\delta < \delta_{int}$ and incomplete melt. Note that while describing results of the PFA simulation with some equations, it is important to have a good coincidence for the position of the minimum of the energy and near this minimum only. Eq. (3.51) with a single fitting parameter $\delta_a$ does not allow a good description of the PFA simulation results while Eq. (3.51) does allow (see e.g., Figs. 3.7 and 3.8). During the fitting procedure for PFA results, $\delta_a$ is determined from the value of the width $\delta$ corresponding to the minimum of the energy (3.53) and $\delta_{int}$ is obtained from the numerical fitting of the energy curve near the minimum. The same is done for the short-range interaction model.

**Short-range interface interaction model.**-The short-range interface interactions are due to non-uniform structure and composition of surfacial/interfacial phases. These repulsive forces play a crucial role in stabilizing the finite width of surfacial/interfacial nanoscale phases in metals and ceramics (Ackler and Chiang, 1999; Luo, 2007). In contrast to long-range interactions that can exist even in a uniform structure, the gradient of the chemical and structural origin has a major contribution to the short-range forces. An energy for the short-range interaction model is defined as

$$G_{sr}(\delta^*) = 2E^{s0} + \Delta G\delta^* - \Delta \gamma \exp \left(-\delta^*/\delta_a\right).$$

(3.54)

Similar to the energy of the long-range interaction, $G_{sr}$ satisfies all the required conditions for the sharp interfaces but should be modified to take into account the finite width of the $SM$
interfaces. The more general function is

$$\tilde{G}_{sr} = 2E^{s0} + \Delta G (\delta - \delta_{int}) - \Delta \gamma \exp \left( -\delta / \delta_a \right). \quad (3.55)$$

which satisfies the same conditions as $\tilde{G}_{lr}$. An actual width $\delta$ is determined by a solution to the equation $\partial \tilde{G}_{sr} / \partial \delta = 0$:

$$\delta = \delta_a \ln \left[ -\Delta \gamma / (\Delta G \delta_a) \right], \quad (3.56)$$

which is independent of $\delta_{int}$, like for the long-range interaction.

**Approximate phase field model.**—Better agreement with PFA can be obtained if we directly include some properties of the PFA solution in the analytical expression for energy. This can be easily done when width of the completely molten region is much larger than $\delta^{s0}$. Utilizing Eq. (3.43), one can approximately evaluate energy of the $S_1MS_2$ system assuming linear distribution of $\vartheta$ within $IM$ (Fig. 3.6):

$$E^* = 2E^{s0} + \Delta G (\delta - \delta_{int}) + 0.5 \beta^2 a_0 / (\delta - \delta_{int}). \quad (3.57)$$

Here $\delta - \delta_{int}$ is the width of complete melt (e.g., where $\Upsilon < 0.01$) and $\delta - \delta_{int}$ is the width over which $\vartheta$ linearly changes from 0 to 1. Then $\nabla \vartheta \simeq \frac{1}{(\delta - \delta_{int})}$ and $\beta^2 a_0 |\nabla \vartheta|^2 = \frac{\beta^2 a_0}{2(\delta - \delta_{int})}$, which explains the third term in Eq. (3.57) that describes interaction between two SM interfaces. It scales with $a_0$, which proves the necessity of keeping $a_0 \neq 0$ for the description of such an interaction. For very large $\delta$, when interaction between two SM interfaces is negligible, this term disappears, as expected. To reduce the number of fitting parameters, we can assume $\delta_{int} \simeq \delta_{int}$, since $\delta \gg \delta_{int}$ and $\delta \gg \delta_{int}$. To approximately expand this equation for a smaller $\delta$ and take into account the short-range interactions, we add the last term from (3.54):

$$G^{pf} = 2E^{s0} + \Delta G (\delta - \delta_{int}) + 0.5 \beta^2 a_0 / (\delta - \delta_{int}) - \Delta \gamma \exp \left( -\delta / \delta_a \right). \quad (3.58)$$

This adds the second fitting constant $\delta_a$, like for other models. We did not use a step function because the term with $1/(\delta - \delta_{int})$ makes this equation applicable for $\delta > \delta_{int}$. Condition $\partial G^{pf} / \partial s = 0$ results in the following equation for an actual width $\delta$:

$$\Delta G - 0.5 \beta^2 a_0 / (\delta - \delta_{int})^2 + \Delta \gamma / \delta_a \exp \left( -\delta / \delta_a \right) = 0. \quad (3.59)$$

During the fitting procedure, both $\delta_{int}$ and $\delta_a$ have been fitted simultaneously.
Figure 3.6: Distribution of the order parameters $\Upsilon$ and $\vartheta$ for $k_\delta = 2.0$, $k_E = 10.0$, $a_0 = 1.0$, and $\theta = 533K$ that led to a formation of a wide complete melt. Variation of $\vartheta$ within $IM$ can be approximated to be linear. Width of the disordered (non-solid) phase $\delta$ is defined as a region where $\Upsilon < 0.99$. Width of the complete melt $\delta - \delta^{\prime}_{int}$ is defined as a region where $\Upsilon < 0.01$, and $\delta - \delta^{\prime}_{int}$ is defined as the width where $\vartheta$ varies linearly.

### 3.5.2 Phase-field simulations of interface interaction

Despite clear advantages of the force-balance models, including their simplicity, they have limitations (Luo, 2007). They assume a uniform film, while it is well known that the structure (and, in a more general case, composition) of the surfacial/interfacial phase vary significantly along the thickness. Furthermore, they are inaccurate when the width of the $IM$ is comparable with the width of $SM$ interface and especially when $IM$ is not complete, i.e., $\Upsilon > 0$ everywhere. The PFA does not have such limitations and it will be utilized here to study the formation of $IM$ and the effect of different parameters, including temperature, interface width ratio, and interfacial interactions. The energy of $IM$ is calculated as a function of $IM$ width for each simulation condition. The three aforementioned force-balance models are used for fitting to simulation data and material parameters for these models are determined. Application range of the model is studied. Three major simulation sets are performed at three different temperatures: (i) close to melting temperature ($\theta = 532K$), (ii) at a high temperature ($\theta = 522K$), and (iii) at $S_1S_2$ equilibrium temperature ($\theta = \theta^{e2}_e = 432K$). For all models we used
Figure 3.7: Comparison between force-balance models and phase field simulations for \( \theta = 532K \) and \( k_\delta = 1.0 \). Phase field results for different \( a_0 \) values (open symbols) are fitted to three force-balance models (solid lines): (a) approximate phase field model, \( G^{PF} \); (b) long-range interaction model, \( \tilde{G}_{lr} \); and (c) short-range interaction model, \( \tilde{G}_{sr} \).

\[ \Delta G = (\Delta G^{10} + \Delta G^{20})/2, \] i.e., \( IM \) appears in the region equally occupied by each of the solid phases. The values of \( \Delta G \) at each specified temperature are: \( \Delta G = 7.2 \ GJ/m^3 \) at \( \theta = 532K \); \( \Delta G = 16 \ MJ/m^3 \) at \( \theta = 522K \), and \( \Delta G = 94 \ MJ/m^3 \) at \( \theta = 432K \). Simulations are performed for \( \beta^{21} = 2.48 \ J/m \), \( k_E = 3.2 \), and \( E^{21} = 1 \ J/m^2 \), which results in \( E^{m0} = 1/3.2 = 0.313 \ J/m^2 \) and \( \Delta \gamma = 0.375 \ J/m^2 \).

Simulations for \( \theta = 532K \) — Results of the PF simulations for \( k_\delta = 1.0 \) and 1.1 for various \( a_0 \) are presented in Figs. 3.7 and 3.8. Solid lines in these plots are fitting curves based on three force-balance models, with fitting parameters \( \delta_a \) and \( \delta_{int} \) presented in Table 3.2. All models reproduce well, not only the value of \( \delta \) corresponding to the energy minimum (which is not surprising since it was directly fitted), but also values of energy minima and the entire curve in a large range of \( \delta \) around the energy minimum. While for large \( \delta \) all models show good fitting, the approximate phase field model shows a broader range of coincidence with simulation results for small \( \delta \), for all \( a_0 \) and both \( k_\delta \). Increasing \( a_0 \) increases the repulsive forces between interfaces and consequently, the equilibrium \( IM \) width.

Comparing Figs. 3.7 and 3.8, it can be concluded that increasing the \( k_\delta \) reduces the equilibrium width of the \( IM \) and slightly reduces the fitting range of the models. Characteristic length
Figure 3.8: Comparison between force-balance models and phase field simulations for $\theta = 532K$ and $k_\delta = 1.1$. Phase field results for different $a_0$ values (open symbols) are fitted to three force-balance models (solid lines): (a) approximate phase field model, $G^{pf}$; (b) long-range interaction model, $G_{lr}$; and (c) short-range interaction model, $G_{sr}$.

$\delta_a$ is much smaller for the approximate phase field model than for the other two models and reduces with increasing $a_0$, while for other models it increases. The width $\delta_{int}$ that corrects values of the energy in comparison with traditional short-range and long-range interaction models is smaller for the short-range interaction and reduces with increasing $a_0$. Thus, the necessity for correction is evident. The width $\delta_{int}$ for the approximate phase field model is between that for the short-range and long-range interaction and also reduces with increasing $a_0$.

Simulations for $\theta = 522K$.—For $k_\delta = 1.1$, $\Upsilon$ vanishes inside the IM and the region of complete melt is very large. The IM free energy versus width $\delta$ is plotted in Fig. 3.9. The values of parameters fitted to each model are shown in Table 3.2. The reduction of temperature in comparison with $\theta = 532K$ increased the IM free energy and decreased the IM width. The smaller IM width has essentially reduced the range of coincidence with simulations for short-range and long-range interaction models. However, our approximate phase field model shows very good agreement with simulations in the entire range of width $\delta$ under study. Both widths $\delta_{int}$ and $\delta_a$ are the smallest for the approximate phase field model and they reduce with an increase in $a_0$. 
Figure 3.9: Comparison between force-balance models and phase field simulations for $\theta = 522K$ and $k_\delta = 1.1$. Phase field results for different $a_0$ values (open symbols) are fitted to three force-balance models (solid lines): (a) approximate phase field model, $G_{pf}$; (b) long-range interaction model, $\tilde{G}_{lr}$; and (c) short-range interaction model, $\tilde{G}_{sr}$.
Table 3.2: Parameters of three force balance models ($\tilde{G}_{lr}$, $\tilde{G}_{sr}$, and $\tilde{G}_{pf}$) determined from the best fit to phase field simulations. The long-range and short-range interaction models failed to fit the simulation results at $\theta = 432 \, K$. However, the approximate phase field model still fits well to the simulation results at $\theta = 432 \, K$.

<table>
<thead>
<tr>
<th></th>
<th>$k_\delta = 1.0, \theta = 532 , K$</th>
<th>$k_\delta = 1.1, \theta = 532 , K$</th>
<th>$k_\delta = 1.1, \theta = 522 , K$</th>
<th>$k_\delta = 1.1, \theta = 432 , K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$</td>
<td>0.1 0.2 0.3 0.4</td>
<td>0.1 0.2 0.3 0.4</td>
<td>0.1 0.2 0.3 0.4</td>
<td>0.1 0.2 0.3 0.4</td>
</tr>
<tr>
<td>$\delta_{lr}$</td>
<td>3.44 4.3 5.2 5.5</td>
<td>3.2 4.2 4.48 5.2</td>
<td>3.5 4.1 5.2 5.7</td>
<td>— — — —</td>
</tr>
<tr>
<td>$\delta_{lr}^{int}$</td>
<td>6.71 5.75 5.72 4.47</td>
<td>5.92 5.67 4.04 3.81</td>
<td>5.14 4.42 4.94 4.46</td>
<td>— — — —</td>
</tr>
<tr>
<td>$\delta_{sr}$</td>
<td>3.52 4.76 5.2 6.2</td>
<td>3.24 4.22 5.06 5.80</td>
<td>3.9 5.56 8.1 9.08</td>
<td>— — — —</td>
</tr>
<tr>
<td>$\delta_{sr}^{int}$</td>
<td>3.92 4.06 2.74 2.92</td>
<td>3.25 2.65 2.12 2.12</td>
<td>4.30 5.12 6.76 6.48</td>
<td>— — — —</td>
</tr>
<tr>
<td>$\delta_{pf}$</td>
<td>2.01 1.9 1.8 1.7</td>
<td>2.01 1.91 1.70 1.6</td>
<td>3.9 5.56 8.1 9.08</td>
<td>2.95 2.17 1.76 1.14</td>
</tr>
<tr>
<td>$\delta_{pf}^{int}$</td>
<td>4.9 4.18 4.11 3.87</td>
<td>4.9 4.18 4.11 3.46</td>
<td>4.30 5.12 6.76 6.48</td>
<td>3.55 3.15 3.12 3.13</td>
</tr>
</tbody>
</table>
Figure 3.10: Comparison between approximate phase field model, Eq. (3.58), solid lines, and phase field simulations (open symbols) for $\theta = 532K$ and $k_\delta = 1.1$. Attempts to fit the simulation results using the other two force-balance models failed.

Simulations for $\theta = \theta_e^{21} = 432K$.— For $k_\delta = 1.1$ and $100K$ below the melting temperature, $\Upsilon > 0$ and melt is incomplete. For this case, none of the force-balance models are expected to describe phase field results. Indeed, our attempts to fit short/long-range interaction models to the simulation results at $\theta = 432K$ have failed. However, approximate phase field model demonstrates reasonably good correspondence with simulations (Fig. 3.10) in some range of $\delta$. Both widths, $\delta_{int}$ and $\delta_a$, are not much smaller than for $\theta = 532K$.

If we assume that for any chosen temperature and corresponding $\delta_{int}$ and $\delta_a$ the chosen force-balance model will well describe the experimental data, we can find corresponding $a_0$ and our PFA model will well describe the same experiment. After finding $a_0(\theta)$, phase field model can describe experiments with more details and in a broader range (in particular, for small IM width and incomplete melt) than the force-balance models.

3.6 Barrierless phase transformation

Effect of interface energy and width ratios, $k_E$ and $k_\delta$.— The effect of $k_E$ on the formation and stability of melt is systematically studied for a number of $k_\delta$ values and $a_0 = 0$ at $\theta_e^{21}$ for the case with pre-existing melt and an initially perturbed solid-solid interface—i.e., solidification and melting processes (Fig. 3.11). To remind, for $k_E > 2$ and melt equilibrium temperature, two $S_1M$ and $S_2M$ interfaces are energetically more favorable than $S_1S_2$ interface. Here we
consider $\theta = \theta_e^{21} = 432 K$, i.e., $\sim 100 K$ below melting temperature. For small $k_\delta$, both initial conditions result in the same steady solution for partial IM. If in a thought experiment one can change continuously $k_E$, e.g., by changing concentration of some alloying elements while keeping other parameters unchanged, then this would produce reversible change in the degree of premelting without any hysteresis. For larger $k_\delta$, two different initial conditions result in the same solution for relatively small and large $k_E$ only, but with two different nanostructures for intermediate $k_E$. One of these two solutions is always just a $S_1S_2$ interface. With increasing $k_E$, there is a jump from the $S_1S_2$ interface (which ceases to exist) to the second solution with partial or complete IM. With decreasing $k_E$, there is an opposite jump, which occurs for $k_E < 2$, i.e., IM persists under conditions at which it is energetically unfavorable. The two solutions produce a hysteresis region. This is in contrast to the sharp interface results that do not possess a scale parameter $k_\delta$ and has just one solution and formation of melt at $k_E > 2$ near melt equilibrium temperature. For both of the aforementioned initial conditions, increasing the value of $k_E$ promotes the formation and persistence of melt. Width of the hysteresis increases with increasing $k_\delta$, starting from zero for small enough $k_\delta$ values. While formation of a (almost) complete melted phase is observed for large $k_\delta$ and large enough $k_E$ values, for smaller $k_\delta$ values, only a partial IM appears for the same $k_E$ value.

Formation of IM as a function of $k_\delta$ has also been studied for a number of $k_E$ values at $\theta_e^{21}$ and $472 K$ and the results were shown in Fig. 3.12 for the same two different initial conditions. It is shown that increasing the value of $k_E$ promotes the formation of IM, which is consistent with results presented in Fig. 3.11. In all these cases, for large $k_\delta$ two solutions exist, one of each is the $S_1S_2$ interface ($\Upsilon_{min} = 1$) for $S_1S_2$ initial conditions and another one is the complete or incomplete IM for $S_1MS_2$ initial conditions. For small $k_\delta$, these solutions coincide, i.e., steady solution is independent of initial conditions. For large $k_E$ ((a) and (c)) and $S_1MS_2$ initial conditions, $\Upsilon_{min}$ for IM continuously reduces with an increase in $k_\delta$ and continuously increases with the reduction in $k_\delta$ along the same line. For $S_1S_2$ initial conditions, with reduction in $k_\delta$, the solution $\Upsilon_{min} = 1$ ceases to exist and a jump occurs to the single solution for IM. For small $k_E$ ((b) and (d)), the behavior is more sophisticated. For small $k_\delta$, a nonmonotonous dependence of $\Upsilon_{min}$ vs. $k_\delta$ is observed, the same for both initial conditions.
Figure 3.11: Intermediate melt formation $\sim 100K$ below melting temperature. a) Minimum steady value of $\Upsilon_{\text{min}}$ within $S_1MS_2$ interface at $\theta = \theta^{21}_\text{c} = 432K$ versus $k_E$, for melting (black graphs) and solidification (red graphs) is plotted for several $k_\delta$. For each $k_\delta \geq 0.7$, two different solutions exist in the range of $k_E$ within hysteresis loop (between arrows directed up and down), one of which is $\Upsilon_{\text{min}} = 1$. Outside this loop, for smaller $k_E$, IM does not exist; for larger $k_E$, $S_1S_2$ interface does not exist. For small $k_\delta$ (e.g. for $k_\delta = 0.3$), both solutions coincides. b) Profile of the equilibrium distribution of the order parameter $\Upsilon$ for $k_\delta = 0.3$ and multiple $k_E$. 
Thus, IM formation is promoted by an increase in the $k_\delta$ up to a certain point, and then it is suppressed for higher $k_\delta$ values, see the $\Upsilon$ profile in Fig. 3.13. For large $k_\delta$, the solution $\Upsilon_{\text{min}} = 1$ always exists and there is no jump to IM. For $S_1 S_2$ initial conditions, $\Upsilon_{\text{min}}$ slightly increases with reducing $k_\delta$ until IM ceases to exist and a jump to $\Upsilon_{\text{min}} = 1$ occurs. For intermediate $k_\delta$, the only existing solution for both initial conditions is $\Upsilon_{\text{min}} = 1$, which is called IM-free gap. The IM-free gap becomes smaller and finally disappears as $k_E$ increases, and is substituted by a continuous reversible PT. In addition, for small $k_E$, the IM does not appear even at low $k_\delta$. Structures of IM for different $k_\delta$ and two temperatures are shown in Fig. 3.13.

Effect of temperature. — The effect of temperature on the formation of IM is studied during melting and solidification for a number of $k_E$ and $k_\delta$ values and $a_0 = 0$ (Fig. 3.14). As expected, increasing temperature promotes the formation of IM for all $k_E$ and $k_\delta$ values independent of the chosen initial conditions. Increasing $k_E$ as well as reducing $k_\delta$ shifts the IM-formation temperature to lower values. For small $k_\delta$ values, a reversible and continuous melting/solidification occurs for all $k_E$ values under study (Fig. 3.14a), at least for $\theta < \theta^{20}_e$. For $\theta^{20}_e < \theta < \theta^{10}_e$ and some $k_E$, hysteretic phenomena are observed, which will be studied in detail elsewhere.

For larger values of $k_\delta$, barrierless jump occurs from $S_1 S_2$ interface to complete IM with increasing temperature. With a reduction in temperature from the IM state, first disordering reduces and then a jump occurs back to $S_1 S_2$ interface. While for $k_E = 3.5$, IM appears below the melting temperatures $\theta^{10}_e$ and $\theta^{20}_e$, for smaller $k_E$ this happens with overheating above the melting temperatures for both solid phases. The IM can be retained much below melting temperatures, and the resolidification temperature reduces for higher $k_E$ values. Width of the temperature hysteresis curve increases by reducing $k_E$ and increasing $k_\delta$. Increasing $k_\delta$ reduces (increases) the solidification (melting) temperature.

Note that when there is no energetic profit from substituting $S_1 S_2$ interface with two SM interfaces (i.e., $k_E \leq 2$) and for a homogeneous solid phase, barrierless nucleation starts at the lattice instability temperature of solid, i.e., significant overheating may occur. When there is energetic profit (i.e., $k_E > 2$) in the sharp interface approach $k_\delta = 0$, melting starts below melting temperature and the width of melt diverges at melting temperature (Levitas et al.,
Figure 3.12: Minimum steady value of $\Upsilon_{\text{min}}$ is plotted as a function of $k_\delta$ at $\theta_e^{21} = 432 K$ ((a) and (b)) and $\theta_e^{21} = 472 K$ ((c) and (d)) and for number of values of $k_E$ in the range $2.0 \leq k_E \leq 2.57$ ((b) and (d)) and in the range $2.59 \leq k_E \leq 3.5$ ((a) and (c)). Simulations are performed for melting (symbol-lines) and solidification (lines). For all cases, for large $k_\delta$ two solutions exist, one of each is $\Upsilon_{\text{min}} = 1$ for $S_1S_2$ initial conditions and another one for $S_1MS_2$ initial conditions. Arrows designate jumps from one solution (which ceases to exist) to another. For small $k_\delta$, these solutions coincide. For small $k_E$ ((b) and (d)), for small $k_\delta$, a nonmonotonous dependence $\Upsilon_{\text{min}}$ vs. $k_\delta$ is observed. For intermediate $k_\delta$, the only existing solution for both initial conditions is $\Upsilon_{\text{min}} = 1$, which is called IM-free gap.
Figure 3.13: Structures of $IM$ as a function of $k_\delta$ and temperature. The $Y$-profile of different $IM$ configurations for various $k_\delta$ values, $k_E = 2.2$ ((a) and (c)) and for $k_E = 2.0$ ((b) and (d)) are plotted at $\theta = 432K$ ((a) and (b)) and $\theta = 472K$ ((c) and (d)). The arrows represent the direction of increase in $k_\delta$ values. It is shown that below $IM$-free gap, decreasing $k_\delta$ first promotes formation of $IM$ up to some $k_\delta$ value and then suppresses $IM$ at lower values. Structure of (almost) complete melt for two different $k_\delta$ is plotted at $\theta = 432K$ (b) and $\theta = 472K$ (d).
Figure 3.14: Effect of temperature on the formation and retaining of IM. The $Y_{\text{min}}$ for (a) $k_\delta = 0.3$, (b) $k_\delta = 1.0$, and (c) $k_\delta = 1.1$ is plotted at different values of $k_E$. Continuous and reversible (without hysteresis) melting/solidification occurs for $k_\delta = 0.3$ and all $k_E$ values, at least for $\theta < \theta_e^{20}$. For $k_\delta = 1.0$ (b) and $k_\delta = 1.1$ (c), melting and solidification represent the first-order transformation with hysteresis loops.

2012). Here, significant overheating above both melting temperatures occurs even for $k_E = 3$ (Fig. 3.14, b and c). This is because of the scale effect, i.e., the effect of the relatively large value of $k_\delta$.

**Interface energy, width and velocity.** In this section, the effect of interface interactions and scale effect on formation of IM, interface energy, width, and velocity have been studied in detail for a wide temperature range by varying $a_0$ and $k_\delta$. Simulations are performed for $k_\delta = 0.3, 1.0, 1.1$ and a large enough $k_E$ value—i.e., $k_E = 4.0$, to ensure formation of IM in a wide temperature range, $0.65\theta_e^{21} < \theta < \theta_e^{20}$ (Figs. 3.15 to 3.18). Solutions for two different initial conditions coincide for all cases in this Section. It is worth noting that almost a complete melt with a width larger than $1\text{nm}$ is formed at $0.65\theta_e^{21}$ and $k_\delta = 1.0$, which is almost $240K$ below melting temperature.

Numerical simulations indicate that the formation of IM is promoted as temperature increases for all $a_0$ values—i.e., $Y_{\text{min}}$ and $S_1MS_2$ energy are reduced while the width $\delta^*$ increases (Figs. 3.15 and 3.16). Energy of IM at elevated temperatures, when IM has a large width $\delta^*$, can be approximated as in Eq. (3.57), i.e., $E^* = 2E^0 + \Delta G\delta^* + 0.5\beta^{21}a_0/\delta^*$. Here $\delta^*$ can be defined as $\delta - \delta_{\text{int}}$ or the distance between points with $Y = 0.5$ at two $S_1M$ and $S_2M$ interfaces: the difference is small for relatively large $\delta^*$. The equilibrium width of IM is determined by $\partial E^*/\partial \delta^* = 0$, which results in $\delta^* = \sqrt{0.5\beta^{21}a_0}/\Delta G$. When $\Delta G \to 0$, IM width $\delta^*$ diverges. Note that since $\Delta G$ was approximated as $\Delta G = (\Delta G^{10} + \Delta G^{20})/2$, divergence should occur
above $\theta^{20}$ but below $\theta^{10}$. This was the case in all simulations (Fig. 3.15). In contrast, in (Levititas and Momeni, 2014) $\Delta G$ was taken for phase with lower melting temperature, which lead to IM width divergence at $\theta^{20}$. Large $\delta^*$ corresponds to the case that extra interface energy due to interaction of SM interfaces, $0.5\delta^{21}a_0/\delta^*$, is negligible. The energy of IM reaches the energy of two SM interfaces, which in this case ($k_E = 4.0$) is $0.5E^{21}$. Smaller $a_0$ enhances the melting at low temperatures—i.e. reduces $\Upsilon_{min}$, while at temperatures higher than $\theta/\theta^{21} > 1.1$, the effect of $a_0$ either disappears for $k_\delta = 0.3$ or getting nonmonotonous for $k_\delta \geq 1$.

Increasing $k_\delta$ reduces the IM energy $E^*$, and modifies its nonlinear relation with temperature at small $k_\delta$ to an approximately linear relation at larger $k_\delta$ (Fig. 3.16). IM energy $E^*$ increases with increasing $a_0$. Width of the IM, $\delta^*$, increases monotonously with increasing temperature, which is consistent with the relation obtained for $\delta^*$. For $k_\delta = 1$, width $\delta^*$ increases with increasing $a_0$ for high temperatures $\theta/\theta^{21} > 0.85$ and reduces for $\theta/\theta^{21} < 0.85$. For $k_\delta = 1.1$, the intersection of $\delta^*$ curves for different $a_0$ occurs in temperature range $\theta/\theta^{21} > 0.82$ width increases with increasing $a_0$ for high temperatures $\theta/\theta^{21} > 0.85$ and reduces for $1.1 > \theta/\theta^{21} < 0.85$. For $k_\delta = 0.3$, $\delta^*$ curves for different $a_0$ are very close, except for $a_0 = 0.5$. There is no direct simplified model nor any indication in other plots ($\Upsilon_{min}$ and $E^*$ vs. $\theta/\theta^{21}$) to describe such behavior for $\delta^*$. Therefore, the data presented in Fig. 3.17 develop new intuition to the problem and indicate the necessity for further investigation close to the crossover point (at $\theta/\theta^{21} \approx 0.85$ for $k_\delta = 1.0$).

For the simple case of direct PT between two phases, the interface velocity can be calculated using the analytical solutions (3.32) and (3.34) and the numerical solution of the GL equations matches them (Fig. 3.5). Formation of IM generally reduces the interface velocity (Fig. 3.18) despite the fact that the kinetic coefficient for solid-melt PT is chosen to be twice of that for $S_1 - S_2$ PT. This reduction grows with increasing $k_\delta$. In contrast to linear temperature dependence of the interface velocity for $S_1S_2$ and SM interfaces, the interface velocity for $S_1S_2$ interface is a nonlinear function of temperature. The interface velocity increases in all cases as the magnitude of interface interaction increases. For small $k_\delta = 0.3$, results for any $a_0$ are very close to the $S_1S_2$ interface velocity, and for large $a_0$ close to the melting temperature the $S_1MS_2$ interface velocity is even higher than the $S_1S_2$ interface velocity (Fig. 3.18a).
Figure 3.15: Minimum steady value of $\Upsilon$ at different temperatures and $a_0$ values, indicating formation of IM for $k_\delta = 0.3$ (a), $k_\delta = 1.0$ (b), and $k_\delta = 1.1$ (c). Increasing $k_\delta$ reduces the $\Upsilon_{\text{min}}$ for corresponding $a_0$.

Figure 3.16: Effect of temperature on the energy of IM, $E^*$, for different $a_0$ values, (a) $k_\delta = 0.3$, (b) $k_\delta = 1.0$, and (c) $k_\delta = 1.1$. While $E^*$ is an almost linear function of temperature for $k_\delta = 1.0$ and $k_\delta = 1.1$, it becomes a nonlinear function of temperature for small $k_\delta$ values ($k_\delta = 0.3$). Reducing $k_\delta$ also increases the energy of IM for corresponding temperature and $a_0$. 
Figure 3.17: Effect of temperature on width of IM, $\delta^*$, for different $a_0$ values, (a) $k_\delta = 0.3$ (logarithmic scale), (b) $k_\delta = 1.0$ (reciprocal scale), and (c) $k_\delta = 1.1$ (reciprocal scale). The $\delta^*$ is directly related to temperature for all $k_\delta$ values. It is also directly related to $a_0$ at higher temperatures but has a cross-over as temperature reduces and becomes inversely related to $a_0$ for low temperatures. The cross-over point shifts to higher temperatures as $k_\delta$ reduces.

Figure 3.18: Effect of formation of IM on the $S_1 S_2$ interface velocity. Solid line is the velocity of $S_1 S_2$ interface obtained using the analytical solution (Eq. (3.43)). Simulations are performed for $k_E = 4$, (a) $k_\delta = 0.3$, $k_\delta = 1$, and $k_\delta = 1.1$. Formation of IM drastically reduces the $S_1 S_2$ interface velocity for large $k_\delta$ values, but has a minor effect for small $k_\delta$. In the latter case formation of IM may even increase $S_1 S_2$ interface velocity for large enough $a_0$. 
3.7 Thermally activated intermediate melting through critical nucleus

As it was found above, two different steady solutions may appear for some parameters depending on initial conditions, i.e., for a melting or solidification process. They correspond to the local energy minima. Two minima are always separated by an energy barrier that should be overcome in order to jump from one minimum to another one. This indicates the existence of a third solution, corresponding to the minimal energy barrier between two steady solutions, which represents the critical $IM$ nucleus.

If the difference between energy of the $IM$ critical nucleus, $E^{cn}$ and the ground state is smaller than $(40 - 80)k_B\theta$, where $k_B$ is the Boltzmann constant, then a thermally activated jump from the ground state to the critical nucleus is energetically possible within reasonable time (Porter, 1981). After this, further growth of the critical nucleus, which evolves to the alternative steady nanostructure. Thus, if the initial condition corresponds to the $S_1S_2$ interface, then the condition $\Delta E_{ss}^{cn} = E^{cn} - E^{21} \leq (40 - 80)k_B\theta$ represents nucleation criterion for the $IM$. If initial structure corresponds to $IM$, then the condition $\Delta E_{ss}^{cn} = E^{cn} - E^* \leq (40 - 80)k_B\theta$ represents kinetic criterion for the disappearance of the $IM$.

Even for the homogeneous nucleation in bulk, the critical nucleus has a size of a few nanometers. An advantage of PFA (nonclassical nucleation model) in comparison with the classical sharp-interface nucleation theory is that the critical nucleus may represent some intermediate structure (e.g., $\Upsilon > 0$) rather than complete product phase, which reduces its energy (Cahn and Hilliard, 1958). Also, at the critical temperature, when the parent phase loses its stability, the energy of the critical nucleus tends to zero in PFA, as expected. This cannot be achieved in the sharp interface approach. For heterogeneous $IM$ nucleation within $S_1S_2$ interface, the nucleus size is limited by the interface width and it is always an incomplete melt; thus sharp interface approach is not applicable. A PFA to heterogeneous solid nucleation from liquid at the wall was considered in (Gránásy et al., 2007; Warren et al., 2009).

Because a critical nucleus represents an unstable stationary solution corresponding to the saddle point of the energy functional (Shen et al., 2008; Chu et al., 2000), its finding represents a separate nontrivial problem. Solving the evolutionary time-dependent phase field equations
leads to the local minima of the system and cannot be used for finding the saddle points. Different methods were introduced for finding the saddle points of the energy functional, including nudged elastic band (Mills and Jönsson, 1994), climb-image nudged elastic band (Shen et al., 2008; Henkelman and Jönsson, 2000; Henkelman et al., 2000), and minimax variational (Zhang et al., 2007) techniques, some of which (Shen et al., 2008; Zhang et al., 2007) have been applied for PFA. We will use a simple approach based on finding a solution to the stationary GL equations by utilizing a numerical solver for stationary problems rather than by solving non-stationary system of equations. Then if initial conditions are chosen to be close to the solution for the critical nucleus, a stationary solution will represent the critical nucleus rather than any other solutions corresponding to the local energy minima. This is similar to the approach utilized in (Gránásy et al., 2007; Warren et al., 2009) for nucleation at the wall. We limit ourselves to $\theta = \theta^e_2$, because for other temperatures the interface is not stationary and the stationary solver cannot be used. Extension of this approach for non-stationary interfaces by utilizing equations in the frame of reference moving together with $S_1MS_2$ interface will be considered elsewhere. Here, a modified Newtonian method (Deuflhard, 1974) is utilized for solving the stationary GL equations from an initial condition close to the final configuration of the critical nuclei. It involves an iterative process with different initial conditions, produced by a chosen function—namely, Eq. (3.60). For finding the critical nucleus in 1D approximation, the initial condition for $\Upsilon$ at the entire $S_1S_2$ interface is prescribed by Eq. (3.60). Such a 1D approximation overestimates an energy of a critical nucleus, which can be reduced by finding a finite size of the nucleus along the $S_1S_2$ interface. Axisymmetric problem formulation with the symmetry axis orthogonal to the interface is an optimal formulation, which allows us to find an actual critical nucleus with economic 2D simulations. For single and multiple 2D axisymmetric critical nuclei, the initial distribution $\Upsilon$ Eq. (3.60) is multiplied by a step function along the $S_1S_2$ interface to limit the length of initial disordered phase along the interface.

The simplest initial condition, which describes $IM$ confined between two solids can be obtained by combining the analytical solutions for two stationary $S_M$ interfaces (Eq. (3.32)):

$$
\Upsilon_{cn} = \left\{ 1 + \exp\left[-(\Upsilon - x_0 - W/2)/\delta^{20}\right]\right\}^{-1} + \left\{ 1 + \exp\left[(\Upsilon + x_0 - W/2)/\delta^{10}\right]\right\}^{-1}$$

(3.60)
Figure 3.19: Initial conditions and effect of system parameters on CN. (a) Profiles for initial conditions for determining the critical nucleus based on Eq. (3.60) for various $x_0$ and $\theta = \theta_{e}^{21} = 432K$. (b) Effect of $k_E$ on the $\Upsilon$-profile of the critical nuclei (upper curves) and stable stationary solution for the $IM$ (lower curves) for a 1D formulation, $k_{\delta} = 1.0$ and $\theta = \theta_{e}^{21} = 432K$, and different $k_E$ values are plotted for 1D problem. The inset shows the zoomed in section of the $IM$ plot.

where $W$ is width of the sample, and $x_0$ determines the width of $IM$. Increasing the values of $x_0$, reduces $\Upsilon_{min}$. The $S_1MS_2$ profile is plotted in Fig. 3.19(a) for multiple $x_0$ values at $\theta = \theta_{e}^{21} = 432K$.

The proper $x_0$ value which leads to the solution corresponding to the critical nucleus is determined iteratively and is about $0.3\delta^{21}$ for the range of studied $k_E$ values. Depending on the initial conditions, three different critical nuclei configurations are found which correspond to 1D plane interface, single 2D axisymmetric, and multiple axisymmetric configurations. The effect of interface energy ratio, $k_E$, on the $\Upsilon$-profile of critical nucleus at $k_{\delta} = 1.0$ and $a_0 = 0$ is studied for 1D planar and 2D axisymmetric problems. For the 1D solution for planar solid-solid interface, the $\Upsilon$-profile for critical nuclei is shown in Fig. 3.19(b) along with the stationary solution for stable $IM$ for the corresponding $k_E$ values. Solutions for the $IM$ are obtained by solving time-dependent GL equations with the initial condition corresponding to perturbed critical nucleus by slightly reducing $\Upsilon$. It is shown that the degree of disordering of the $IM$ (or critical nucleus) increases (or decreases) with increasing $k_E$. The size of the critical nucleus also gets smaller as $k_E$ increases.
Figure 3.20: Effect of $k_E$ on the structure of the critical nucleus. The 2D distribution of $\Upsilon$ and its planar cut along the $S_1S_2$ interface is shown for a $40 \times 60\, nm$ sample at $\theta = \theta_2^{21} = 432K$, $k_\delta = 1$, and multiple $k_E$ values. The $S_1S_2$ interface between $\beta$-phase (bottom) and $\delta$-phase (top) is at the center of the sample.

The critical nucleus is also found for a 2D axisymmetric problem in a $40 \times 60\, nm$ sample. Two initial conditions are considered: (i) initial disordered phase is elongated a few nanometers along the $S_1S_2$ interface, and (ii) initial disordered phase is elongated tens of nanometers along the $S_1S_2$ interface but does not cover the entire $S_1S_2$ interface. The $\Upsilon$-distributions for critical nucleus for cases (i) and (ii) are shown for different $k_E$ values in Figs. 3.20 and 3.21, respectively. While Fig. 3.20 shows the formation of a single critical nucleus, Fig. 3.21 demonstrates the formation of multiple nuclei along the solid-solid interface similar to the oscillatory solution of GL equations for the 1D case (Falk, 1983; Levitas et al., 2003). Fig. 3.20 demonstrates the reduction in the size and degree of disordering of the critical nucleus as $k_E$ increases. Multiple nuclei have much larger energy than the single nucleus at the center of the sample and that is why their appearance due to thermal fluctuations is improbable.

Solving the GL equations using the distribution for CN as the initial conditions, does not change its $\Upsilon$-distribution. However, if the initial conditions are deviated slightly toward $S_1S_2$ interface or $S_1MS_2$ interface, the solution of the GL equations evolves to the corresponding local energy minima, as shown in Fig. 3.22. It proves that the obtained solution is indeed the critical nucleus and corresponds to the saddle point of the total free energy function.
Figure 3.21: Multiple critical nuclei solution for $\theta = \theta_e^{21} = 432K$, $k_\delta = 1$, and $k_E = 3.0$ for a 40 × 60 nm sample.

Figure 3.22: (a) The critical nucleus for 40 × 60 nm sample at $\theta = \theta_e^{21} = 432K$, $k_\delta = 1$, and $k_E = 3$. (b) Snapshot of the subcritical nucleus obtained during evolution of the critical nucleus slightly perturbed toward $S_1 S_2$ interface. (c) Snapshot of the supercritical nucleus obtained during evolution of the critical nucleus slightly perturbed toward $S_1 M S_2$ interface. The subcritical nucleus finally disappears, while supercritical nucleus forms an IM at the $S_1 S_2$ interface. Corresponding distribution of $\vartheta$ is shown in (d)-(f).
Figure 3.23: Formation energy of the critical nucleus versus $k_E$, from $S_1S_2$ ground state, $\Delta E_{cn}^{ss}$ (solid black line), and from $S_1MS_2$ ground state, $\Delta E_{cn}^{sms}$ (red dashed line), for the 40 $\times$ 60 nm sample for $\theta = \theta_2^{21} = 432K$, $k_\delta = 1$. Nucleation is possible when kinetic nucleation criterion is met, i.e., below horizontal blue dotted line corresponding to $80k_B\theta$.

Fig. 3.23 shows the formation energy of the critical nucleus versus $k_E$, from $S_1S_2$ and $S_1MS_2$ ground states. Nucleation is possible when kinetic nucleation criterion, $\Delta E_{cn} < 80k_B\theta$ is satisfied, i.e., below the horizontal line corresponding to $80k_B\theta$. The intersection of energy lines with axis $\Delta E_{cn} = 0$ determines $k_E$ for barrierless nucleation. Thus, nucleation of IM due to thermal fluctuations is possible for $k_E > 3.0$, and above $k_E > 3.05$ for barrierless nucleation. Similarly, the disappearance of the IM due to thermal fluctuations is possible for $k_E < 2.52$, slightly above $k_E > 2.51$ for barrierless nucleation.

3.8 Comparison with some existing models and possible future applications

We are not aware of any PFA for propagating interface between two phases containing intermediate phase, except (Levitas and Momeni, 2014); comparison with (Levitas and Momeni, 2014) is given in Section 3.1. The PFAs for premelting in grain boundaries (Kobayashi et al., 2000; Lobkovsky and Warren, 2002a; Tang et al., 2006a) also consider intermediate melt (disordered phase) between two phases (grains) and structure of interface (i.e., variation of order parameters) is qualitatively similar. However, details of the thermodynamic potentials are different in (Kobayashi et al., 2000; Lobkovsky and Warren, 2002a; Tang et al., 2006a)
than here due to different physics. In particular, there is no thermal energy difference for
grain boundary movement and the linear term in the gradient of grain orientation angle ($\vartheta$ in
the designations of the current paper) is included in energy. However, the key difference is that
in (Kobayashi et al., 2000; Lobkovsky and Warren, 2002a; Tang et al., 2006a) the gradient of
the grain orientation angle $\nabla \vartheta$ in complete melt is not penalized because orientation in melt
has no meaning. This is equivalent to $a_0 = 0$ in our model which as we discussed leads to
an ill-posed problem, catastrophically mesh dependent solutions, and the impossibility to de-
scribe interaction between two interfaces. These problems have not been realized in (Kobayashi
et al., 2000; Lobkovsky and Warren, 2002a) probably because complete melting in the grain
boundary was not the main focus. Also, detectable premelting in these works takes place just
several degrees below melting temperature (the same for both grains), while the intermediate
melting in experiments (Levitas et al., 2004, 2006a; Levitas, 2005; Levitas et al., 2012; Randzio
and Kutner, 2008) and here, occurs several hundreds of degrees below melting temperatures
of both phases. It was not even clear that PFA is able to describe such phenomena. In (Tang
et al., 2006a), quadratic contribution to the energy $|\nabla \vartheta|^2$ was omitted and sharp $\vartheta$ interface
was explicitly introduced in analytical treatment. Since this interface should not be resolved
numerically, the problem of ill-posedness of the formulation did not arise. However, such an
approach is equivalent to setting $a_0 = 0$ and does not include interaction between interfaces.

Multiphase models are routinely utilized to study phase transformations between three
and more phases (Tiaden et al., 1998; Folch and Plapp, 2005a), between austenite and multi-
ple martensitic variants (Artemev et al., 2001a; Chen, 2002a; Levitas et al., 2003, 2013), for
nucleation of competing solid phases from melt (Tóth et al., 2011), and for grain boundary
premelting (Mishin et al., 2009). The first main advantage of the current model in comparison
with (Tiaden et al., 1998; Folch and Plapp, 2005a; Artemev et al., 2001a; Chen, 2002a; Lev-
itas et al., 2003, 2013; Mishin et al., 2009; Tóth et al., 2011) is that each of the three phase
transformations is described by a single-order parameter, without additional constraints on the
order parameters. The second advantage is that we explicitly treat interaction between two
interfaces via intermediate third phase. Also, one of the goals of the multiphase formulation
was to avoid any intermediate phases at the interface between two phases (Mishin et al., 2009;
Folch and Plapp, 2005a). In (Tóth et al., 2011) a structure of the solid phase critical nucleus was obtained which contains traces of the second solid phase at the nucleus surface. The model in (Tóth et al., 2011) corresponds to $a_0 = 0$ and $k_\delta = 1$. Since width of two-phase interface is not well known for most of phases but it has an order of magnitude of 1 nm, it is typical to assume that $k_\delta = 1$. However, as we demonstrated, variation of $k_\delta$ may drastically change the results. In (Artemev et al., 2001a; Chen, 2002a; Levitas et al., 2003; Levitas and Javanbakht, 2011a) the interfaces between two martensitic variants are described by simultaneous variation of two order parameters. That is why there is no analytical solution for such interfaces and their energy and width depend on temperature (through driving force for austenite-martensite PT) in an uncontrollable way. In (Levitas and Javanbakht, 2011a) the product of gradients of two different order parameters was introduced in the energy functional in order to vary energy of martensite-martensite interface independent of the energy of austenite-martensite interface. For low martensite-martensite interface energy and close to austenite-martensite equilibrium temperature, pre-austenite and austenite appeared at the martensite-martensite interface (Levitas and Javanbakht, 2011a). Still, in (Levitas and Javanbakht, 2011a) martensite-martensite interface is described by simultaneous variation of two order parameters and there is no analytical solution for such an interface. This drawback is eliminated with the help of hyperspherical order parameters (which reduce to polar order parameters utilized here for a three phase system) in (Levitas et al., 2003, 2013). However, in (Levitas et al., 2003, 2013) all solid phases (martensitic variants) have the same thermal energy, $a_0 = 0$, and an intermediate phase was not considered. Since our model is reduced to three-phase model in (Levitas et al., 2013) by putting $a_0 = 0$ and equal thermal energies of phases, and model (Levitas et al., 2013) describes qualitatively and quantitatively well some observed nanostructures, this also adds credibility to our current model.

Models (Falk, 1983; Levitas et al., 2003) for the one-dimensional case have analytical solutions which show the appearance of pre-austenite and austenite at the martensite-martensite interface. However, all three phases are described by the single order parameter $\eta$ and the path from one variant $\eta = 1$ to another $\eta = -1$ passes through austenite $\eta = 0$. Premelting at the external surface (Lipowsky, 1982; Levitas and Samani, 2011a,b) and surface-induced marten-
sitic phase transformation (Levitas and Javanbakht, 2010) are also governed by the reduction in surface energy during transformation. This is, however, just two-phase models that do not include moving solid-solid interface. In (Levitas and Javanbakht, 2011b) the finite width of the external surface is introduced with the help of a separate order parameter in addition to the order parameter describing phase transformation. While this was a very simplified model in comparison with the current one, the strong scale effect described by $k_\delta$ was revealed.

All of the above models and phenomena, namely for grain boundary melting (Kobayashi et al., 2000; Lobkovsky and Warren, 2002a; Tang et al., 2006a; Mishin et al., 2009), multivariant martensitic and reconstructive PTs (Artemev et al., 2001a; Chen, 2002a; Levitas et al., 2003; Levitas and Javanbakht, 2011a; Levitas et al., 2013), surface-induced melting and solid-solid transformations, including moving condensed phase - vapor interface (Lipowsky, 1982; Levitas and Javanbakht, 2010; Levitas and Samani, 2011a,b; Levitas and Javanbakht, 2011b), solid-solid transformation via surface-induced or grain boundary-induced intermediate melting (Levitas et al., 2012), and general multiphase models (Tiaden et al., 1998; Folch and Plapp, 2005a) may benefit from introducing some results of the current study. They include introducing polar order parameters, the satisfaction of stability conditions, elaborating on gradient energy contributions, and the description of interface interaction. Amorphization via IM (Levitas, 2005) can be described in a similar way. In general, it is not necessarily that IM completely wets solid phases. In particular, the critical nucleus did not exhibit complete wetting and does not spread along the entire interface (Figs. 3.20 and 3.21). Similarly, in the finite-width external surface model (Levitas and Javanbakht, 2011b), morphological transitions from the complete wetting to incomplete wetting and different shapes of the product nucleus is observed for different $k_\delta$. Thus, mutually beneficial interaction between works on wetting of the external and internal surfaces, e.g., (Cahn, 1977; Baram et al., 2011; Luo, 2007; Luo and Chiang, 2008; Luo, 2012) and our approach, is desirable. The developed approach can be generalized for the description of diffusive PTs in a multicomponent system with evolving concentration (Mishin et al., 2009; Luo, 2007; Luo and Chiang, 2008; Luo, 2012). An important recent direction is a study of formation of interfacial and intergranular crystalline or amorphous phases (called complexions) (Luo, 2007; Luo and Chiang, 2008; Luo, 2012; Baram et al., 2011; Luo and
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Chiang, 2000; Avishai and Kaplan, 2005; Avishai et al., 2005; Cantwell et al., 2014; Qian et al., 2008; Chung and Kang, 2003; ?; Frolov et al., 2013b) in ceramic and metallic systems and developing corresponding interfacial phase diagrams (Luo, 2007; Luo and Chiang, 2008; Luo, 2012). Our PFA after proper generalization and specification can be utilized for such studies. Note that other methods have been utilized to model phase transformations and premelting in grain boundaries, including molecular dynamics (?Frolov et al., 2013b) and phase field crystal (Heo et al., 2011; Mellenthin et al., 2008; Adland et al., 2013; Goldenfeld et al., 2005) methods. They can be applied to the problem under study as well.

3.9 Concluding remarks

A three-phase PFA to solid-solid PT via an intermediate phase is developed and utilized to perform a detailed numerical study of the main IM features using finite element method. A thermodynamic potential is formulated with the help of polar order parameters, which satisfies all desired phase equilibrium and stability conditions. By setting \( \Upsilon = 1 \) or \( \vartheta = 0 \) or 1, this potential reduces to the same two-phase potential suggested in (Levitas and Preston, 2002a) and the same corresponding GL equations. Necessity to introduce the gradient energy for solid-solid interface within complete melt, which at first glance seems contradictory, is justified by necessity to have a well-posed problem and to describe the interaction between two solid-melt interfaces. Previous force-balance models for short range and long range interaction forces between two interfaces are generalized for the case that includes finite width interfaces. A new force-balance model is suggested that better describes results of the phase field simulations significantly below the melting temperatures. We demonstrated that our PFA is able to capture the relation between IM energy and width described by all force balance models in some range by choosing proper \( a_0 \). With the same values \( a_0 \), PFA should realistically describe interfacial interactions and IM width for the cases when sharp interface models do not work, namely for small IM width or incomplete IM.

Detailed study of the effect of four parameters, namely, \( k_\delta \), \( k_E \), \( a_0 \), and temperature, on the structure, width, energy of the IM, and velocity of \( S_1MS_2 \) interface is performed by solving time dependent GL equations. While temperature and energy ratio \( k_E \) (or \( k_E \)-related
parameters) are parameters that are traditionally considered in surface or grain boundary premelting and melting (Lipowsky, 1982; Lobkovsky and Warren, 2002a; Tang et al., 2006a; Levitas and Samani, 2011a,b), two other parameters were unexplored. That is why many results are unexpected and counterintuitive. Thus, for small $k_\delta$ barrierless $IM$ is reversible and hysteresis-free, and single steady solution exists independent of initial conditions. For large $k_\delta$, in particular, $k_\delta \geq 1$, three solutions exist: stable, metastable, and a critical nucleus between them (unstable), one of them is dry $S_1S_2$ interface. For neglected thermal fluctuations, significant overheating even above the melting temperature of solid phases and overcooling to very low temperature is observed, i.e., significant hysteresis in melting/solidification exists. The effect of $k_\delta$ is very nontrivial and depends on $k_E$, $a_0$, and temperature. For relatively large $k_E$, an increase in $k_\delta$ reduces the degree of disordering down to complete melt in the case of $S_1MS_2$ initial conditions; at the same time it leads to the appearance of the dry $S_1S_2$ solution starting with some $k_\delta$. For relatively small $k_E$ and for small $k_\delta$, dependence of $\Upsilon_{\min}$ on $k_\delta$ is nonmonotonous. Thus, for reversible barrierless melting, $\Upsilon_{\min}$ first reduces and then increases reaching 1. For larger $k_\delta$ barrierless melting does not occur for $S_1S_2$ interface initial conditions. At large $S_1S_2$, $IM$ can be obtained for $S_1MS_2$ initial conditions. For intermediate $k_\delta$, $IM$ does not exist for any initial condition forming $IM$-free gap. Solutions for critical nucleus were found utilizing a stationary solver for time-independent GL equations with the proper choice of initial condition in axisymmetric formulation. Kinetic criterion for its appearance leads to conditions at which thermally activated nucleation is possible. While multiple critical nuclei have been obtained as well, their energy is much larger than energy of the single nucleus near the symmetry axis and their appearance is improbable. Note that the discussed force-balance interaction models have just one energy minimum with respect to $IM$ width. Consequently, they are not applicable to the case with three solutions, for which force-balance interaction models should have two minima separated by a maximum. Development of such models will be considered in the future. That is why based on intuition developed by studying force-balance models, the appearance of partial melt more than 100 K below melting temperature and retaining melt more than 200 K below the melting temperature, as well as significant overheating above the melt temperatures of solid phases without melting, looks unexpected.
and counterintuitive. Numerical simulations show a significant reduction in the $S_1S_2$ interface velocity as $IM$ forms at moderate to high $k_5$ values. However, a slight increase in the $S_1S_2$ interface velocity is observed for small $k_3$ at a high temperature and large $a_0$ values. The interface velocity is a nonlinear function of $a_0$ and increases as $a_0$ increases.

Some possible generalizations and applications of the developed PFA are discussed in Section 3.8. As the next step, the effect of internal stresses will be included in the model in a way outlined in (Levitas and Momeni, 2014). This will, in particular, allow us to attempt to quantitatively describe interface propagation velocity vs. temperature for $\beta - \delta$ PT in HMX crystals, observed experimentally (Henson et al., 2002; Smilowitz et al., 2002; Levitas et al., 2006b). This will include the formation of the critical nucleus (because interface kinetics is well described by the phenomenological model for thermally activated propagation), the generation and relaxation of internal stresses and interface stresses within propagating interface. Also, the statement that the interface with $IM$ should be insensitive to the stress field of defect and consequently, exhibit zero athermal resistance, will be checked depending on the degree of disordering within the interface.

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CHAPTER 4. THE STRONG INFLUENCE OF INTERNAL STRESSES ON THE NUCLEATION OF A NANOSIZED, DEEPLY UNDERCOOLED MELT AT A SOLID-SOLID PHASE INTERFACE

The effect of elastic energy on nucleation and disappearance of a nanometer size intermediate melt (IM) region at a solid-solid ($S_1S_2$) phase interface at temperatures 120$K$ below the melting temperature is studied using a phase-field approach. Results are obtained for broad range of the ratios of $S_1S_2$ to solid-melt interface energies, $k_E$, and widths, $k_\delta$. It is found that internal stresses only slightly promote barrierless IM nucleation but qualitatively alter the system behavior, allowing for the appearance of the IM when $k_E < 2$ (thermodynamically impossible without mechanics) and elimination of what we termed the IM-free gap. Remarkably, when mechanics is included within this framework, there is a drastic (16 times for HMX energetic crystals) reduction in the activation energy of IM critical nucleus. After this inclusion, a kinetic nucleation criterion is met, and thermally activated melting occurs under conditions consistent with experiments for HMX, elucidating what had been, to-date, mysterious behavior. Similar effects are expected to occur for other material systems where $S_1S_2$ phase transformations via IM take place, including electronic, geological, pharmaceutical, ferroelectric, colloidal, and superhard materials.

In this study, we investigate the appearance of phases at an $S_1S_2$ boundary, detailing the influence of processes within few nanometer thick phase interface, including its structure and stress state. It is found that the $S_1S_2$ interface tends to reduce its energy via elastic stress relaxation and restructuring. Specifically, restructuring can occur via the nucleation of a nm-scale IM at the $S_1S_2$ boundary, at temperatures well below the bulk melting temperature. This

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mechanism was proposed for $\beta \leftrightarrow \delta$ phase transformations (PTs) in energetic organic HMX crystals (Levitas et al., 2004, 2006a) at undercoolings of 120K in order to explain puzzling experimental data in Refs. (Henson et al., 2002; Smilowitz et al., 2002). The appearance of the IM at these temperatures allowed for a relaxation of elastic energy at the $S_1S_2$ phase interface, making the transition energetically favorable. This mechanism explained, both quantitatively and qualitatively, 16 nontrivial experimental phenomena. (Levitas et al., 2006a) In addition to stress relaxation and elimination of interface coherency, the IM eliminates athermal friction and alters the interface mobility. Along related lines, the mechanism of crystal-crystal and crystal-amorphous PTs via intermediate (or virtual) melting for materials (like water) where increasing the pressure leads to a reduction in the melting temperature was suggested in Ref. (Levitas, 2005). Amorphization via virtual melting was claimed in experiments for Avandia (Rosiglitazone), an anti-diabetic pharmaceutical, in Ref. (Randzio and Kutner, 2008). Also, solid-solid PT via IM and surface-induced IM in PbTiO$_3$ nanofibers was observed experimentally and treated thermodynamically in Ref. (Levitas et al., 2012). In this case, melting within the $S_1S_2$ interface was caused by reduction in the total interface energy and relaxation of internal elastic stresses. And, in subsequent investigations, it was found that relaxation of external deviatoric stresses under very high strain rate conditions could cause melting at undercoolings of 4000 K (Levitas and Ravelo, 2012). The important role of these phenomena in the relaxation of stress in crystalline systems is given in Ref. (Ball, 2012). Most recently, the transition between square and triangular lattices of colloidal films of microspheres via an IM was directly observed in Ref. (Peng et al., 2015). However, there are some essential inconsistencies in the thermodynamic and kinetic interpretation of this phenomenon in Ref. (Peng et al., 2015). While it is stated that crystal-crystal transformation occurs below the bulk melting temperature $T_m$, the bulk driving force for melting is considered to be positive, which is possible above $T_m$ only. In contrast to the statement in Ref. (Peng et al., 2015), crystal-crystal transformation via intermediate (virtual) melting have been discussed for a decade, indeed significantly below melting temperature (Levitas et al., 2004; Levitas, 2005; Levitas et al., 2006a; Randzio and Kutner, 2008; Levitas et al., 2012; Levitas and Ravelo, 2012; Ball, 2012; Momeni and Levitas, 2014; Levitas and Momeni, 2014), and with much more general thermodynamic and kinetic
In the above treatments of this phenomena, the theoretical approach was limited to simplified continuum thermodynamics. Recently, however, we introduced a phase-field approach for the $S_1S_2$ phase transformation via $IM$ and the formation of disordered interfacial phases both without (Momeni and Levitas, 2014) and with (Levitas and Momeni, 2014) mechanical effects. This approach yielded a more detailed picture of the interface, including the appearance of a “partial” $IM$ and the substantial influence of the parameter $k_\delta$, an effect necessarily not present in sharp-interface theories. In Refs. (Momeni and Levitas, 2014; Levitas and Momeni, 2014) the effect of relaxation of internal stresses was briefly investigated for the case of barrierless $IM$ nucleation, and nucleation via a critical nucleus (CN) was not explored. In fact, results in Ref. (Momeni and Levitas, 2014) for CN appeared to eliminate it as a mechanism for stress relaxation, as the CN had too high an activation energy to explain observation of macroscopic kinetics of $\beta \leftrightarrow \delta$ PTs in HMX crystals (Levitas et al., 2004, 2006a; Henson et al., 2002; Smilowitz et al., 2002).

In this letter, we employ our phase field approach to study effect of mechanics, i.e., internal stresses (for different ratios $k_E$ and $k_\delta$) on the thermodynamics, kinetics, and structure of $IM$ within a $S_1S_2$ interface, describing its appearance and disappearance due to barrierless and thermally activated processes $120K$ below bulk melting temperature in a model HMX system. It is found that internal stresses only slightly promote barrierless $IM$ nucleation but qualitatively alter the system behavior, allowing for the appearance of the $IM$ when $k_E < 2$ (thermodynamically impossible without mechanics) and elimination of what we termed the $IM$-free gap. Remarkably, when mechanics is included within this framework, there is a drastic (16 times for HMX energetic crystals) reduction in the activation energy of $IM$ critical nucleus. After this inclusion, a kinetic nucleation criterion is met, and thermally activated melting occurs under conditions consistent with experiments for HMX, elucidating what had been, to-date, mysterious behavior. (Levitas et al., 2004, 2006a). CN at the surface of a sample is also studied.
4.1 Model

For description of PTs between three phases, a phase-field model introduced in Ref. (Levitas and Momeni, 2014) (and presented in Supporting Information) employs two polar order parameters: radial $\Upsilon$ and angular $\vartheta$, where $\pi \vartheta/2$ is the angle between the radius vector $\Upsilon$ and the positive horizontal axis in the polar order parameter plane. The melt is represented by $\Upsilon = 0$ for all $\vartheta$. Solid phases correspond to $\Upsilon = 1$; phase $S_1$ is described by $\vartheta = 0$ and phase $S_2$ is described by $\vartheta = 1$. This representation of the three phases sits in contrast to other multiphase models (Tiaden et al., 1998; Folch and Plapp, 2005b; Tóth et al., 2011; Mishin et al., 2009) that used three order parameters with a constraint that they always sum to a constant. Unlike the prior approaches, the polar variable approach has desirable property that each of the PTs: $M \leftrightarrow S_1$, corresponding to variation in $\Upsilon$ between 0 and 1 at $\vartheta = 0$; $M \leftrightarrow S_2$, corresponding to variation in $\Upsilon$ between 0 and 1 at $\vartheta = 1$, and $S_1 \leftrightarrow S_2$, corresponding to variation in $\vartheta$ between 0 and 1 at $\Upsilon = 1$, is described by single order parameter with the other fixed, which allowed us to utilize analytical solutions for each of the nonequilibrium interfaces and determine their width, energy, and velocity (Momeni and Levitas, 2014; Levitas and Momeni, 2014). Similar to sharp-interface study of phase transformations in HMX, which is consistent with experiments,(Levitas et al., 2004, 2006a) we assume that internal stresses cannot cause nucleation of dislocations. The model was implemented in the finite element package COMSOL®. 2011. Version 4.2. COMSOL, Inc., Burlington, MA, USA, ). Material parameters have been chosen for organic HMX energetic crystal (Tables 1 and 2 in Supporting Information). Problems have been solved for different $k_E$ and $k_\delta$ values at equilibrium temperature of two HMX solid phases, $\theta_e = 432 K$, which is $120 K$ below the melting temperature of the $\delta$ phase, which melts and resolidifies into $\beta$ phase during $\beta \rightarrow \delta$ PT. Here the values of $k_E$ and $k_\delta$ are explored to determine their influence, partly as they are unknown; but also we expect that these parameters will be sensitive in experiments to impurities and other ”alloying” effects, and thus can be experimentally controlled to some degree.

For barrierless processes, a rectangular $40 \text{ nm} \times 300 \text{ nm}$ with the symmetry plane at its left vertical edge, fixed lower left corner, and a stress-free boundary on the right side are
considered. A vertical initial interface was placed in the middle of the sample. Two types of initial conditions have been used: (i) A stationary $S_1S_2$ interface, which is obtained by placing an analytical solution for a stationary stress-free interface as an initial condition (see Eq. (19) in Supporting information), and (ii) a pre-existing melt confined between two solid phases (designated as $S_1MS_2$), which is obtained as a stationary solution with initial data corresponding to $S_1MS_2$ with a complete IM that is broader than in stationary solution. Parameters $k_\delta$ and $k_E$ are explicitly defined in the Supporting Information (see Eq. (20) therein). Plane strain conditions in the out-of-plane direction are assumed. The domain is meshed with five elements per $S_1S_2$ interface width, using quadratic Lagrange elements. An implicit time-stepping integrator with variable-step-size backward differentiation is used, with initial time step of 1 ps and a relative tolerance of $10^{-4}$. The numerical model is verified by solving the time-dependent Ginzburg-Landau equations (phase fields) for the PT between two phases at different temperatures without mechanics and comparing the results with analytical solutions for the interface energy, width, velocity, and profile (Momeni and Levitas, 2014), which indicate perfect match.

### 4.2 Barrierless nucleation

Here, the effect of thermal fluctuations is neglected and barrierless PTs are studied. The IM exhibits itself as deviation of the order parameter $\Upsilon$ within otherwise $S_1S_2$ interface from 1. If the minimum value $\Upsilon_{min}$ reaches zero, then IM is complete; otherwise, it is incomplete IM. In figs. 4.1 and 4.2 the minimum value $\Upsilon_{min}$ is presented for the steady state solution using two initial conditions (states): stationary $S_1S_2$ and $S_1MS_2$ interfaces.

Results for small $k_\delta$ values in fig. 4.1a revealed continuous pre-melting/resolidification with increasing/decreasing $k_E$ and presence of only a single solution independent of initial conditions. Allowing for internal stresses generated by misfit strain at the $S_1S_2$ interface promotes melt formation, i.e., reduces $\Upsilon_{min}$. In other words, melting results in the partial or complete relaxation in internal stresses, or stress results in an additional thermodynamic driving force for melting. Mechanics also shifts the minimum value of $k_E$ for initiation of disordering, even below $k_E < 2.0$, which is energetically impossible without mechanics (because energy of two
Figure 4.1: Effect of internal elastic stresses on thermodynamically equilibrium solutions as function of $k_E$. Initial conditions are shown in boxes and correspond to $S_1S_2$ (designated as SS) and $S_1MS_2$ (designated as SMS) interfaces. Value of $\Upsilon_{min}$ is shown for problems without and with mechanics at $\theta = \theta_e = 432K$, which is $120K$ below the melting temperature. (a) Continuous pre-melting/resolidification for small $k_\delta = 0.3$, and (b) jump-like $IM$ and resolidification for $k_\delta = 0.7$. Allowing for elastic energy that relaxes during intermediate melting promotes melting for all cases.

$SM$ stress-free interfaces is larger than energy of $SS$ interface). For larger $k_\delta = 0.7$ (fig. 4.1b) a range of $k_E$ values is found for which two different stationary solutions exist depending on the chosen initial conditions. Solutions for $\Upsilon_{min}$ experience jumps from 1 to small values after reaching some critical $k_E$ and then change continuously with increasing or decreasing $k_E$. Starting with $IM$ state, decreasing $k_E$ leads to jump to $\Upsilon_{min} = 1$. Thus, in contrast to fig. 4.1a, there is a clear hysteresis behavior. Internal elastic stresses reduce $\Upsilon_{min}$ and shift the critical $k_E$ values for loss of stability of $S_1S_2$ and $S_1MS_2$ interfaces to lower values of $k_E$, as well as increase hysteresis region, thus promoting $IM$.

A much richer picture is observed when $\Upsilon_{min}$ is plotted versus scale parameter $k_\delta$ for different fixed $k_E$ (fig. 4.2). fig. 4.2b for $k_E = 2.6$ shows that for small $k_\delta$ values, $S_1S_2$ interface does not exist and the only continuous reversible intermediate melting/ordering occurs with increasing/decreasing $k_\delta$. Elastic stresses promote $IM$ again by reducing $\Upsilon_{min}$. With further increases in $k_\delta$ for the same $S_1MS_2$ interface, the degree of disordering increases (and reversibly decreases with decreasing $k_\delta$), the effect of mechanics diminishes and disappears when $\Upsilon_{min}$ reaches zero. However, for large $k_\delta$, an alternative solution $\Upsilon_{min} = 1$ exists and if $S_1S_2$ interface is the initial state, it does not change. Below some critical $k_\delta$, a jump from $S_1S_2$ interface to
Figure 4.2: Mechanics and scale effects on thermodynamically equilibrium solutions $\Upsilon_{\text{min}}$ at $\theta = \theta_e = 432K$ for three values of $k_E$. Elastic energy promotes formation of melt and changes qualitatively types of behavior for some parameters.

$S_1MS_2$ interface occurs with reducing $k_\delta$ and the elastic energy increases slightly this critical value. A reverse jump is impossible, thus $S_1MS_2$ interface does not transform to $S_1S_2$ interface barrierlessly.

For smaller $k_E = 2.0$ and 2.3, the effect of the scale parameter $k_\delta$ is nonmonotonous and thus more complex (fig. 4.2a). For $k_E = 2.0$ without mechanics, the only solution is the $S_1S_2$ interface. Elastic energy changes result qualitatively. Thus, for small $k_\delta$ the only solution contains IM; however, the degree of disordering reversibly reduces with increasing $k_\delta$ (opposite to the case with larger $k_E$ in fig. 4.2b) and eventually disappears. For large $k_\delta$, there are both (almost) complete $S_1MS_2$ and $S_1S_2$ solutions. While initial $S_1S_2$ does not change in this range, $IM$ reduces degree of disordering with reducing $k_\delta$, until $IM$ discontinuously disappears. For intermediate $k_\delta$ the only solution is the $S_1S_2$ interface. This region between two other regions where $IM$ exists we called the $IM$-free gap. For $k_E = 2.3$, $IM$-free gap exists without mechanics but disappears with mechanics. Now, with mechanics, the behavior is qualitatively similar to that for $k_E = 2.6$ (fig. 4.2b). Without mechanics, for small $k_\delta$ the value $\Upsilon_{\text{min}}$ first decreases and then increases up to $\Upsilon_{\text{min}} = 1$ (i.e., exhibits local minimum), followed by $IM$-free gap and then by two solutions. Thus, mechanics qualitatively changes types of barrierless behavior. However, quantitatively values $\Upsilon_{\text{min}}$ are not drastically affected.
4.3 Thermally activated nucleation

The presence of two stationary solutions in fig. 4.1b, corresponding to local minima of the energy, indicates existence of the third, unstable, solution equivalent to the “min-max” of energy functional corresponding to a CN between them. Critical nuclei are studied at $\theta = \theta_e = 432K$ for $k_E = 2.6$ and $k_\delta = 0.7$, i.e., in the range of parameters where two solutions exist for both cases without and with mechanics (fig. 4.1b). Due to thermodynamic instability, CN solutions are highly sensitive to the initial conditions of the system and can be obtained by solving stationary Ginzburg-Landau and mechanics equations using an affine invariant form of the damped Newton method with initial conditions close to the final configuration of the CN.

We consider a cylindrical sample of $R = 20\, nm$ in radius, $100\, nm$ in length along the axis of symmetry (z-axis), and capped by two so-called ”perfectly matched” layers of $10\, nm$ in length at the top and bottom that are used in the COMSOL code (COMSOL Multiphysics®. 2011. Version 4.2. COMSOL, Inc., Burlington, MA, USA,) to mimic an infinite sample length. Here, we focused on the effect of internal stresses and assumed that all external surfaces are stress-free. Boundary conditions for both order parameters are imposed in the form of zero normal components of the gradient of the order parameters, which will guarantee that the outer surface energy remain fixed during a PT. Two CN were considered, in one, CN$_1$, the IM is at the center of a sample, and in the other, CN$_2$, the IM is at the surface. Initial conditions for the simulations are obtained from the analytical solution for a two-phase interface profile for $\vartheta$ and two back-to-back interface profiles for $\Upsilon$ (see these conditions in the Supporting Information and Ref. (Momeni and Levitas, 2014)).

In fig. 5.11, for solutions that are without (do not consider) mechanics (fig. 5.11a,b) and those with (that do consider) mechanics (fig. 5.11c,d), we plot the distributions of the order parameters, $\Upsilon$ and $\vartheta$, revealing the structure of CN for the case when IM is at the center of a sample. Similar results for CN$_2$ are presented in fig. 5.12. The solutions were tested to make sure that they correspond to the energy min-max of the system. This test was done by taking the calculated solutions for CN and slightly perturbing the CN solutions toward $S_1S_2$ and $S_1MS_2$ solutions, obtaining nominally super- and sub-critical nuclei. These are then used
Figure 4.3: Structure for the CN$_1$ with IM at the center of a sample. Simulations are performed at $\theta_e = 432 K$, $k_\delta = 0.7$, and $k_E = 2.6$ for the cases without (a,b) and with mechanics (c,d). Profile of the order parameter $\Upsilon(r)$ along the horizontal line $z = 30 \, \text{nm}$ is plotted in the top insets. Vertical insets show the profile of $\Upsilon(z)$ (top plots) and $\vartheta(z)$ (bottom plots) at $r = 0$. Solid line in the $\Upsilon$ plots corresponds to $\Upsilon = 0.9$ and determines the boundary of disordered CN of IM within the $S_1S_2$ interface. Dotted line in the $\vartheta$ plots indicates the level line of $\vartheta = 0.5$ and corresponds to the sharp $S_1S_2$ interface.

as the initial conditions for the time-dependent Ginzburg-Landau and mechanics equations. As required for the unstable CN, the solutions with sub- and supercritical IM nuclei evolved to the two stable $S_1S_2$ and $S_1MS_2$ interfaces, respectively.

For models both without and with mechanics, the CN$_1$ with the IM at the center has an ellipsoidal shape with $\Upsilon_{min} = 0.24$ and 0.30, respectively. The larger $\Upsilon_{min}$ value for the sample with mechanics is due to additional driving force associated with the relaxation of elastic energy during melting. Allowing for mechanics led to the formation of curved (bent) $S_1S_2$ interface, which is due to monotonically increasing volumetric transformation strain across the $S_1S_2$ interface. This bending cannot be realized within the usual sharp-interface approaches, suggesting that sharp-interface models should be improved to include this phenomenon, e.g., in Refs. (Javili and Steinmann, 2010; Levitas, 2014a). The same interface bending is observed for CN$_2$ (fig. 5.12). Both CN change local interface structure in terms of narrowing $S_1S_2$ interface in $\vartheta$ distribution within CN.

By construction, the energy of both bulk solid phases is equal at their equilibrium temperature (with and without mechanics), and thus the excess interface energy is calculated with
Figure 4.4: Structure for the CN$_2$ with IM at the surface of the sample. Simulations are performed at $\theta_e = 432K$, $k_\delta = 0.7$, and $k_E = 2.6$ for the case without (a,b) and with mechanics (c,d). Profile of order parameter $\Upsilon(r)$ along the horizontal line $z = 30\,nm$ is plotted in the top insets. Vertical insets show the profile of $\Upsilon(z)$ (top plots) and $\vartheta(z)$ (bottom plots) at $r = 20nm$.

respect to any of homogeneous solid phase by integration of total energy distribution over the sample. In such a way, we determine the energy $E_{ss}$ of the $S_1S_2$ and the energy $E_{sms}$ of the $S_1MS_2$ ground states. Similarly, we define the energy $E_{1CN}$ of the CN$_1$ and the energy $E_{2CN}$ of the CN$_2$. The difference between the energy of each CN$_1$ and CN$_2$, and each ground state gives the activation energies for the corresponding PTs. Thus, the activation energy of the $S_1MS_2$ CN$_1$ at the center within $S_1S_2$ interface is $Q_{1sms}^1 = E_{1CN}^1 - E_{ss}$ and for CN$_2$ at the surface is $Q_{2sms}^2 = E_{2CN}^2 - E_{ss}$. Similar, the activation energy of the $S_1S_2$ CN$_1$ within $S_1MS_2$ interface is $Q_{ss}^1 = E_{1CN}^1 - E_{sms}$ and for CN$_2$ is $Q_{sm}^2 = E_{2CN}^2 - E_{sms}$. Each of the above mentioned energies, which we will designate by $\Psi$ for conciseness, is the sum of three contributions: thermal energy $\Psi^\theta$, gradient energy $\Psi^\nabla$, and elastic energy $\Psi^e$. Our calculations for the energies of ground states and critical nuclei are listed in table 5.1.

A thermally activated process can be experimentally observed if the activation energy of CN is smaller than $(40 - 80)k_B\theta$ (Ref. (Porter, 1981)), where $k_B$ is the Boltzmann constant. This is equal to $0.24 - 0.48 \times 10^{-18}J$ at $\theta_e = 432K$. The results indicate that the only possible thermally activated process is the formation of CN$_1$ of IM within the $S_1S_2$ interface at the center of a sample when mechanics is included. Since the activation energy for resolidification is much larger than the magnitude of thermal fluctuations for both CN, the IM persists. Perhaps
Table 4.1: Total energy, $\Psi = \Psi^\theta + \Psi^\nabla + \Psi^e$, and its individual contributing terms, thermal $\Psi^\theta$ plus gradient $\Psi^\nabla$ energies, and elastic $\Psi^e$ energy, calculated for ground states, $E_{ss}$ and $E_{sms}$, as well as for interfaces with CN, $E^{CN}_1$ with the IM at the center of a sample and $E^{CN}_2$ with the IM at the surface. Activation energies $Q$ for appearance of the CN are the difference between energies of interfaces with CN and ground states. Simulations are performed for the cases without and with mechanics at $\theta_e = 432$ K for $k_\delta = 0.7$ and $k_E = 2.6$. All the energies are expressed in ($\times 10^{-18} J$).

<table>
<thead>
<tr>
<th></th>
<th>Without mechanics</th>
<th>With mechanics</th>
</tr>
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<tbody>
<tr>
<td>$\Psi$</td>
<td>1256.64</td>
<td>1269.281</td>
</tr>
<tr>
<td>$\Psi^\theta + \Psi^\nabla$</td>
<td>1269.281</td>
<td>21.4274</td>
</tr>
<tr>
<td>$\Psi^e$</td>
<td>1291.0786</td>
<td>1290.7084</td>
</tr>
<tr>
<td>$E_{ss}$</td>
<td>1162.2663</td>
<td>1172.7927</td>
</tr>
<tr>
<td>$E^{CN}_1$</td>
<td>1323.0063</td>
<td>1277.2457</td>
</tr>
<tr>
<td>$Q_{sms}^1$</td>
<td>6.05</td>
<td>0.163</td>
</tr>
<tr>
<td>$Q_{sms}^2$</td>
<td>160.74</td>
<td>104.453</td>
</tr>
<tr>
<td>$Q_{sms}^2$</td>
<td>66.3663</td>
<td>7.965</td>
</tr>
<tr>
<td>$Q_{ss}$</td>
<td>100.418</td>
<td>96.6513</td>
</tr>
<tr>
<td>$Q^{CN}_2$</td>
<td>105.56</td>
<td>8.908</td>
</tr>
<tr>
<td>$Q^{ss}$</td>
<td>66.3663</td>
<td>7.965</td>
</tr>
</tbody>
</table>

The most surprising result is that including the energy of elastic stresses reduced the activation energy for IM critical nucleus at the center of a sample, by a factor of 16, making nucleation possible despite large undercoolings. Similarly, internal stresses significantly reduced energy of IM critical nucleus at the surface (by $\sim 62 \times 10^{-18} J$ or by a factor of 15) and the energy of the SS critical nucleus with solid at the center (by $\sim 51 \times 10^{-18} J$). Although elastic energy makes a positive contribution to the energy of ground states and CN, it increases the energy of ground states more than it increases the energy of CN. The proximate cause of this phenomenon is the slight change in the structure of the CN and alteration of the interface geometry during appearance of the CN. Thus, a small change in two large numbers ($E^{CN}_1$ and $E_{ss}$) significantly changes their small difference $Q_{sms}^1$. To ensure that our conclusions are physical rather than due to numerical errors, we used different integration volumes enclosing IM critical nucleus. The calculations are insensitive to the integration volume as long as boundaries of this volume are far (> 5 nm) from the boundaries of CN. We note that mechanics surprisingly increases activation energy for resolidification for CN$_1$. 
Without and with mechanics, activation energies for both the IM critical nucleus and the CN of a solid-solid interface are much smaller (by \( \sim 60 \times 10^{-18} J \)) for the CN\(_1\) at the center in comparison with the CN\(_2\) at the surface. While results for CN\(_1\) are independent of the sample size and boundary conditions for the order parameter (because CN\(_1\) is much smaller than the sample), this is not the case for the CN\(_2\) at the surface. Reducing the sample size reduces volume of the CN\(_2\) and its activation energy, and for some critical size, nucleation of the IM at the surface may be kinetically possible. Also, if surface energy of the melt is smaller than the surface energy of the solid, it promotes thermally activated nucleation of the IM at the surface and may also lead to barrierless nucleation. This can be studied using methods similar to those in Ref. (Levitas and Samani, 2011b; Levitas and Javanbakht, 2011b, 2010; Levitas and Samani, 2014). A tensorial transformation strain for melting (Levitas and Samani, 2011a) and the effect of an external load can be easily included as well. All these factors may lead to new results and phenomena.

Previous results (Momeni and Levitas, 2014) without mechanics showed very high activation energy and the practical impossibility of thermally activated intermediate melting, which contradicted the experimentally observed thermally activated interface kinetics and the overall kinetics for HMX (Levitas et al., 2004, 2006a). The inclusion of elastic stresses in the model results in a drastic reduction of activation energy, resolving this discrepancy.

### 4.4 Concluding remarks

We have developed a phase-field approach, and applied it to study the effect of mechanics on barrierless and thermally activated nucleation and disappearance of nanoscale IM within an \( S_1S_2 \) interface during \( S_1S_2 \) PTs 120K below the melting temperature. For different ratios \( k_E \) and \( k_\delta \), various types of behavior, mechanics and scale effects are obtained. Barrierless intermediate melting/resolidification can be continuous (reversible), jump-like in one direction and continuous in another, and jump-like in both directions (hysteretic); partial and complete; with monotonous and nonmonotonous dependence on \( k_\delta \) and with IM-free gap region between two IM regions along \( k_\delta \) axis. Internal elastic stresses only slightly promote barrierless IM nucleation but change type of system behavior, including appearance of IM for \( k_E < 2 \) (which
is thermodynamically impossible without mechanics) and elimination of IM-free gap region. To study thermally activated nucleation, solutions for CN at the center and surface of a sample are found, activation energies are calculated and compared with the required values from a kinetic nucleation criterion. We revealed an unanticipated, drastic (16 times for HMX energetic crystals) reduction in the activation energy of IM critical nucleus when elastic energy is taken into account. This reduction results in the system meeting the kinetic nucleation criterion for the CN$_1$ at the center of a sample, consistent with experiments for HMX. Since thermally activated resolidification is kinetically impossible, IM persists during $S_1MS_2$ interface propagation. For smaller sample diameters and/or reduction of surface energy during melting, mechanics can induce IM nucleation at the surface as well. Similar effects are expected to occur for other material systems where solid-solid phase transformations via IM takes place, including electronic (Si and Ge), geological (ice, quartz, and coesite), pharmaceutical (avandia), ferroelectric (PbTiO$_3$), colloidal, and superhard (BN) materials. Similar approach can be developed for grain-boundary melting (Lobkovsky and Warren, 2002a), and formation of interfacial and intergranular crystalline or amorphous phases (complexions) (Luo, 2007; Luo and Chiang, 2008; Baram et al., 2011; Frolov et al., 2013b) in ceramic and metallic systems and developing corresponding interfacial phase diagrams.

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CHAPTER 5. A PHASE-FIELD APPROACH TO SOLID-SOLID PHASE TRANSFORMATIONS VIA INTERMEDIATE INTERFACIAL PHASES UNDER STRESS TENSOR

Thermodynamically consistent phase-field (PF) theory for phase transformations (PTs) between three different phases is developed with emphases on the effect of a stress tensor and interface interactions. The phase equilibrium and stability conditions for homogeneous phases are derived and a thermodynamic potential which satisfies all these conditions is introduced using polar order parameters. Solid-solid (SS) interface propagation containing nanometer-sized intermediate disordered interfacial phases (IP) and particularly an interfacial intermediate melt (IM) is studied for an HMX energetic material using the developed PF model. The scale effects (ratio of widths of SS to solid-melt (SM) interfaces, $k_\delta$), effect of the energy ratio of SS to SM interfaces ($k_E$), and the temperature, on the formation and stability of IMs are studied. An interaction between two SM interfaces via an IM, which plays a key role in defining a well-posed problem and mesh-independent solution, is captured using a special gradient energy term. The influence of the elastic energy on the formation and retainment of IM and its structure, hundreds of degrees below the melting temperature, is investigated. Elastic energy promotes barrierless IM in terms of an increasing degree of disordering, interface velocity, and width of IM, but it surprisingly increases nucleation temperature for the IM. The key result however, is the drastic reduction (by a factor of 16) of the energy of the critical nuclei (CN) of the IM within the SS interface, which caused by the mechanics. The developed PF model is applicable for the general case of PT between three phases and can be applied (adjusted) to other physical phenomena, such as premelting/disordering at grain boundaries, martensitic PTs, surface-induced premelting and PTs, and developing the interfacial phase diagrams.

This chapter is adapted from (Momeni and Levitas, ).
5.1 Introduction

The formation and stabilization of \textit{IP} (e.g., surfacial amorphous films and intergranular amorphous films) have many important applications, e.g., in the electronic industry (Luo and Chiang, 2008). Interfacial phases also play an important role in sintering, alloying, and strengthening ceramic materials (Luo et al., 1999; Becher et al., 2000). In addition, the properties of \textit{IP} are different from the constituent homogeneous phases. A sample with a large volume fraction of \textit{IP} show different overall properties (e.g. creep, superplasticity, and electrical conductivity), compared to the sample of homogeneous phases (Cantwell et al., 2014). Therefore, any advancement in the theoretical and computational modeling of \textit{IP} can have a significant scientific and industrial impact.

Interfaces between different phases can undergo PTs similar to bulk materials and can be treated as quasi-two-dimensional phases. The chemical and structural properties of the interfaces change abruptly or continuously during their PT during a variation of the corresponding driving forces. Although the interfaces can be analyzed using equilibrium thermodynamics, the equilibrium \textit{IPs} have varying properties. The Gibbs definition of a phase cannot be applied because of their inhomogeneous structure and composition (Cantwell et al., 2014). Presence of \textit{IPs} can change thermodynamic properties of materials and lead, e.g., to liquid-metal embrittlement (Luo et al., 2011). It also alters the kinetics of processes, e.g., PTs and grain growth (Dillon et al., 2007). Interfacial phases emerge in a wide range of processes such as premelting and prewetting, surface-induced premelting and PT (Levitas and Samani, 2011a,b; Levitas and Javanbakht, 2011b, 2010), intrinsic PT that occurs in pure materials, and extrinsic PT that happens in non-pure materials involving an adsorption of an impurity or dopant (Frolov et al., 2013b,a).

Solid-solid PT via a nanometer-sized intermediate disordered \textit{IP} called intermediate melt, \textit{IM}, at temperatures much below melting temperature ($\theta_{e}^{m}$) has been predicted thermodynamically (Levitas et al., 2004, 2006b; Levitas, 2005; Levitas et al., 2012) and confirmed experimentally for HMX energetic material (Smilowitz et al., 2002; Henson et al., 2002; Levitas et al., 2004, 2006b), \textit{PbTiO$_3$} piezoelectric nanowires (Levitas et al., 2012), and for amorphization
in an insulin enhancer pharmaceutical substance called avandia (Randzio and Kutner, 2008). The PT via formation of IM was also suggested as the mechanism for crystal-crystal PT and amorphization for materials with reducing melting temperature under pressure (e.g., ice, Si, and Ge) (Levitas, 2005). Furthermore, stresses may also be due to an applied external loading. Formation of IM under a high strain rate loading was predicted thermodynamically and confirmed using MD simulations for aluminum and copper (Levitas and Ravelo, 2012).

The thermodynamic condition for the appearance of an IM between solid-1 and solid-2 \( (S_1MS_2 \text{ interface}) \) is \( E^{21} - E^{10} - E^{20} - E^e > (G^0 - G^s)\delta^* \) (See Ref. (Levitas and Momeni, 2014)). Here, \( E^{10}, E^{20}, \) and \( E^{21} \) are the energies of the \( S_1M, S_2M, \) and \( SS \) interfaces, respectively; \( E^e \) is the elastic energy of the coherent \( SS \) interface; \( \delta^* \) is the width of the IM, and \( G^0 \) and \( G^s \) are the bulk thermal energies of melt and the solid phase with a smaller melting temperature \( \theta^m \), respectively. Reduction of the total interface energy and relaxation of the elastic energy are the driving forces for the formation of melt significantly below \( \theta^m \). Theoretical models based on the sharp-interface approach (Levitas et al., 2012, 2006a; Levitas, 2005; Levitas et al., 2004) have neglected the change in interface energy during melting as well as the interfacial interactions. The main driving force for the formation of IM in these models was the relaxation of internal stresses due to large volumetric transformation strains. This driving force vanishes as soon as melt forms, which results in a supercooled melt and immediate resolidification of melt to the stable solid phase. This intermediate transient melt is a special form of IM which is called virtual melt (Levitas et al., 2004, 2006b). Formation of the virtual melt is predicted in materials with large volumetric transformations that generate large elastic energy, when other stress relaxing mechanisms, such as plastic deformation and twinning, are suppressed; e.g., in materials with complex molecular or atomic structures.

Different techniques are utilized for characterizing and modeling the IP. The models developed are based on the sharp-interface approach which consider zero-thickness interfaces, are oversimplified because the IP has a width in the range of a few nanometers, which is comparable with the width of a SS interface. Furthermore, sharp-interface approach considers a bulk phase sandwiched between two interfaces of zero-thickness and cannot capture formation of the IP with partial melting. Molecular dynamics (MD) simulations have been utilized to
investigate interfacial PTs in pure materials (Frolov et al., 2013b). However, investigating such PTs in multiphase materials using the MD technique is limited by inevitable long simulation time for producing equilibrated composition profiles. Properties of IP have also been studied using ab initio techniques (Painter et al., 2002; Rulis et al., 2005; Shibata et al., 2004). A phase-field crystal model (Elder and Grant, 2004) was also used to investigate the effect of IP such as grain boundary premelting (Mellenthin et al., 2008).

An advanced PF approach to formation of the IM was developed in Ref. (Momeni and Levitas, 2014) but without mechanics. The interaction between two SM interfaces through melt are modeled using an SS interface energy contribution within complete melt. A new force-balance model was introduced that could match the results of PF simulations up to temperatures much bellow the melting temperature. Shifting from a jump-like first-order to a continuous second-order PT that is separated by an IM-free region was captured during IM-formation as $k_\delta$ reduced. The presence of three solutions associated with stable and metastable IM, as well as CN of IM were revealed. A retainment of IM at temperatures much below melting temperature for $k_E < 2.0$ was also illustrated. The dependence of the interface energy on $a_0$ and $k_\delta$ in the presence of IM was demonstrated using the numerical simulations.

The goal of this paper is to generalize a model (Momeni and Levitas, 2014) for when elastic energy and stresses are important. Advanced PF approach to PTs with strong focus on the effect of the stress tensor has been developed for martensitic PT (Levitas et al., 2003; Levitas and Preston, 2002a,b; Levitas et al., 2009; Cho et al., 2012; Levitas, 2013b), surface-induced PT in solids (Levitas and Javanbakht, 2011b, 2010), melting (Slutsker et al., 2006; Levitas and Samani, 2011a,b), dislocation evolution (Levitas and Javanbakht, 2013), and interaction between PT and dislocations (Levitas and Javanbakht, 2012, 2014). Here, thermodynamically consistent phase field approach for IM at the SS interface under a general stress tensor will be developed, combining our PF approaches to PT in solids, melting, and the model (Momeni and Levitas, 2014) without mechanics. Some preliminary results with mechanics have been presented as a short communication in Ref. (Levitas and Momeni, 2014).

The remainder of this paper is organized as follows. In Section 5.2, a strict thermodynamic approach is developed for the thermodynamic potential that depends on the polar order param-
eters and their gradients, as well as elastic strain and temperature. The constitutive equations are derived for the general case of a three-phase material under a stress tensor. Specific expressions for the Helmholtz free energy and thermal and transformation strains are presented, which (as we will show in Section 5.4) satisfy all the formulated thermodynamic equilibrium and stability conditions for homogeneous states. The time-dependent GL equations are derived in Section 5.3 for a nonequilibrium propagating interface. In Section 5.4 thermodynamic stability conditions are derived in the general form and for our specific model. A detailed description of the numerical implementations of the model, including the initial conditions used to study the kinetics and capture the CN, are described in Section B. The developed model is then tailored to the properties of an HMX energetic material, and the effects of different parameters on the formation of $IM$ and $SS$ PT are studied in Section 5.5. In Section 5.6, formation and structure of the CN of $IM$ within $S_1S_2$ interface and CN of the $S_1S_2$ interface within $S_1MS_2$ interface are studied in detail for the models without and with mechanics. Finally, the results of this study are summarized in Section 5.7.

We have designated the contraction of tensors $A$ and $B$ over one and two indices with $A\cdot B$ and $A:B$, respectively. The subscripts $s$ and $a$ label the symmetric and the skew-symmetric part of a second-rank tensor. Elastic, thermal, and transformational parts of the strain tensor are designated with subscripts $e$, $\theta$, and $t$, respectively. The unit tensor and Kronecker delta are designated by $I$ and $\delta_{ij}$, respectively; $\nabla$ is the gradient operator.

5.2 Thermodynamic theory

Polar order parameters. Following Refs. (Levitas et al., 2003; Momeni and Levitas, 2014), the polar order parameters, the radial $\Upsilon$ and the angular $\vartheta$, are introduced in a plane (Fig. 5.1). Geometrically, $\pi \vartheta/2$ is the angle between the radius vector $\Upsilon$ and the axis 1. The origin of the coordinate system, described by $\Upsilon = 0$ for any $\vartheta$, corresponds to the reference phase 0. In the current paper, it is a melt $M$; however, it can be any phase for general three-phase system, in particular, austenite for multivariant martensitic transformations (Levitas and Preston, 2002b; Levitas et al., 2003, 2013). Points ($\Upsilon = 1$ and $\vartheta = 0$) and ($\Upsilon = 1$ and $\vartheta = 1$) correspond to solid phases $S_1$ and $S_2$, respectively. Transformations $S_s \leftrightarrow M$ are described by the variation
of \( \Upsilon \) between 0 and 1 at \( \vartheta = 0 \) or 1; Transformations \( S_1 \leftrightarrow S_2 \) occur by variation of \( \vartheta \) between 0 and 1 at \( \Upsilon = 1 \). In our applications, phases \( S_1 \) and \( S_2 \) correspond to HMX \( \delta \) and \( \beta \) phases, respectively.

**Kinematics.** In the small-strain approximation, the additive decomposition of the strain tensor is

\[
\varepsilon = (\nabla \mathbf{u})_s = \varepsilon_e + \varepsilon_t(\Upsilon, \vartheta) + \varepsilon_\vartheta(\Upsilon, \vartheta, \theta), \tag{5.1}
\]

where \( \mathbf{u} \) is displacement vector, \( \varepsilon_e, \varepsilon_t, \) and \( \varepsilon_\vartheta \) are the elastic, transformational, and thermal strains, respectively.

### 5.2.1 Laws of thermodynamics

The first law of thermodynamics for an arbitrary volume \( V \) of a three-phase material with a boundary \( S \) is

\[
\int_S (p \cdot \mathbf{v} - \mathbf{h} \cdot \mathbf{n}) \, dS + \int_S (Q_\Upsilon \dot{\Upsilon} + Q_\vartheta \dot{\vartheta}) \cdot \mathbf{n} \, dS + \int_V \rho (f \cdot \mathbf{v} + r) \, dV = \frac{d}{dt} \int_V \rho (U + 0.5 \mathbf{v} \cdot \mathbf{v}) \, dV, \tag{5.2}
\]

where \( p \) is the traction vector, \( \mathbf{v} \) is the particle velocity, \( \mathbf{h} \) is the heat flux, \( \mathbf{n} \) is the outward unit normal to \( S \), \( U \) is the internal energy per unit mass, \( f \) represents the body forces per unit mass, and \( r \) is the specific volumetric heat supply rate per unit mass, and \( \rho \) is the mass density, which will be considered as a constant within small-strain approximation. The introduced generalized forces \( Q_\Upsilon \) and \( Q_\vartheta \) originate from the dependence of the thermodynamic potential on \( \nabla \Upsilon \) and \( \nabla \vartheta \), respectively. These thermodynamic forces allow us to write the energy equation for an arbitrary volume and consequently transform the global energy balance to its local form.

Applying the second law of thermodynamics in the global form of the entropy balance along with the Clausius-Duhem inequality gives

\[
\frac{d}{dt} \int_V \rho \, s \, dV - \int_V \rho \frac{r}{\vartheta} \, dV + \int_S \frac{\mathbf{h}}{\vartheta} \cdot \mathbf{n} \, dS \geq 0, \tag{5.3}
\]

where \( s \) is the entropy per unit mass. Utilizing the Gauss theorem and conservation of mass \( (d(\rho V)/dt = 0) \), both thermodynamics law, after some mathematical manipulations, transform
to integrals over the volume

\[
\int_V \left( \sigma : \dot{\varepsilon} - \rho \dot{U} - \nabla \cdot h + \rho r + \nabla \cdot (Q_T \dot{Y} + Q_\theta \dot{\theta}) \right) dV + \int_V (\nabla \cdot \sigma + \rho f - \rho \dot{\psi}) \cdot \mathbf{v} dV = 0 ; \quad (5.4)
\]

\[
\int_V \left( \rho \dot{s} - \rho \frac{r}{\theta} + \nabla \cdot \frac{h}{\theta} \right) dV \geq 0 . \quad (5.5)
\]

The constitutive equations must be objective and independent of the motion of the observer. Therefore Eq. (5.4) should be invariant with respect to superposition of the rigid body motion. In particular, substituting the velocity vector \( \mathbf{v} \) with a vector \( \mathbf{v} - \mathbf{v}' \), where \( \mathbf{v}' \) is the constant velocity, should not alter Eq. (5.4). This can only be achieved if the term in parenthesis of the second integral in Eq. (5.4) is identically zero,

\[
\nabla \cdot \sigma + \rho f = \rho \dot{\psi} . \quad (5.6)
\]

Thus, introducing thermodynamic forces \( Q_T \) and \( Q_\theta \) does not affect the local momentum balance. Since Eqs. (5.4) and (5.5) are valid for an arbitrary volume, they have to be valid for all individual points in that volume:

\[
\sigma : \dot{\varepsilon} - \rho \dot{U} - \nabla \cdot h + \rho r + \nabla \cdot (Q_T \dot{Y}) + \nabla \cdot (Q_\theta \dot{\theta}) = 0 ; \quad (5.7)
\]

\[
\rho \dot{S} = \rho \dot{s} - \rho \frac{r}{\theta} + \nabla \cdot \frac{h}{\theta} = \rho \dot{s} - \rho \frac{r}{\theta} + 1 \frac{1}{\theta} \nabla \cdot h - \frac{\nabla \theta}{\theta^2} \cdot h \geq 0 , \quad (5.8)
\]

where \( \dot{S} \) is local total entropy production rate per unit mass. Defining the local dissipation rate as \( \mathcal{D} = \theta \dot{S} \), multiplying Eq. (5.8) by \( \theta \) gives \( \rho \mathcal{D} \). Eliminating \( \rho r - \nabla \cdot h \) from Eqs. (5.7) and (5.8) results in the local dissipation inequality,

\[
\rho \mathcal{D} := \sigma : \dot{\varepsilon} - \rho \dot{U} + \rho \theta \dot{s} + \nabla \cdot (Q_T \dot{Y}) + \nabla \cdot (Q_\theta \dot{\theta}) - \frac{\nabla \theta}{\theta^2} \cdot h \geq 0 . \quad (5.9)
\]

Assuming independence of the heat conduction and other thermodynamic processes, Eq. (5.9) splits into the Fourier’s inequality, \( -\frac{\nabla \theta}{\theta^2} \cdot h \geq 0 \) and the remaining inequality without the last term (for which we keep using the \( \mathcal{D} \) designation):

\[
\rho \mathcal{D} = \sigma : \dot{\varepsilon} - \rho \dot{\psi} - \rho s \dot{\theta} + \nabla \cdot (Q_T \dot{Y}) + \nabla \cdot (Q_\theta \dot{\theta}) \geq 0 , \quad (5.10)
\]

where the Helmholtz free energy, \( \psi = U - \theta s \), was introduced.
\[5.2.2 \text{ Constitutive equations}\]

We postulate that \( \psi = \psi(\varepsilon, \Upsilon, \vartheta, \theta, \nabla \Upsilon, \nabla \vartheta) \). The derivation process would be more concise if the Helmholtz free energy \( \psi \) was expressed in terms of \( \varepsilon \) rather than \( \varepsilon_e \),

\[
\psi = \psi(\varepsilon, \Upsilon, \vartheta, \theta, \nabla \Upsilon, \nabla \vartheta) = \psi(\varepsilon - \varepsilon_e(\Upsilon, \vartheta), \Upsilon, \vartheta, \theta, \nabla \Upsilon, \nabla \vartheta) = \bar{\psi}(\varepsilon, \Upsilon, \vartheta, \theta, \nabla \Upsilon, \nabla \vartheta).
\]

(5.11)

The last two terms in Eq. (5.10) can be expanded as

\[
\nabla \cdot (Q \dot{\Upsilon}) = (\nabla \cdot Q) \dot{\Upsilon} + Q \cdot \nabla \dot{\Upsilon} + \partial \cdot (Q \dot{\vartheta}) = (\nabla \cdot Q_{\vartheta}) \dot{\vartheta} + Q_{\vartheta} \cdot \nabla \dot{\vartheta}.
\]

Also, \( \nabla \cdot \dot{\Upsilon} = \nabla \dot{\Upsilon} \) and \( \nabla \dot{\vartheta} = \nabla \dot{\vartheta} \) due to small strain approximation. Then, inserting Eq. (5.11) in Eq. (5.10), we have:

\[
\rho \mathcal{D} = (\sigma - \rho \frac{\partial \bar{\psi}}{\partial \varepsilon}) : \dot{\varepsilon} - (\rho s + \rho \frac{\partial \bar{\psi}}{\partial \theta}) \dot{\theta} - \left( \frac{\partial \bar{\psi}}{\rho \Upsilon} - \nabla \cdot Q \right) \dot{\Upsilon} + (Q \Upsilon - \rho \frac{\partial \bar{\psi}}{\partial \nabla \Upsilon}) \cdot \nabla \dot{\Upsilon} - \left( \frac{\partial \bar{\psi}}{\rho \vartheta} - \nabla \cdot Q_{\vartheta} \right) \dot{\vartheta} + (Q_{\vartheta} - \rho \frac{\partial \bar{\psi}}{\partial \nabla \vartheta}) \cdot \nabla \dot{\vartheta} \geq 0;
\]

(5.12)

Assuming the dissipation rate to be independent of \( \dot{\varepsilon}, \dot{\theta}, \nabla \dot{\Upsilon}, \) and \( \nabla \dot{\vartheta} \) leads to the elasticity rule, equation for the entropy, and definition of thermodynamic forces \( Q_{\Upsilon} \) and \( Q_{\vartheta} \):

\[
\sigma = \rho \frac{\partial \bar{\psi}}{\partial \varepsilon}; \quad s = -\frac{\partial \bar{\psi}}{\partial \theta};
\]

(5.13)

\[
Q_{\Upsilon} = \rho \frac{\partial \bar{\psi}}{\partial \nabla \Upsilon}; \quad Q_{\vartheta} = \rho \frac{\partial \bar{\psi}}{\partial \nabla \vartheta}.
\]

(5.14)

Dissipative (viscous) stresses can be introduced in a standard way (see, e.g., Ref. (Levitas, 2013c)). Substituting Eq. (5.14) back in Eq. (5.12), we obtain the residual dissipative inequality

\[
\rho \mathcal{D} = X_{\Upsilon} \dot{\Upsilon} + X_{\vartheta} \dot{\vartheta} \geq 0;
\]

(5.15)

with the definition of generalized forces

\[
X_{\Upsilon} = -\rho \frac{\partial \bar{\psi}}{\rho \Upsilon} + \nabla \cdot \left( \rho \frac{\partial \bar{\psi}}{\partial \nabla \Upsilon} \right);
\]

(5.16)

\[
X_{\vartheta} = -\rho \frac{\partial \bar{\psi}}{\rho \vartheta} + \nabla \cdot \left( \rho \frac{\partial \bar{\psi}}{\partial \nabla \vartheta} \right).
\]

(5.17)

To satisfy the inequality Eq. (5.15), one has to prescribe proper kinetic equations \( X_{\Upsilon} = X_{\Upsilon}(\dot{\Upsilon}) \) and \( X_{\vartheta} = X_{\vartheta}(\dot{\vartheta}) \), which together with definitions (5.16) and (5.17) result in the generalized
Ginzburg-Landau equations for the evolution of the order parameters. Onsager’s cross effects will be neglected for simplicity.

**Boundary conditions for the order parameters.** One of the boundary conditions that we will use is $\Upsilon = 0$ or 1 and $\vartheta(t) = 0$ or 1, which corresponds to the prescribed phases at the boundaries. Alternatively, we can prescribe the normal component of the introduced generalized forces $\mathbf{Q}_\Upsilon$ and $\mathbf{Q}_\vartheta$ (similar to the traction, heat or mass flux):

$$
n \cdot \mathbf{Q}_\Upsilon = n \cdot \rho \frac{\partial \psi}{\partial \Upsilon} = H_\Upsilon; \quad n \cdot \mathbf{Q}_\vartheta = n \cdot \rho \frac{\partial \psi}{\partial \vartheta} = H_\vartheta,
$$

where $H_\Upsilon$ and $H_\vartheta$ are given functions. Also, one can prescribe periodic boundary conditions for the order parameters, which is always the case when spectral methods of solutions of the boundary value problems are used (Wang et al., 2001; Chen, 2002b). Functions $H_\Upsilon$ and $H_\vartheta$ can be expressed in terms of variation of the surface energy during a phase transformation under study (Levitas and Samani, 2014, 2011a,b; Lipowsky, 1984; Pluis et al., 1990; Levitas and Javanbakht, 2010). In this study we are not interested in surface-induced phenomena and will use $H_\Upsilon = H_\vartheta = 0$, which corresponds to the same surface energy of all phases.

### 5.2.3 Helmholtz free energy for SS phase transformation via IM

The Helmholtz energy function per unit mass is defined as

$$
\psi = \psi^e + \psi^\Upsilon + \psi^\vartheta + \psi^\nabla = \psi^l + \psi^\nabla;
$$

with the elastic energy

$$
\rho \psi^e = 0.5 \epsilon^e : \mathbf{C}(\Upsilon, \vartheta) : \epsilon^e;
$$

$$
\mathbf{C}(\Upsilon, \vartheta) = \mathbf{C}_0 + [\mathbf{C}_S(\vartheta) - \mathbf{C}_0] q(\Upsilon, a_C);
$$

$$
\mathbf{C}_S(\vartheta) = \mathbf{C}_1 + (\mathbf{C}_2 - \mathbf{C}_1) q(\vartheta, a_{cS});
$$

thermal driving force

$$
\psi^\Upsilon = G_{00}^\Upsilon(\vartheta) + \Delta G^\Upsilon(\vartheta, \vartheta) q(\Upsilon, 0);
$$

$$
\Delta G^\Upsilon(\vartheta, \vartheta) = \Delta G_{10}^\Upsilon + \Delta G_{21}^\Upsilon q(\vartheta, 3);
$$
triple-well barrier

\[ \psi^\theta = A^{s_0}(\theta, \vartheta) m(\Upsilon) + A^{21}(\theta) q(\Upsilon, a_\phi) m(\vartheta); \]  \hspace{1cm} (5.25)

\[ A^{s_0}(\theta, \vartheta) = A^{10}(\theta) + [A^{20}(\theta) - A^{10}(\theta)] q(\vartheta, a_\phi); \]  \hspace{1cm} (5.26)

and the gradient energy

\[ \psi^\nabla = \frac{1}{2\rho} \left[ \beta^{s_0}(\vartheta) |\nabla \Upsilon|^2 + \beta^{21}(\Upsilon, a_\phi, a_0) |\nabla \vartheta|^2 \right]; \]  \hspace{1cm} (5.27)

\[ \beta^{s_0}(\vartheta) = \beta^{10} + (\beta^{20} - \beta^{10}) q(\vartheta, a_\beta), \]  \hspace{1cm} (5.28)

where \( \psi^l \) is the local energy. Elastic energy has the simplest form corresponding to the linear elasticity rule. All other terms are justified in Ref. (Momeni and Levitas, 2014). They reduce to the equations in Ref. (Levitas, 2013c) for any two phases.

In Eqs. (C.4)-(5.28), \( \mathbf{C}_i \) is the elastic modulus tensor of phase \( i \), \( G_0^\theta \) is the thermal energy of melt; \( \Delta G_0^{\theta} \) is the change in thermal energy between solid and melt; \( \Delta G_{s_0}^\theta \) \( (s = 1, 2) \) is the difference in thermal energy between the solid \( S_s \) and \( M \); \( \Delta G_{21}^\theta \) is the difference in thermal energy between solid \( S_2 \) and \( S_1 \); \( A^{s_0} \) and \( A^{21} \) are the \( SM \) and \( SS \) energy barriers, respectively; \( \beta^{s_0} \) and \( \beta^{21} \) are \( SM \) and \( SS \) gradient energy coefficients, respectively. While the capital \( S \) in the super- and subscripts refers to solid and usually designates some function of \( \vartheta \), small \( s \) \((s = 1, 2)\), designates a specific solid \( S_s \); the value of the phase indicator \( i \) is 0 for \( M \), 1 for \( S_1 \), and 2 for \( S_2 \).

The monotonous interpolating functions connecting properties of phases are justified in Ref. (Momeni and Levitas, 2014):

\[ q(y, a) = ay^2 - 2(a - 2)y^3 + (a - 3)y^4 = y^2 \left[ a(y - 1)^2 + (4 - 3y) \right]; \]  \hspace{1cm} (5.29)

\[ \phi(\Upsilon, a_\phi, a_0) = a_\phi \Upsilon^2 - 2[a_\phi - 2(1 - a_0)] \Upsilon^3 + [a_\phi - 3(1 - a_0)] \Upsilon^4 + a_0, \]  \hspace{1cm} (5.30)

which have the following derivatives

\[ \partial q(y, a)/\partial y = 2y(y - 1) [2(a - 3)y - a]; \]  \hspace{1cm} (5.31)

\[ \partial \phi(\Upsilon, a_\phi, a_0)/\partial \Upsilon = 2 \Upsilon (\Upsilon - 1) \left\{ 2 [a_\phi + 3(a_0 - 1)] \Upsilon - a_\phi \right\}. \]  \hspace{1cm} (5.32)

The double-well function \( m(y) \) that participates in the triple-well function (C.6) is defined as

\[ m(y) = y^2(1 - y)^2, \]  \hspace{1cm} (5.33)
and has the following derivative

\[ \frac{dm(y)}{dy} = 2y(y - 1)(2y - 1). \]  

(5.34)

The derivatives in Eqs. (5.31), (5.32), and (5.34) will appear in the GL equations (see Sec. 5.3).

In the interpolation function \( q(y, a) \) for \( y = \vartheta \) or \( \Upsilon \), parameters \( a (a_\vartheta, a_\beta, ... \) vary depending on the material and material property. These functions satisfy the following conditions:

\[
\begin{align*}
\phi(0, a_\phi, a_0) &= a_0; & \phi(1, a_\phi, a_0) &= 1; & \frac{\partial \phi(0, a_\phi, a_0)}{\partial \vartheta} = \frac{\partial \phi(1, a_\phi, a_0)}{\partial \Upsilon} &= 0; & 0 \leq a_\phi \leq 6.
\end{align*}
\]  

(5.35)

\[
\begin{align*}
\phi(0, a_\phi, a_0) &= a_0; & \phi(1, a_\phi, a_0) &= 1; & \frac{\partial \phi(0, a_\phi, a_0)}{\partial \vartheta} = \frac{\partial \phi(1, a_\phi, a_0)}{\partial \Upsilon} &= 0; & 0 \leq a_\phi \leq 6.
\end{align*}
\]  

(5.36)

The first two conditions result in the proper change of material properties, the second two conditions guarantee fulfilment of the thermodynamic equilibrium conditions for each phase for all temperatures and stress tensors, see Section 5.3, and the last inequality guarantees a monotonous behavior of the connecting functions. For \( a_0 = 0 \) both functions coincide, \( \phi(y, a, 0) = q(y, a) \). The parameter \( a_0 \) is included for gradient energy only (Eq. (5.27)) and penalizes solid-solid gradient energy even in melt (\( \Upsilon = 0 \)), which is proportional to \( a_0 \), \( \psi^\nabla = \beta^{21} a_0 |\nabla \vartheta|^2 \). Otherwise, the width of the IM is zero and the problem is ill-posed (see Ref. (Momeni and Levitas, 2014)). The parameter \( a_0 \) controls the interaction between \( S_1 M - S_2 M \) interfaces, which significantly affects the final structure of IM. Also, the above equations satisfy the desired instability conditions, which represent PT criteria (see Section 5.4). The double-well connecting function \( m(y) \) has a zero value and derivative at \( y = 0 \) and \( 1 \), to satisfy the thermodynamic equilibrium conditions and also avoid introducing any contribution to the energy function of homogeneous phases.

The transformation strain \( \varepsilon_t \) and thermal strain \( \varepsilon_\theta \) tensors are defined as

\[
\begin{align*}
\varepsilon_t(\Upsilon, \vartheta) &= [\varepsilon_{t1} + (\varepsilon_{t2} - \varepsilon_{t1}) q(\vartheta, a_{t\vartheta})] q(\Upsilon, a_{t\Upsilon});
\varepsilon_\theta(\theta, \Upsilon, \vartheta) &= \varepsilon_{\theta0} + [\varepsilon_{\theta1} - \varepsilon_{\theta0} + (\varepsilon_{\theta2} - \varepsilon_{\theta1}) q(\vartheta, a_{\theta\vartheta})] q(\Upsilon, a_{\theta\Upsilon}); & \varepsilon_{\theta i} &= \alpha_i (\theta - \theta_0). \end{align*}
\]  

(5.37)

(5.38)

where \( \alpha_i \) is the tensor of the linear thermal expansion coefficient of phase \( i \) and \( \theta_0 \) is the reference temperature for all three phases for both thermal expansion and transformation strain. If
\( \theta_0 \) belongs to the region of metastability of all three phases, then transformation strain represents an actual jump in the stress-free strain (interpolated with the help of thermal expansion coefficients) at \( \theta = \theta_0 \). If some of the phases do not exist at \( \theta = \theta_0 \), then transformation strain is defined as the jump in stress-free strain extrapolated (utilizing thermal expansion coefficients) to \( \theta = \theta_0 \). Because the splitting of the total inelastic strain into thermal and transformational parts depends on the choice of the reference temperature \( \theta_0 \) and is therefore to some extent arbitrary, the same extrapolating functions will be used for them, i.e., \( a_{\theta\theta} = a_{t\theta} \) and \( a_{\theta\Sigma} = a_{t\Sigma} \).

It is clear that for melt the thermal expansion is isotropic, \( \alpha_0 = \alpha_0 \mathbf{I} \). Usually, transformation strain for solidification/melting is also considered isotropic and is determined by the change in mass density. In Refs. (Levitas and Samani, 2011a,b) the deviatoric part of the transformation strain for melting/solidification was introduced, which is proportional to the deviatoric stresses and describes their relaxation within a solid-melt interface. For simplicity, we will neglect this type of deviatoric transformation strain here. However, because we need to distinguish between crystal lattices of two solid phases and because transformation strain between these lattices, \( \varepsilon_{t2} - \varepsilon_{t1} \), is well defined, we have to define tensorial transformation strains \( \varepsilon_{t1} \) and \( \varepsilon_{t2} \) for the solidification of each phase. The transformation strain of cubic lattices from melt is isotropic, \( \varepsilon^c_t = 1/3 \varepsilon_{t0} \mathbf{I} \), where \( \varepsilon_{t0} \) is the volumetric transformation strain. If \( \varepsilon_{t0} = 0 \), then there is no difference from continuum geometric point of view between melt and cubic lattice. We will use this for the definition of tensorial transformation strain for solidification/melting.

The effect of stresses can be illustrated using the local part of the Gibbs potential, \( G(\sigma, \theta, \Sigma, \vartheta) \)

\[ = \psi(\varepsilon, \theta, \Sigma, \vartheta) - \frac{1}{2} \rho \sigma : \varepsilon, \] where the stress tensor is an independent variable. For simplicity, i.e., to focus on transformation strain rather than on elastic compliances, we will use in Figs. 5.1 and 5.2 the shifted Gibbs potential \( \tilde{G}(\sigma, \theta, \Sigma, \vartheta) = G(\sigma, \theta, \Sigma, \vartheta) + \frac{1}{2} \rho \sigma : C : \sigma = -\frac{1}{2} \rho \sigma : \varepsilon_t(\Sigma, \vartheta) + \psi^\theta + \psi^\vartheta \) for pure hydrostatic and shear loading, respectively. Each phase is designated along with contour plots for different material parameters.

Using the constitutive Eq. (5.13) and the developed Helmholtz free energy, Eqs. (C.4)-
Figure 5.1: Plot of the shifted Gibbs potential $\tilde{G}(\sigma, \theta, \Upsilon, \vartheta)$ for HMX at $\theta = \theta_\text{c}^{21}$ and 1 MPa volumetric compressive stress for different $\theta_\text{c}^\text{m} = \theta_\text{c}^{10}$ and $\theta_\text{c}^\text{m} = \theta_\text{c}^{20}$ values, in the polar system of the order parameters $\Upsilon$ and $\vartheta$. The 3D plot of the potential surface is shown in (e) along with its contour plot, for the same critical temperatures as plotted in (a).

Figure 5.2: Plot of the shifted Gibbs potential $\tilde{G}(\sigma, \theta, \Upsilon, \vartheta)$ for HMX at $\theta = \theta_\text{c}^{21}$ and principal stress of $\sigma = \{1, -1, -3\}$ MPa for different $\theta_\text{c}^\text{m} = \theta_\text{c}^{10}$ and $\theta_\text{c}^\text{m} = \theta_\text{c}^{20}$ values, in the polar system of the order parameters $\Upsilon$ and $\vartheta$. The 3D plot of the potential surface is shown in (e) along with its contour plot, for the same critical temperatures as plotted in (a).
(5.30), the relation for the stress tensor is
\[
\sigma = \rho \frac{\partial \bar{\psi}}{\partial \epsilon_e} = \rho \frac{\partial \bar{\psi}}{\partial \epsilon_e} \frac{\partial \epsilon_e}{\partial \epsilon_e} = \rho \frac{\partial \psi^e}{\partial \epsilon_e} = \mathcal{C}(\Upsilon, \vartheta) : \epsilon_e. \tag{5.39}
\]

For a two-phase system the developed potential can be simplified significantly by substituting \( \vartheta = 0 \) (or 1) in Eqs. (C.4)-(5.30) for \( M-S_s \) PT and \( \Upsilon = 1 \) for \( S_1-S_2 \) PT, respectively. This potential function for \( M-S_s \) PT is
\[
\psi^{s0} = \frac{1}{2\rho} \epsilon_e : \mathcal{C}(\Upsilon, s) : \epsilon_e + \Delta G_{s0}^\theta(\theta) q(\Upsilon, 0) + A^{s0}(\theta) \Upsilon^2 (1 - \Upsilon)^2 + \frac{\beta^{s0}}{2\rho} \left| \nabla \Upsilon \right|^2; \tag{5.40}
\]
and for \( S_1-S_2 \) PT is
\[
\psi^{21} = \frac{1}{2\rho} \epsilon_e : \mathcal{C}(1, \vartheta) : \epsilon_e + \Delta G_{10}^\theta + \Delta G_{21}^\theta q(\vartheta, 0) + A^{21}(\theta) \vartheta^2 (1 - \vartheta)^2 + \frac{\beta^{21}}{2\rho} \left| \nabla \vartheta \right|^2; \tag{5.42}
\]
which coincide with Ref. (Levitas et al., 2003). Equations (5.40) and (5.42) are equivalent (except an unimportant constant shift \( \Delta G_{10}^\theta \)), and are one-to-one with the models proposed in Ref. (Levitas and Samani, 2011a) for melting and in Ref. (Levitas and Preston, 2002a) for austenite-martensite PT.

### 5.3 Ginzburg-Landau equations

The governing equations for the evolution of order parameters (GL equations) can be obtained by assuming a linear relation between time the derivative of the order parameters and their corresponding dissipative driving force,
\[
\begin{align*}
\frac{\dot{\Upsilon}}{L_\Upsilon} &= -\rho \frac{\partial \bar{\psi}}{\partial \Upsilon} + \nabla \cdot \left( \rho \frac{\partial \bar{\psi}^\epsilon}{\partial \epsilon_e} \right) = -\rho \frac{\partial \bar{\psi}^\epsilon}{\partial \Upsilon} \bigg|_{\Upsilon} + \frac{\beta^{21}}{2} \frac{\partial \phi(\Upsilon, a_\phi, a_0)}{\partial \Upsilon} \left| \nabla \vartheta \right|^2 + \nabla \cdot \left( \beta^{s0}(\vartheta) \nabla \Upsilon \right); \\
\frac{\dot{\vartheta}}{L_\vartheta} &= -\rho \frac{\partial \bar{\psi}}{\partial \vartheta} + \nabla \cdot \left( \rho \frac{\partial \bar{\psi}^\epsilon}{\partial \epsilon_e} \right) = -\rho \frac{\partial \bar{\psi}^\epsilon}{\partial \vartheta} \bigg|_{\vartheta} + \frac{\beta^{20} - \beta^{10}}{2} \frac{\partial q(\vartheta, a_\beta)}{\partial \vartheta} \left| \nabla \Upsilon \right|^2, \\
&\quad + \nabla \cdot \left[ \beta^{21} \phi(\Upsilon, a_\phi, a_0) \nabla \vartheta \right] \tag{5.44}
\end{align*}
\]
where subscript \( \epsilon \) emphases that the derivative is evaluated at fixed \( \epsilon \), and \( L_\Upsilon \) and \( L_\vartheta \) are the kinetic coefficients. To obtain a more explicit expression for the local driving force, we utilize the definition in Eqs. (5.11) and (5.39) to elaborate:
\[
\frac{\partial \psi}{\partial t} |_{\epsilon} = -\frac{1}{\rho} \sigma^t \frac{\partial \varepsilon_t(Y, \theta)}{\partial \psi} - \frac{1}{\rho} \sigma^\theta \frac{\partial \varepsilon_\theta(Y, \theta)}{\partial \psi} + \frac{\partial \psi}{\partial \psi} |_{\epsilon} = -\frac{1}{\rho} \sigma^t \frac{\partial \varepsilon_t}{\partial \psi} - \frac{1}{\rho} \sigma^\theta \frac{\partial \varepsilon_\theta}{\partial \psi} \\
+ \frac{1}{2\rho} \frac{\partial \psi(Y, a\epsilon)}{\partial \psi} \varepsilon^c: [C_S(Y) - C_0] : \varepsilon_e + \frac{\partial \psi^\theta}{\partial \psi} + \frac{\partial \psi^\theta}{\partial \psi} \\
= -\frac{1}{\rho} \sigma^t [\varepsilon_{t1} + \varepsilon_{t0}] + \varepsilon_e + \frac{\partial \psi^\theta}{\partial \psi} + \frac{\partial \psi^\theta}{\partial \psi} \\
= \frac{1}{2\rho} \frac{\partial \psi(Y, a\epsilon)}{\partial \psi} \varepsilon^c: [C_S(Y) - C_0] : \varepsilon_e + \Delta G^\theta(Y, \theta) \frac{\partial \psi(Y, a\epsilon)}{\partial \psi} \\
+ A^{20}(\theta, a\epsilon) \frac{m(Y)}{\partial \psi} \frac{\partial m(Y)}{\partial \psi}. 
\]

Following the same approach,
\[
\frac{\partial \psi}{\partial \psi} |_{\epsilon} = -\frac{1}{\rho} \sigma^t \frac{\partial \varepsilon_t(Y, \theta)}{\partial \psi} - \frac{1}{\rho} \sigma^\theta \frac{\partial \varepsilon_\theta(Y, \theta)}{\partial \psi} + \frac{\partial \psi}{\partial \psi} |_{\epsilon} = -\frac{1}{\rho} \sigma^t \frac{\partial \varepsilon_t}{\partial \psi} - \frac{1}{\rho} \sigma^\theta \frac{\partial \varepsilon_\theta}{\partial \psi} \\
+ \frac{1}{2\rho} \frac{\partial \psi(Y, a\epsilon)}{\partial \psi} \varepsilon^c: [C_S(Y) - C_0] : \varepsilon_e + \frac{\partial \psi^\theta}{\partial \psi} + \frac{\partial \psi^\theta}{\partial \psi} \\
= -\frac{1}{\rho} \sigma^t [\varepsilon_{t2} - \varepsilon_{t1} + \varepsilon_{t0}] + \varepsilon_e + \frac{\partial \psi^\theta}{\partial \psi} + \frac{\partial \psi^\theta}{\partial \psi} \\
= \frac{1}{2\rho} \frac{\partial \psi(Y, a\epsilon)}{\partial \psi} \varepsilon^c: [C_S(Y) - C_0] : \varepsilon_e + \Delta G^\theta(Y, \theta) \frac{\partial \psi(Y, a\epsilon)}{\partial \psi} + [A^{20}(\theta) - A^{10}(\theta)] \frac{\partial \psi(Y, a\epsilon)}{\partial \psi} m(Y) \\
+ A^{21}(\theta) \frac{m(Y)}{\partial \psi} \frac{\partial m(Y)}{\partial \psi}. 
\]

Substituting Eqs. (5.45) and (5.46) in Eqs. (5.44) and (5.44), respectively, results in a more detailed form of GL equations:
\[
\frac{1}{L_T} \frac{\partial Y}{\partial t} = \sigma [\varepsilon_{t1} + \varepsilon_{t0} + \varepsilon_e + \varepsilon_{t2} - \varepsilon_{t1} + \varepsilon_{t0}] \frac{\partial \psi(Y, a\epsilon)}{\partial Y} - 0.5 \frac{\partial \psi(Y, a\epsilon)}{\partial Y} \varepsilon_e - \rho \Delta G^\theta(Y, \theta) \frac{\partial \psi(Y, 0)}{\partial Y} - \rho A^{20}(\theta, \theta) \frac{\partial m(Y)}{\partial Y} \\
- \rho A^{21}(\theta, \theta) \frac{\partial m(Y, a\epsilon)}{\partial \psi} m(Y) - \frac{\beta^{21} \partial \psi(Y, a\epsilon)}{2} \frac{\partial \psi(Y, a\epsilon)}{\partial Y} |\nabla \psi|^2 \\
+ \nabla \cdot [\beta^{10} (\beta^{20} - \beta^{10}) \varepsilon_e(Y)] + \nabla \cdot [\beta^{21} \varepsilon_e(Y, a\epsilon) \nabla \psi]. 
\]
Local thermodynamic equilibrium conditions. It is evident that each of three homogeneous phases, $M \equiv \{ \Upsilon = 0 \text{ and any } \vartheta \}$, $S_1 \equiv \{ \Upsilon = 1 \text{ and } \vartheta = 0 \}$ and $S_2 \equiv \{ \Upsilon = 1 \text{ and } \vartheta = 1 \}$, makes the thermodynamic driving forces for change in $\Upsilon$ and $\vartheta$ (i.e., the right-hand side of Eqs. (5.45) and (5.46)) equal to zero for any stress and temperature; i.e., they correspond to the local thermodynamic equilibrium. This was one of the main requirements to the thermodynamic potential, which in particular imposed zero derivatives of approximating functions in Eqs. (5.35)-(5.36) for each of three phases. Note that since melt is defined as $\Upsilon = 0$ for any $\vartheta$, then the disappearance of the term with $|\nabla \vartheta|^2$ in Eqs. (5.44) for melt requires $\partial \phi(0, a_\vartheta, a_0)/\partial \Upsilon = 0$, which does not have a counterpart in the previous theories (Levitas et al., 2003; Levitas and Preston, 2002a,b). At the same time, for homogeneous solid phases all gradients should be zero and condition $\partial \phi(1, a_\vartheta, a_0)/\partial \Upsilon = 0$ in Eq. (5.36) does not follow from the condition of thermodynamic equilibrium. It is just a convenient condition that provides $q(y, a) = \phi(y, a, 0)$. The $\phi(y, a_\vartheta, a_0)$ function describes the nature of interaction between two $SM$ interfaces in vicinity of each other. Although, different functions can be chosen for describing this interaction, the chosen function need to be representative of the real system. Here, we have chosen $\phi(y, a_\vartheta, a_0)$, Eq. (5.30), such that results in interactions matching the available sharp interface models (see Ref. (Momeni and Levitas, 2014)).

Solving $\partial \psi^l / \partial \Upsilon |_{\epsilon} = 0$ for $\vartheta = 0$ and $\vartheta = 1$ gives three roots corresponding to the extremum points along the $S_\epsilon M$ phase transformation path:

$$
\Upsilon^I = 0; \quad \Upsilon^{II} = 1;
\Upsilon^{III} = 0.5 \left\{ A^0(\theta) - a_{\epsilon \Upsilon} / \rho \sigma: (\epsilon_{ts} + \epsilon_{\vartheta s} - \epsilon_{0}) - 0.5 a_C \epsilon_e: (C_0 - C_s) : \epsilon_e / \rho \right\} /
\left\{ A^0(\theta) - 3 \Delta G^0_{s0} - (a_{\epsilon \Upsilon} - 3) / \rho \sigma: (\epsilon_{ts} + \epsilon_{\vartheta s} - \epsilon_{0}) - 0.5 (a_C - 3) \epsilon_e: (C_0 - C_s) : \epsilon_e / \rho \right\}.
$$

Two of these roots are associated with the local minima (stable/metastable solid or melt); the third root corresponds to the maximum (unstable equilibrium state) of the potential. The Gibbs energy barriers for the $M \leftrightarrow S_\epsilon$ PTs are $G(\Upsilon^{III}) - G(\Upsilon^I)$ and $G(\Upsilon^{III}) - G(\Upsilon^{II})$. Following the same procedure for the path between two solids, $\Upsilon = 1$ and $0 \leq \vartheta \leq 1$, the roots
of equation $\partial \psi / \partial \theta \big|_{\varepsilon} = 0$ are:

$$\vartheta^I = 0; \quad \vartheta^{II} = 1; \quad (5.51)$$

$$\vartheta^{III} = 0.5 \left[ A^{21}(\theta) + a_{t\theta}/\rho \sigma: (\varepsilon_{t1} + \varepsilon_{\theta1} - \varepsilon_{t2} - \varepsilon_{\theta2}) + 0.5 a_{cS} \varepsilon_c: (C_2 - C_1) \varepsilon_c/\rho \right] / \left[ A^{21}(\theta) - 3\Delta G_{21}^0 + (a_{t\theta} - 3)/\rho \sigma: (\varepsilon_{t1} + \varepsilon_{\theta1} - \varepsilon_{t2} - \varepsilon_{\theta2}) - 0.5 (a_{cS} - 3) \varepsilon_c: (C_1 - C_2) \varepsilon_c/\rho \right]. \quad (5.52)$$

The Gibbs energy barriers for the $S_1 \leftrightarrow S_2$ PTs are $G(\vartheta^{III}) - G(\vartheta^{I})$ and $G(\vartheta^{III}) - G(\vartheta^{II})$.

When $\Upsilon^{III} = \Upsilon^I$ or $\Upsilon^{III} = \Upsilon^{II}$, an energy barrier disappears and the corresponding phase loses its thermodynamic stability and transforms to an alternative phase under the combination of $\sigma$ and $\theta$ that follows from these equalities. For the stress-free case, this happens at the corresponding instability temperature (see a few lines below). The same is valid when $\vartheta^{III} = \vartheta^I$ or $\vartheta^{III} = \vartheta^{II}$. Instability conditions will considered in more detail in Section 5.4.

**Some specifications.** Further specification of the temperature-dependent parameters is outlined below and described in more details in Ref. (Momeni and Levitas, 2014). Thus, we assume $\Delta C_{s0}^0 = -\Delta s_{s0}(\theta - \theta_{s0}^e)$ ($s = 1, 2$), where $\Delta s_{s0}$ is the jump in entropy between solid phase $S_s$ and melt $M$, and $\theta_{s0}^e$ is the thermodynamic equilibrium melting temperature of $S_s$. Then for $SS$ transformation, $\Delta G_{21}^0 = \Delta G_{20}^0 - \Delta G_{10}^0 = -\Delta s_{21}(\theta - \theta_{e}^2)$ with $\Delta s_{21} = \Delta s_{20} - \Delta s_{10}$ and $\theta_{e}^2 = (\Delta s_{20} \theta_{e}^2 - \Delta s_{10} \theta_{e}^{10})/\Delta s_{21}$.

For parameters defining the height of the energy barriers between equilibrium phases we assume a linear temperature dependence, shows a good match with experiments in a wide range of temperatures (Levitas and Preston, 2002a): $A^{s0}(\theta) = A_c^{s0}(\theta - \theta_{c0}^s)$ and $A^{21}(\theta) = \tilde{A}_c^{21}(\theta) + A_c^{21}(\theta - \theta_{c}^{21})$, where $\theta_{c0}^s$ (and $\theta_{c}^{21}$) is the critical temperature at which stress-free $M$ (and $S_1$) loses its stability toward $S_s$ (and $S_2$) (which follows directly from Eqs. (5.67)-(5.70) below). For the PT between two phases with the same thermal properties, such as two variants of martensite or twins, critical temperature $\theta_{c}^{21}$ does not exist and $A^{21}(\theta) = \tilde{A}_c^{21}(\theta)$.

For all other phases with different thermal properties, one has to set $\tilde{A}_c = 0$ in order to make the stress-free instability condition (5.68) below satisfied first at $\theta = \theta_{e}^{21}$ (Ref. (Momeni and Levitas, 2014)).

**Interface profile, energy, width, and velocity.** Solving the GL equations without mechanics
for PT between two phases lead to the following relations for the interface profile, energy \((E)\), width \((\delta)\), velocity \((v)\) (Levitas et al., 2003):

\[
\vartheta(x) = \frac{1}{1 + e^{-p(x-v_{21}t)/\delta^{21}}}; \quad \Upsilon(x) = \frac{1}{1 + e^{-p(x-v_{s0}t)/\delta^{s0}}};
\]

\[
E^{21} = \sqrt{2\beta^{21} \left[ A^{21}(\theta) - 3\Delta G^{\theta}_{21}(\theta) \right]} / 6; \quad E^{s0} = \sqrt{2\beta^{s0} \left[ A^{s0}(\theta) - 3\Delta G^{\theta}_{s0}(\theta) \right]} / 6; \quad (5.53)
\]

\[
\delta^{21} = \left\{ dq \left[ \vartheta(x), 3 \right] / dx \right\}_{max}^{-1} = p\sqrt{\beta^{21} / \left\{ 2 \left[ A^{21}(\theta) - 3\Delta G^{\theta}_{21}(\theta) \right] \right\}};
\]

\[
\delta^{s0} = \left\{ dq \left[ \Upsilon(x), 3 \right] / dx \right\}_{max}^{-1} = p\sqrt{\beta^{s0} / \left\{ 2 \left[ A^{s0}(\theta) - 3\Delta G^{\theta}_{s0}(\theta) \right] \right\}}; \quad (5.54)
\]

\[
v_{21} = 6L_{21}\delta^{21}\Delta G^{\theta}_{21}(\theta)/p; \quad v_{s0} = 6L_{s0}\delta^{s0}\Delta G^{\theta}_{s0}(\theta)/p, \quad (5.55)
\]

where \(p = 2.415\) (Levitas et al., 2003). The main parameters of the system that determine formation and stability of \(IM\) are the energy ratio \((k_E)\) and width ratio \((k_\delta)\) of the \(SS\) to \(SM\) interfaces. These parameters are determined using Eqs. (5.54) and (5.55), which are functions of temperature (Levitas and Momeni, 2014) unless \(A_{ij}^{ij} = -3\Delta s_{ij}\):

\[
k_E = \frac{E^{21}}{E^{s0}} = \sqrt{\frac{\beta^{21}}{\beta^{s0}} \frac{\Delta s_{21}(\theta_{21} - \theta_{e})}{\Delta s_{s0}(\theta_{c} - \theta_{e})}}; \quad k_\delta = \frac{\delta^{21}}{\delta^{s0}} = \sqrt{\frac{\beta^{21}}{\beta^{s0}} \frac{\Delta s_{21}(\theta_{c} - \theta_{s0})}{\Delta s_{21}(\theta_{c} - \theta_{e})}}. \quad (5.56)
\]

In the numerical simulations, we have considered \(SS\) interface width to have a fixed value of 1 nm (Porter, 1981) and width of \(SM\) interface is determined by fixing \(k_\delta\). The energy of the interface with \(IM\) is defined as (Levitas, 2013c)

\[
E^* = \int_{-\infty}^{x_{\phi=0.5}} \rho(\psi - \psi_{s1})dx + \int_{x_{\phi=0.5}}^{\infty} \rho(\psi - \psi_{s2})dx,
\]

where \(x_{\phi}\) is the location of the sharp interface (Gibbsian dividing surface), which should be determined using a static equivalence approach (Levitas, 2014b; Levitas and Attariani, 2014; Levitas, 2014a). For the interface without \(IM\) and 2-3-4 potential that is symmetric with respect to \(\vartheta = 0.5\), the location of the corresponding sharp interface is \(x_{\phi} = 0.5\). Here, we assume the same position of the dividing surface for the case with \(IM\) and will treat this problem in a stricter way in the future.

### 5.4 Thermodynamic stability conditions

The PT criteria between different phases in the phase-field theory are derived using the condition for a loss of stability of the homogeneous crystal lattice under spontaneous variation of
the order parameters. Instability analyses of the crystal lattice have been used for determining the ultimate strength of perfect crystals (Milstein and Hill, 1979; Hill and Milstein, 1977; Hill, 1975; Born and Fürth, 1940; Born and Misra, 1940; Misra, 1940; Born, 1940), melting (Born, 1939; Wang et al., 1993; Ida, 1969), and crystal to amorphous transition (Wang et al., 1993; Li and Johnson, 1993). Investigating the stability of a loaded crystal requires a specification of the loading type – i.e., conservative, extrinsic, or intrinsic loadings. The extrinsic loading accounts for the rotation of the specimen during the loading process as in conventional mechanical tests. The intrinsic loading assumes that the stresses follow the material boundaries. The stability of a crystalline lattice under conservative external loading have been studied using the continuum mechanics approach and large deformation formulation by applying the Lagrange stability criteria (Milstein and Hill, 1979; Hill and Milstein, 1977; Hill, 1975). Stability of the crystalline systems under a special type of nonconservative loading was studied in Refs. (Wang et al., 1995, 1993). A strict thermodynamic approach for a stability analysis of the homogeneous crystalline material under external loading and finite rotations is developed in Refs. (Levitas and Preston, 2005; Levitas, 2013b).

Here, we limit ourselves to small strain formulation and specify an approach from Ref. (Levitas, 2013b) to determine conditions for instability of homogeneous crystalline phases \( S_s \), and extend this approach to describe instability of homogeneous melt toward solidification. We formulate the following thermodynamic definition of instability under the prescribed stress tensor \( \sigma \): equilibrium phases \((\vartheta_{eq} = s - 1 \text{ for } S_s \text{ and } \Upsilon_{eq} = 0 \text{ or } 1) \) are unstable under prescribed stress tensor \( \sigma \) if a spontaneous deviation of order parameters results in a non-negative dissipation rate – i.e., \( \mathcal{D} \geq 0 \):

\[
X_T(\sigma, \varepsilon_e + \Delta \varepsilon_e, \Upsilon_{eq} + \Delta \Upsilon, \vartheta_{eq} + \Delta \vartheta, \theta)\dot{\Upsilon} + X_\vartheta(\sigma, \varepsilon_e + \Delta \varepsilon_e, \Upsilon_{eq} + \Delta \Upsilon, \vartheta_{eq} + \Delta \vartheta, \theta)\dot{\vartheta} \geq 0.
\]

(5.59)

Here, \( \Delta \varepsilon_e \) is the change in elastic strain due to changing of elastic moduli that depend on the order parameters. Using Taylor series expansion around the equilibrium phases and imposing
$X_T = X_\theta = 0$ for each equilibrium phase, Eq. (5.59) can be approximated by

$$
\frac{\partial X_T(\sigma, \varepsilon, \Upsilon_{eq}, \vartheta_{eq})}{\partial \Upsilon} \ddot{\Upsilon} + \frac{\partial X_T(\sigma, \varepsilon, \Upsilon_{eq}, \vartheta_{eq})}{\partial \vartheta} \dot{\vartheta} + \frac{\partial X_\theta(\sigma, \varepsilon, \Upsilon_{eq}, \vartheta_{eq})}{\partial \vartheta} \dot{\vartheta}^2 \geq 0,
$$

(5.60)

where $\theta$ was not shown for compactness. In Eq. (5.60), all the derivatives are calculated at constant stress. For homogeneous states, the expressions for $X_T$ and $X_\theta$ are given in Eqs. (5.16)-(5.17). Utilizing them, Eq. (5.60) expands to

$$
\begin{align*}
\sigma: & \frac{\partial^2(\varepsilon_l(\Upsilon_{eq}, \vartheta_{eq}) + \varepsilon_\theta(\Upsilon_{eq}, \vartheta_{eq}))}{\partial \Upsilon^2} - \rho \frac{\partial^2 \psi^l(\varepsilon, \Upsilon_{eq}, \vartheta_{eq})}{\partial \Upsilon^2} - \rho \frac{\partial^2 \psi^l(\varepsilon, \Upsilon_{eq}, \vartheta_{eq})}{\partial \varepsilon \partial \Upsilon} \frac{\partial \varepsilon}{\partial \Upsilon} \dot{\Upsilon}^2 + \\
2\sigma: & \frac{\partial^2(\varepsilon_l(\Upsilon_{eq}, \vartheta_{eq}) + \varepsilon_\theta(\Upsilon_{eq}, \vartheta_{eq}))}{\partial \vartheta \partial \Upsilon} - 2\rho \frac{\partial^2 \psi^l(\varepsilon, \Upsilon_{eq}, \vartheta_{eq})}{\partial \varepsilon \partial \vartheta} - \rho \frac{\partial^2 \psi^l(\varepsilon, \Upsilon_{eq}, \vartheta_{eq})}{\partial \varepsilon \partial \vartheta} \frac{\partial \varepsilon}{\partial \vartheta} \dot{\Upsilon} \dot{\vartheta} + \\
& - \rho \frac{\partial^2 \psi^l(\varepsilon, \Upsilon_{eq}, \vartheta_{eq})}{\partial \varepsilon \partial \vartheta} \frac{\partial \varepsilon}{\partial \vartheta} \dot{\vartheta}^2 \geq 0.
\end{align*}
$$

(5.61)

Note that since in Eq. (5.61) $\rho \frac{\partial \varepsilon}{\partial \vartheta} = \sigma = \text{const}$, all terms that involve these derivatives disappear:

$$
\begin{align*}
\sigma: & \frac{\partial^2(\varepsilon_l(\Upsilon_{eq}, \vartheta_{eq}) + \varepsilon_\theta(\Upsilon_{eq}, \vartheta_{eq}))}{\partial \Upsilon^2} - \rho \frac{\partial^2 \psi^l(\varepsilon, \Upsilon_{eq}, \vartheta_{eq})}{\partial \Upsilon^2} \dot{\Upsilon}^2 \\
+ & \left(2\sigma: \frac{\partial^2(\varepsilon_l(\Upsilon_{eq}, \vartheta_{eq}) + \varepsilon_\theta(\Upsilon_{eq}, \vartheta_{eq}))}{\partial \vartheta \partial \Upsilon} - 2\rho \frac{\partial^2 \psi^l(\varepsilon, \Upsilon_{eq}, \vartheta_{eq})}{\partial \varepsilon \partial \vartheta} \dot{\Upsilon} \dot{\vartheta} + \\
& + \left(\sigma: \frac{\partial^2(\varepsilon_l(\Upsilon_{eq}, \vartheta_{eq}) + \varepsilon_\theta(\Upsilon_{eq}, \vartheta_{eq}))}{\partial \vartheta^2} - \rho \frac{\partial^2 \psi^l(\varepsilon, \Upsilon_{eq}, \vartheta_{eq})}{\partial \vartheta^2} \dot{\vartheta}^2 \geq 0,
\end{align*}
$$

(5.62)

Utilizing Sylvester’s criterion for a positive-definite matrix one can easily find the explicit instability conditions, which are, however, quite complicated. It is very difficult to design a thermodynamic potential $\psi$ and transformation and thermal strains for which such sophisticated conditions reduce to simple conditions for each of three PTs, when they are considered separately. Similar to the sharp-interface approach, it is natural to assume that PT criteria between two phases are independent of the third phase. This can be satisfied if and only if all mixed derivatives in Eq. (5.62) vanish:

$$
\frac{\partial^2 \varepsilon_l(\Upsilon_{eq}, \vartheta_{eq})}{\partial \vartheta \partial \Upsilon} = 0; \quad \frac{\partial^2 \varepsilon_\theta(\Upsilon_{eq}, \vartheta_{eq})}{\partial \vartheta \partial \Upsilon} = 0; \quad \frac{\partial^2 \psi^l(\varepsilon, \Upsilon_{eq}, \vartheta_{eq})}{\partial \vartheta \partial \Upsilon} = 0.
$$

(5.63)
Note that these constraints are imposed for equilibrium phases only; for intermediate values of \( \Upsilon \) and \( \vartheta \) there are no restrictions on the mixed derivatives. Eqs. (C.4)-(5.30) have been formulated in such a way that conditions (5.63) are satisfied. Therefore, the conditions for the loss of stability of melt and solid reduce to

\[
\frac{\partial X_T(\sigma, \varepsilon_e, \Upsilon_{eq}, \vartheta_{eq})}{\partial \Upsilon} = \sigma: \frac{\partial^2(\varepsilon_i(\Upsilon_{eq}, \vartheta_{eq}) + \varepsilon_\theta(\Upsilon_{eq}, \vartheta_{eq}))}{\partial \Upsilon^2} - \rho \frac{\partial^2 \psi_i(\sigma, \Upsilon_{eq}, \vartheta_{eq})}{\partial \Upsilon^2} \geq 0 \tag{5.64}
\]

\[
\frac{\partial X_\vartheta(\sigma, \varepsilon_e, \Upsilon_{eq}, \vartheta_{eq})}{\partial \vartheta} = \sigma: \frac{\partial^2(\varepsilon_i(\Upsilon_{eq}, \vartheta_{eq}) + \varepsilon_\theta(\Upsilon_{eq}, \vartheta_{eq}))}{\partial \vartheta^2} - \rho \frac{\partial^2 \psi_i(\sigma, \Upsilon_{eq}, \vartheta_{eq})}{\partial \vartheta^2} \geq 0 \tag{5.65}
\]

Elaborating Eqs. (5.64)-(5.65) for the accepted Eqs. (C.4)-(5.30), the conditions for each phase to lose its stability toward any of the other phases (i.e., phase transformation criteria) are:

**M \rightarrow S_s:** \( \partial X_T(\Upsilon = 0, \vartheta = s - 1)/\partial \Upsilon \geq 0 \rightarrow \)

\[
\rho A^{s0}(\theta) \leq a_{t\Upsilon} \sigma: (\varepsilon_{ts} + \varepsilon_{\theta s} - \varepsilon_{\theta 0}) + 0.5 a_C \varepsilon_e: (C_0 - C_s) : \varepsilon_e; \tag{5.66}
\]

**S_s \rightarrow M:** \( \partial X_T(\Upsilon = 1, \vartheta = s - 1)/\partial \Upsilon \geq 0 \rightarrow \left[ 6 \Delta C_{s0}^\theta - A^{s0}(\theta) \right] \rho \geq (6 - a_{t\theta}) \sigma: (\varepsilon_{ts} + \varepsilon_{\theta s} - \varepsilon_{\theta 0}) + 0.5 (6 - a_C) \varepsilon_e: (C_0 - C_s) : \varepsilon_e; \tag{5.67}
\]

**S_1 \rightarrow S_2:** \( \partial X_\vartheta(\Upsilon = 1, \vartheta = 0)/\partial \vartheta \geq 0 \rightarrow \)

\[
\rho A^{21}(\theta) \leq a_{t\vartheta} \sigma: (\varepsilon_{t2} + \varepsilon_{\theta 2} - \varepsilon_{t1} - \varepsilon_{\theta 1}) - 0.5 a_{cS} \varepsilon_e: (C_2 - C_1) : \varepsilon_e; \tag{5.68}
\]

**S_2 \rightarrow S_1:** \( \partial X_\vartheta(\Upsilon = 1, \vartheta = 1)/\partial \vartheta \geq 0 \rightarrow \left[ 6 \Delta C_{s21}^\theta - A^{21}(\theta) \right] \rho \geq (a_{t\vartheta} - 6) \sigma: (\varepsilon_{t2} + \varepsilon_{\theta 2} - \varepsilon_{t1} - \varepsilon_{\theta 1}) - 0.5 (6 - a_{cS}) \varepsilon_e: (C_2 - C_1) : \varepsilon_e. \tag{5.69}
\]

Formally, Eqs. (5.66)-(5.69) are similar to the instability conditions in Refs. (Levitas et al., 2003; Levitas and Preston, 2002a,b). For zero stresses, they reduce to instability conditions in Ref. (Momeni and Levitas, 2014). An essential difference should be elaborated for the melt instability condition (5.66), because applied stresses reduce to the hydrostatic pressure \( p_0 = -1 / 3 I : \sigma \) and elastic strain reduces to volumetric strain \( \varepsilon^v_e \). Therefore, Eq. (5.66) can be rewritten as

\[
M \rightarrow S_s : A^{s0}(\theta) \rho \leq -a_{t\Upsilon} p_0 (\varepsilon^v_{ts} + \varepsilon^v_{\theta s} - \varepsilon^v_{\theta 0}) + 0.5 a_C (\varepsilon^v_e)^2 / (K_0 - K_s), \tag{5.70}
\]

where \( \varepsilon^v_{ts}, \varepsilon^v_{\theta s}, \varepsilon^v_{\theta 0} \) are the volumetric transformation and thermal strains; and \( K \) is the bulk modulus. Phase transformation criteria (5.67)-(5.70) have the desired form: transformation work exceeds the thermal threshold plus the threshold related to jump in elastic compliances.
The analytical stability conditions (5.66)-(5.69) are derived for the simple case of PT between two homogeneous phases in absence of a third phase. However, in the case of an SS phase transformation via IM, the conditions for the loss of stability are more complex and the heterogeneity of the initial state and interaction between two SM interfaces in the same vicinity play an important role. Formation of IM and its stability at different conditions are studied in this paper numerically using the developed PF model. During the formation of the $S_1MS_2$ diffuse interface, $\Upsilon$ reduces from 1 to some smaller value (in particular, to 0 for complete melt) and increases back to 1, while $\vartheta$ varies from 0 to 1 inside the IM.

5.5 Barrierless nucleation and disappearance of IM

Different PT processes are studied in this section such as barrierless and jump-like first order PTs. The effect of system parameters on the formation and stability of IM are investigated for a wide range of temperatures. Two different initial conditions are considered for each simulation – i.e., a perturbed SS interface and a pre-existing melt confined between two solids $S_1MS_2$. The presented results revealed multiple phases, which have different properties and can play a key role in designing advanced materials with new applications.

Effect of $k_E$ and $k_\delta$ — The effect of two main dimensionless parameters will be studied: (i) ratio of SS interface energy to the energy of the SM interface ($k_E$) and (ii) ratio of SS interface width to SM interface width ($k_\delta$). The first parameter characterizes the change in the interface energy during IM formation and the second one characterizes change in energy distribution and is responsible for the scale effects.

Effect of $k_E$ on the formation and stability of IM is studied for different values of $k_\delta$ at a fixed temperature $\theta = \theta_{21}^2 = 432K$. The results for melting and solidification processes for models without and with mechanics are shown in Fig. 5.3. The results show that increasing $k_E$ promotes formation and retention of disordered IM. Decreasing $k_\delta$ changes a first-order PT to a continuous reversible PT. Furthermore, range of stability and retention of IM decreases (i.e., width of IM hysteresis reduces) with decreasing $k_\delta$ (Fig. 5.3). While IM with $0 < \Upsilon < 0.15$ is captured for $k_\delta = 0.7$, this range is broaden to $0 < \Upsilon < 0.8$ for $k_\delta = 1.1$. Although the sharp interface approach imposes a $k_E > 2$ condition as a requirement for the formation of IM, our
Figure 5.3: Effect of $k_E$ and $k_\delta$ on the formation and retention of the IM. The stationary minimum values of $\Upsilon$, i.e., $\Upsilon_{\min}$, are plotted at $\theta = \theta_{21}^e = 432K$ and $a_0 = 0.01$, for different $k_\delta$ values for a model without mechanics (a) and with mechanics (b).

Phase field simulations indicate the emergence and retention of IM for $k_E < 2$ by appropriate choice of $k_\delta$ values. Comparison of the results presented in Fig. 5.3b with the results for the system with no elastic energy (Fig. 5.3a) demonstrates promotion of the IM formation in the presence of elastic energy: all lines are shifted to smaller $k_E$. Distribution of the order parameters $\Upsilon$ and $\vartheta$ at the SMS interface, which indicates the structure of IM, is shown for cases without and with mechanics in Fig. 5.4.

Distribution of elastic stress components $\sigma^y_e$ and $\sigma^z_e$ are plotted in Fig. 5.5 for $S_1S_2$ and $S_1MS_2$ interfaces. Stresses in bulk which are determined by thermal and transformation strains in a clamp in the $z$-direction sample, do not change during formation of the IM. However, stresses in melt relax which provides an additional driving force for the IM appearance.

Formation and retainment of IM as a result of the scale effect is studied in detail by performing simulations for a wide range of $k_\delta$ values at a fixed temperature ($\theta = \theta_{21}^e = 432K$) for different $k_E$ values. The results are presented in Fig. 5.6 for the problem formulation without and with mechanics. In both cases, for small $k_\delta$, after the initial jump of $\Upsilon$ from 1 down to some value, continuous change in $\Upsilon_{\min}$ with change in $k_\delta$ in both directions is observed. For large $k_\delta$, IM cannot nucleate from $\Upsilon = 1$; however, for pre-existing IM, there is a jump from small $\Upsilon$ up to $\Upsilon = 1$. For intermediate $k_\delta$, an IM-free gap is revealed, which separates these two types of behavior. Including the elastic energy reduces the width of the IM-free
Figure 5.4: Scale effects on the structure of the IM. Effect of the scale parameter \( k_\delta \) on the distribution of \( \Upsilon \) and \( \vartheta \) at the SMS interface is studied for \( a_0 = 0.01, k_E = 2.3 \), and different \( k_\delta \) values at \( \theta = \theta_0^{21} = 432K \), i.e., stationary interface. Structure of the stationary IM is shown for partially disordered phases obtained barrierlessly from the perturbed SS interface (top row) and retained complete IM obtained from a broader pre-existing IM (bottom row). The results are plotted for the model without mechanics (a and c) and with mechanics (b and d). Allowing for mechanics significantly increases the degree of disordering of the IM (a vs. b). The structure of IM is no longer symmetric with respect to \( \Upsilon_{\text{min}} \) for the model with mechanics, due to different transformation strains of each phase.
Figure 5.5: $S_1S_2$ interface profile (a) and corresponding stress distributions (c) and $S_1MS_2$ interface profile (b) and corresponding stress distributions (d). Stress distribution is considered in the middle of the sample ($y = 20\text{ nm}$). The results indicate relaxation of elastic stresses when melt is formed. Simulations are performed at $\theta = \theta^e = 432\ K$ for $a_0 = 0.01$, $k_E = 4.0$, and $k_\delta = 1.0$. 
Figure 5.6: Scale effect and formation of IM. Scale parameter \( k_\delta \) was varied to study the formation and persistence of IM for \( \theta = \theta_0^{21} = 432K \) and \( a_0 = 0.01 \) at different \( k_E \) values. Results are obtained using models without mechanics (a) and with mechanics (b).

Gap and causes the IM for smaller \( k_E \) in comparison with the case without mechanics. As \( k_E \) increased, the width of this IM-free gap reduces and finally disappears for large enough \( k_E \) values. Comparing the results of simulations with and without elastic energy, a drastic change in trend of \( \Upsilon_{min} \) for small \( k_\delta \) is found. Without mechanics, the variation of \( \Upsilon_{min} \) as a function of \( k_\delta \) is nonmonotonic indicating existence of a \( k_\delta \) with maximum disordered IM. However, \( \Upsilon_{min} \) increases monotonically in the presence of elastic energy with increasing \( k_\delta \).

Effect of the thermal driving force — Effect of thermal driving force on the energy \( E^* \) and width \( \delta^* \) of IM, as well as interface velocity is studied for two different parameters of the interfacial interactions – namely, \( a_0 = 0.01 \) and 0.1. Simulations are performed for \( k_\delta = 1.0 \) and \( k_E = 4.0 \) to ensure formation of IM in a wide range of temperatures, independent of initial conditions. Two different cases without and with elastic energy are considered. Formation of an IM (\( \Upsilon_{min} \sim 0.07 \)) with a width of \( \sim 1.4 \) nm is captured at \( \sim 0.8 \theta_0^{21} \), which is almost 185 K below the melting temperature. This is consistent with the simplified thermodynamic predictions and experimental evidences (Levitas et al., 2004, 2006b). Phase-field simulations demonstrate the enhancing effect of temperature on the formation of IM, in which \( \Upsilon_{min} \) and \( E^* \) reduce while \( \delta^* \) increases for all case studies (Figs. 5.7-5.9). All the velocities are calculated for a steady-state moving interface, which the profile of IM does not change during the interface propagation. The square points in Figs. 5.7-5.10, indicate the temperature below which, IM does not form barrierlessly within the SS interface.
Elastic energy plays a dual role: it reduces $\Upsilon_{\text{min}}$ promoting IM but surprisingly increases nucleation temperature for the IM, i.e., suppresses IM (Fig. 5.7). Increase in nucleation temperature for IM is caused by the extra elastic energy that needs to be overcome during the initial stage of IM-formation before it can be compensated by relaxation of the elastic energy during melting.

The interface profile and velocity during the PT between two phases with negligible elastic energy are studied numerically. The results of numerical simulations quantitatively match the analytical solutions which indicates validity of the developed numerical model (Momeni and Levitas, 2014). This model is then utilized to perform the simulations for the samples with elastic energy. The simulation results indicate that the interface velocity increases with increasing temperature and interfacial interaction coefficient $a_0$. The simulations for the model without elastic energy indicate a zero $S_1M_S2$ interface velocity at equilibrium temperature $\theta = \theta_e^{21}$ and its magnitude increases with deviation from $\theta_e^{21}$ in both directions. However, the elastic energy increases the $S_1M_S2$ interface velocity from metastable to stable solid phases and produces nonzero interface velocities at $\theta_e^{21}$ (Fig. 5.10). With elastic energy, $S_1M_S2$ interface velocity is positive only, because IM does not appear at a lower temperature that may cause negative velocity.

Figure 5.7: Effect of mechanics on temperature dependence of $\Upsilon_{\text{min}}$ for $k_E = 4.0$, $k_\delta = 1.0$, and two $a_0$ values. Points designate temperatures at which IM nucleates barrierlessly within SS interface. Elastic energy plays a dual role: it increases nucleation temperature of the IM but reduces $\Upsilon_{\text{min}}$. 

![Figure 5.7: Effect of mechanics on temperature dependence of $\Upsilon_{\text{min}}$ for $k_E = 4.0$, $k_\delta = 1.0$, and two $a_0$ values. Points designate temperatures at which IM nucleates barrierlessly within SS interface. Elastic energy plays a dual role: it increases nucleation temperature of the IM but reduces $\Upsilon_{\text{min}}$.](image-url)
Figure 5.8: Effect of mechanics on temperature dependence of the normalized energy of IM, $E^*$, for $k_E = 4.0$, $k_\delta = 1.0$, and two different $a_0$ values. Stresses do not affect IM energy for smaller $a_0$ and reduce it for larger $a_0$. Also, stresses increase nucleation temperature of the IM. The IM energy is almost a linear function of temperature.

Figure 5.9: Effect of mechanics on temperature dependence of the normalized width of IM, $\delta^*$, for $k_E = 4.0$, $k_\delta = 1.0$, and for two different $a_0$. Elastic stresses increase the width of IM, $\delta^*$, which varies almost linearly with temperature in the reciprocal scale, $y = 1/\delta$. 
Figure 5.10: Effect of IM formation on the interface velocity. Black dashed line is the velocity of SS interface when elastic energy is negligible, which is obtained using an analytical solution. The upper line is the velocity of the SS interface with allowing for mechanics. All other lines with dots (indicating nucleation temperature of the IM) are for velocities of $S_1MS_2$ interfaces. Simulations are performed for $k_E = 4.0$ and $k_\delta = 1.0$. For these parameters, the magnitude of the velocity of SS interface is larger than velocity of $S_1MS_2$ interface. Allowing for mechanics increases the magnitude of all interface velocities.

5.6 Nucleation and disappearance of IM via thermally activated processes and critical nucleus

The results on the effect of different system parameters (Sec. 5.5) revealed the presence of two different steady solutions for IM corresponding to the local energy minima, which are separated by an energy barrier. This barrier corresponds to the third solution or min-max of the energy functional and represents the CN. The presence of multiple minima emphasises the importance of thermally activated processes and kinetics on the final structure of an interface. The method to study CN for the IM without mechanics was developed in Ref. (Momeni and Levitas, 2014). In this section, a generalized version of this method for the case with mechanics is utilized for CN of the $S_1S_2$ interface within $S_1MS_2$ interface, and study the morphology and energetics of the CN during a heterogeneous nucleation at the interface between two solid phases (see the Appendix for details of numerical procedure).

Structure and composition of the CN$_1$ and CN$_2$ are plotted in Figs. 5.11 and 5.12, respectively, for cases without and with mechanics. The value of $T_{min}$ for the CN$_1$ is 0.24 for the model without mechanics, and 0.30 for the model with mechanics. It is logical, because for the model with mechanics, the elastic energy provides additional driving force for the formation
Figure 5.11: Effect of elastic energy on the CN$_1$ of the IM within SS interface at the center of the sample. The 2D profile of CN$_1$ ($\Upsilon(r, z)$) for a model without elastic energy (a) and with elastic energy (c) are shown at $\theta = \theta_c^{21} = 432K$, for $k_\delta = 0.7$, and $k_E = 2.6$. The insets in the top row show the profile of order parameter $\Upsilon(r)$ along the horizontal $z = 30 nm$ (top line-plots) and $\Upsilon(z)$ along the vertical $r = 0$ (right line-plots) cross-sections of the CN$_1$. (b) and (d) are corresponding plots for the profile of order parameter $\vartheta(r, z)$, which determines the width of the SS interface along with its cross-section profiles (right line-plots). Dotted line in the $\vartheta$ plots indicates the level line of $\vartheta = 0.5$, which corresponds to the sharp SS interface. The value of $\Upsilon_{min}$ for the problem without and with elastic energy are 0.24 and 0.30, respectively.
Figure 5.12: Effect of elastic energy on CN\(_2\) of \(IM\) within \(S_1S_2\) interface at the outer surface of sample. The 2D profile of CN\(_2\) (i.e., the wide \(SS\) interface near the symmetry axis of the sample) for a model without elastic energy (a) and with elastic energy (c) are presented at \(\theta = \theta_{21} = 432K\), \(k_3 = 0.7\), and \(k_E = 2.6\). The insets in the top row show the profile of order parameter \(\Upsilon(r)\) along the horizontal \(z = 30\, nm\) (top line-plots) and \(\Upsilon(z)\) along the vertical \(r = 20\, nm\) (right line-plots) cross-sections of the CN\(_2\). (b) and (d) are corresponding plots for the profile of order parameter \(\vartheta(r,z)\), which determines the width of the \(SS\) interface along with its cross-section profiles at \(r = 20\, nm\) (right line-plots). Dotted line in the \(\vartheta\) plots indicates the level line of \(\vartheta = 0.5\).
of IM and results in a CN with lower $\Upsilon_{min}$. An oval-shaped CN of the IM is formed in all these cases. The CN of the IM for the model without an elastic energy has the smaller aspect ratio. The width of the $S_1S_2$ interface narrows down inside the CN of the IM. Although the $S_1S_2$ interface is along the radial direction in the model without any elastic energy, it is curved when the effect of elastic energy is considered. This is nontrivial and is due to radial stresses in the cylindrical sample. The volumetric transformation strain increases monotonously across the solid-solid interface as we move away from the symmetry axis of the sample, which results in larger driving force for the phase transformation. Thus, there would be a mismatch between the rates of transformation from center toward the external surface that results in the formation of such complex curved interface.

We utilize the following definitions of the energies. Energy of the ground states with stationary $S_1S_2$ and $S_1MS_2$ interfaces are $E_{ss} = \int \rho \psi_{ss} dV$ and $E_{sms} = \int \rho \psi_{sms} dV$, respectively. The energy for CN$_1$ is $E^{CN_1} = \int \rho \psi_{CN_1} dV$, and energy of the CN$_2$ is $E^{CN_2} = \int \rho \psi_{CN_2} dV$. Then the activation energy for CN$_1$ of $S_1MS_2$ within $S_1S_2$ interface is $\Delta E^{CN_1}_{ss} = E^{CN_1} - E_{ss}$ and the activation energy for CN$_2$ of $S_1MS_2$ within $S_1S_2$ interface is $\Delta E^{CN_2}_{ss} = E^{CN_2} - E_{ss}$. Similarly, we define the activation energy for CN$_1$ and CN$_2$ of $S_1S_2$ within $S_1MS_2$ interface as $\Delta E^{CN_1}_{sms} = E^{CN_1} - E_{sms}$ and $\Delta E^{CN_2}_{sms} = E^{CN_2} - E_{sms}$, respectively. Three contributions to each of the above energies, due to the thermal energy $\psi^\theta + \tilde{\psi}^\theta$, gradient energy $\psi^\nabla$, and elastic energy $\psi^e$ parts of the free energy will be designated with $\Psi^\theta, \Psi^\nabla, \text{and } \Psi^e$, respectively, where $\Psi = \Psi^\theta + \Psi^\nabla + \Psi^e$ (see Tables 5.1 and 5.2). We also define effective energies for the stationary $S_1S_2$ interface, $E^{21} = E_{ss}/A_{int}$, solid-melt-solid interface, $E^{SMs} = E_{sms}/A_{int}$ and their contributions. Here, the interface area $A_{int}$ is defined as $A_{int} = \int dS_{\vartheta=0.5}$, where $S_{\vartheta=0.5}$ is the level set of the points with $\vartheta = 0.5$. Since calculations are performed for $S_1S_2$ phase equilibrium temperature, these definitions should be close to the definition based on Eq.(5.58), which is indeed the case (Table 5.3) for $E^{21}$ in the model without mechanics: it is equal to $S_1S_2$ interface energy of Eq. (5.54)$_1$.

To experimentally detect a thermally activated process within a reasonable time, the activation energy of CN should be smaller than $(40 - 80)k_B\theta$ (Ref. (Porter, 1981)), where $k_B$ is the Boltzmann constant. After forming the CN, thermal fluctuations may lead to further
Table 5.1: Energies of the ground states with stationary $S_1S_2$ (i.e., $E_{ss}$) and $S_1MS_2$ ($E_{sms}$) interfaces, as well as the energy of $S_1S_2$ interface with CN$_1$ ($E_{CN1}$) at the center and CN$_2$ ($E_{CN2}$) at the surface of the sample, are calculated for $k_B = 0.7$, $k_E = 2.6$, and $\theta = \theta_e = 432$ K. Contributions to each energy due to the thermal part $\Psi^\theta$, gradient energy $\Psi^\nabla$, and elastic energy $\Psi^e$ are included; $\Psi = \Psi^\theta + \Psi^\nabla + \Psi^e$. All the values are in $\times 10^{-18}$ J.

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<tbody>
<tr>
<td></td>
<td>$\Psi^\theta$</td>
<td>$\Psi^\nabla$</td>
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<tr>
<td>$E_{ss}$</td>
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<td>631.34</td>
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<tr>
<td>$E_{sms}$</td>
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<td>580.95</td>
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<td>$E_{CN1}$</td>
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<td>634.3279</td>
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<tr>
<td>$E_{CN2}$</td>
<td>662.36</td>
<td>660.65</td>
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Table 5.2: The activation energy of the CN$_1$ and CN$_2$ within $S_1S_2$ interface, $\Delta E_{ss}^{CN_1}$ and $\Delta E_{ss}^{CN_2}$, and $S_1MS_2$ interface, $\Delta E_{sms}^{CN_1}$ and $\Delta E_{sms}^{CN_2}$. Contributions to each energy due to the thermal part $\Psi^\theta$, gradient energy $\Psi^\nabla$, and elastic energy $\Psi^e$ are included; $\Psi = \Psi^\theta + \Psi^\nabla + \Psi^e$. Simulations are performed for $k_B = 0.7$, $k_E = 2.6$, and $\theta = \theta_e = 432$ K.

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<th>Without mechanics</th>
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<tr>
<td></td>
<td>$\Psi^\theta$</td>
<td>$\Psi^\nabla$</td>
</tr>
<tr>
<td>$\Delta E_{ss}^{CN_1}$ ($\times 10^{-18}$ J)</td>
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<td>2.99</td>
</tr>
<tr>
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<td>53.38</td>
</tr>
<tr>
<td>$\Delta E_{sms}^{CN_2}$ ($\times 10^{-18}$ J)</td>
<td>81.03</td>
<td>79.71</td>
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Table 5.3: Energies per unit area ($J/m^2$) of the ground states with stationary $S_1S_2$ (i.e., $E^{21} = E_{ss}/A_{int}$) and $S_1MS_2$ (i.e., $E^{SMS} = E_{sms}/A_{int}$) interfaces calculated for $k_B = 0.7$, $k_E = 2.6$, and $\theta = \theta_e = 432$ K. Contributions to each energy due to the thermal part $\Psi^\theta$, gradient energy $\Psi^\nabla$, and elastic energy $\Psi^e$ are included; $\Psi = \Psi^\theta + \Psi^\nabla + \Psi^e$.

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<tr>
<td></td>
<td>$\Psi^\theta/A_{int}$</td>
<td>$\Psi^\nabla/A_{int}$</td>
</tr>
<tr>
<td>$E^{21}$</td>
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<td>0.5024</td>
</tr>
<tr>
<td>$E^{SMS}$</td>
<td>0.4626</td>
<td>0.4623</td>
</tr>
</tbody>
</table>
growth of CN and formation of the alternative stable steady nanostructure. Therefore a thermally activated PT occurs when the activation energy of CN is smaller than \((40 - 80)k_B\theta\). At \(\theta = \theta^e = 432 \, K\), the energy of thermal fluctuations is \(80k_B\theta = 0.48 \times 10^{-18} \, J\). The calculated activation energies and their components are listed in Table 5.2. The minimum activation energy is obtained for the CN1 of the IM at the center of the sample within \(S_1S_2\) interface, \(\Delta E^{CN1}_{ss}\), with mechanics is smaller than the magnitude of thermal fluctuations. Therefore, \(S_1S_2 \to S_1MS_2\) phase transformation occurs as a thermally activated process. The activation energy of \(S_1MS_2 \to S_1S_2\) phase transformation in the model with mechanics is much larger than the energy of thermal fluctuations for CN1 and CN2, thus the formed IM is metastable and retains.

One has to mention that the effect of the mechanics on the barrierless PTs is nontrivial but moderate for the chosen material parameters. Elastic energy makes a larger contribution to both activation energies of \(S_1S_2\) parent phase than two other contributions together. However, it changes the distribution of the order parameters and geometry of the CN in comparison with the case without mechanics, which significantly reduces contributions of \(\Psi^\theta\) and \(\Psi^V\) to the activation energies in comparison with the case without mechanics.

The most unexpected and intriguing result of this paper is the drastic reduction in the activation energies of CN1 and CN2 due to mechanics without drastic changes in geometry of CN, which are by a factor of \(~16\) and \(~15\), receptively. Although the elastic energy reduces effective interface energies \(E^{21}\) and \(E^{SMS}\), it increases energy of each ground state and each CN. For the case with mechanics, energies of the critical nuclei are marginally increased because their structure are only slightly changed. However mechanics increases energies of the ground states more than it increases the energy of critical nuclei, which results in drastic reduction of their difference that corresponds to activation energies.

We have to be sure that the small activation energies are obtained as the difference of two large numbers and are not the result of numerical errors. Since away from the CN the ground state solution is not disturbed, we can evaluate activation energy as \(\Delta E^{CNi}_{ss} = \int \rho(\psi^{CNi} - \psi_{ss}) \, dV^* \) \( (i = 1, 2)\), where \(V^* \ll V\) is the volume around the CN, where the ground state solution is changed due to the CN. By varying \(V^*\), we found that the calculated activation
energy is not sensitive to the chosen volume $V^*$ as long as the boundaries of the $V^*$ enclose the CN and are few nanometers away from the boundaries of CN. The same is true for $\Delta E_{sm}^{CN}$.

In summary, considering mechanics is crucial for the correct determination of the activation energy for both critical nuclei, description of thermally activated nucleation and disappearance of the $IM$, as well as kinetics of the $S_1MS_2$ and $S_1S_2$ interface propagation.

5.7 Concluding remarks and future directions

In the paper, a thermodynamically consistent PF approach for PTs between three different phases is developed using polar order parameters. It includes the effect of the stress tensor, interface interactions via $IP$, and phase equilibrium and stability conditions for homogeneous phases. Explicit expressions for the Helmholtz free energy and transformation and thermal strains, which satisfy all formulated conditions are derived. The GL equations are derived and coupled to the full system of equations of continuum mechanics. They are implemented in the FE package COMSOL Multiphysics. Propagation and equilibrium of $SS$ interface containing nanometer-sized intermediate disordered $IP$ and, particularly, an interfacial $IM$ are studied in detail for HMX energetic material. Melting releases the energy of internal stresses at a coherent $SS$ interface, which provides an additional thermodynamic driving force that promotes $IM$ significantly below the bulk melting temperature. The main focus of the study is on the effect of mechanics on the structure of the $IM$ and parameters at which it nucleates and disappears, either barrierlessly or via CN and thermal fluctuations. However, results depend strongly on the ratio of widths of $SS$ to $SM$ interfaces, $k_\delta$, energy ratio of $SS$ to $SM$ interfaces, $k_E$, temperature, and parameter $a_0$ that describes the interaction of two $SM$ interfaces via an $IM$. Most of results are presented for temperatures that are more than hundreds of degrees below bulk melting temperature. In particular, formation of the $IM$ ($Y_{min} \sim 0.07$) with a width of $\sim 1.4 \text{ nm}$ is captured at $\sim 0.8\theta_e^{21} = 0.65\theta_e^{02}$, which is almost 185 K below the melting temperature. This is consistent with the simplified thermodynamic predictions and experimental evidences (Levitas et al., 2004, 2006b). Size-dependent melting hysteresis, transition from a first-order jump-like $IM$ to a second-order continuous and reversible $IM$, and formation of an $IM$-free gap are obtained without and with mechanics. Unexpectedly, mechanics plays a dual
role in barrierless IM nucleation: it promotes IM in terms of decreasing stationary value of $\Upsilon_{\text{min}}$ and energy and increasing interface velocity and width of IM but it increases the temperature for barrierless IM nucleation. An increase in nucleation temperature for IM is caused by the extra elastic energy that needs to be overcome during the initial stage of IM-formation before it can be compensated by relaxation of the elastic energy during melting. Although the sharp interface approach predicts the formation of IM for $k_E > 2$, our PF simulations demonstrated the nucleation and retainment of IM for $k_E < 2$ even without mechanics. With mechanics, the critical $k_E$ for IM nucleation reduces. The difference in the results is because the sharp-interface model assumes bulk properties of the melt while PF approach operates with incomplete intermediate nanostructures and includes the scale effect parameter $k_\delta$. The results on the scale effect and presence of an IM-free gap is not limited to the specific modeled material (i.e., HMX); they are expected for a wide range of materials, such as Si, Ge, and other materials with reducing melting temperature as a function of applied pressure (Levitas, 2005).

The most important and surprising result is in the revealed strong (by a factor of 16) reduction of the activation energy of the CN of the IM within SS interface and CN of SS interface within interface with IM due to mechanics in comparison with the model without mechanics. The main reason for drastic reduction of the activations energies is that mechanics increases energies of the ground states more than the energies of the CN. Since activation energy for the $S_1M S_2$ CN, $\Delta E_{\text{sm:s}}^{CN}$, is much smaller than each of the energies $E_{\text{sm:s}}^{CN}$ and $E_{ss}$, even a small difference in the effect of mechanics on $E_{\text{sm:s}}^{CN}$ and $E_{ss}$ significantly reduces $\Delta E_{\text{sm:s}}^{CN}$. The same is true for $S_1S_2$ CN.

Despite the appearance of additional contribution due to elastic energy, this reduction in the total activation energy is related to adjustment of the geometry and structure of the critical nucleus.

For simplicity, simulations have been performed assuming the same interface energy and width for both SM interfaces, as well as weak linear dependence of the SM interface interactions on gradient energy of SS interface inside the melt. Also, pure volumetric transformation strain tensors and temperature-independent energy and width of each individual interface were accepted. These limitations can be avoided in more detailed simulations and when correspond-
ing experimental data will be available. Also, relaxation of the elastic stresses at solid-melt interface can be introduced, similar to that in Ref. (Levitas and Samani, 2011a). The effect of IM formation on the elimination of the athermal friction (Levitas et al., 2006b) and amorphization via IM formation (Levitas, 2005) will be studied in the future. Note that change of the material parameters ($k_\delta$, $k_E$, and $a_0$) may change some of the conclusions of the current paper.

The developed model can be adjusted and implemented to study the PT between any three non-equilibrium phases (Tiaden et al., 1998; Folch and Plapp, 2005b), austenite and multiple martensitic variants (Levitas et al., 2013, 2003; Artemev et al., 2001b; Chen, 2002b), grain boundary pre-melting (Lobkovsky and Warren, 2002b; Tang et al., 2006a; Mishin et al., 2009), and surface induced PT and pre-melting (Levitas and Samani, 2011b; Levitas and Javanbakht, 2010), especially, for the finite width of the external surface (Levitas and Javanbakht, 2011b; Levitas and Samani, 2014). It will advance the above studies by adding the effect of the stress tensor and new scale parameters, like $k_\delta$ and $a_0$. The diagrams on the effect of system parameters such as temperature, $k_\delta$, and $k_E$ can be utilized as a guideline to develop new materials and alloys.

Our model can also be used to study the nucleation of solid phases from melt (T ’oth et al., 2011), heterogeneous nucleation at the interface or an external surface (Gránásy et al., 2007), as well as the effect of mechanics on the morphology and structure of nuclei and nucleation kinetics. One potential direction of research would be extending the current model to capture diffusive PTs in multi-component systems. Other areas of inquiry could encompass the study of interfacial and inter-granular phases (also called complexions) and their phase diagrams (Cantwell et al., 2014; Tang et al., 2006b), as well as a comparison with the results obtained using other simulation techniques such as MD (Frolov et al., 2013b) and phase-field crystal (Heo et al., 2011; Adland et al., 2013; Mellenthin et al., 2008; Goldenfeld et al., 2005).

**Acknowledgments**

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CHAPTER 6. GENERAL CONCLUSION

We developed an advanced phase-field model to study the effect of elastic energy, scale, and interface energy on the formation of interfacial disordered structures, and their role in the solid-solid phase transformation via these intermediate phases. Solid-solid phase transformation via intermediate disordered phase, and specifically intermediate melt, is important for materials with complex crystal structure, materials with decreasing melting temperature as a function of pressure and materials under large loading rates where other stress relaxation mechanisms such as plastic deformation is suppressed. In chapter 2, details of the thermodynamics potential that is used for modeling SS PT via IM is described. The evolution equation for the order parameters describing the SS and SM PT are derived and solved analytically for the case without stresses. Two dimensionless parameters are introduced describing the energy and width ratios of SS to SM interfaces, $k_E$ and $k_\delta$. Effect of these two main parameters on the formation of IM at the SS interface is studied in detail for different temperatures. Multiple new and surprising phenomena are captured which indicate the formation of melt 120K below melting temperature, presence of two solutions indicating the existence of a third solution associated to the unstable solution (known as critical nucleus), and presence of an IM-free range of parameters which the IM does not form for any $k_E$ and $k_\delta$ value. Transition from a first-order jumplike PT to a continuous PT due to scale effects was revealed. Furthermore, we demonstrated the formation and stability of IM at conditions which were not accessible using sharp-interface approach. The developed phase-field model, considers the interaction between two SM interfaces when they are in close vicinity of each other. We have shown that the interaction between two SM interfaces can affect the width, energy, and structure of IM as well as the velocity of the propagating SMS interface. Considering elastic energy, produces additional driving force for the melt formation and further reduces the critical $k_E$ and temperature for the loss of stability of SS interface.
In chapter 3, the developed model is used to perform a detailed study of the transformation between three nonequilibrium phases. It is shown that the energy of SS inside the melt at a SMS interface needs to be considered, otherwise the solutions will be highly mesh-dependent. This additional energy contribution is introduced by a non-trivial gradient energy function, which corresponds to interaction of two SM interfaces in vicinity of each other. The phase-field simulation results were compared with the available sharp interface models for interface interactions, which indicate an excellent match with these classic models at temperatures close to melting temperature of the solid phases. However, as degree of undercooling exceeds, the classic sharp-interface models no longer fit the phase field simulation results. We suggested a new sharp interface model based on the simplified version of the proposed phase-field model for large IM width values. The proposed sharp-interface model for the interfacial interactions fits well with the phase-field simulation results both at temperatures close to melting temperature and even 120K below it. The proposed sharp-interface model brings new insight into the nature of interfacial interactions. Structure of CN is studied by solving stationary GL equations which revealed presence of two critical nuclei for a cylindrical sample. One is the CN of IM at the SS interface and the other is the CN of SS within the SMS interface. The results indicate that the energy of CN is larger than the energy of thermal fluctuations at the equilibrium temperature of two solids. Furthermore, it is proved that for a complex SMS interface the energy of local and gradient terms are equal for the sample without elastic energy.

In chapter 4, we have studied the effect of elastic energy and internal stresses at the interface, on the formation and stability of IM. The equilibrium and stability conditions for the homogeneous phases are derived and a thermodynamic potential function was developed that satisfies all these conditions. It was shown that presence of elastic energy promoted the formation of IM, increases the interface velocity, and width of IM. It is shown that for the plane strain sample, the relaxation of elastic energy provides an additional deriving force which results in the motion of SS interface even at SS equilibrium temperature. Effect of elastic energy on the nucleation of IM phase at the SS interface is also studied, which indicates significant reduction (16 times for HMX energetic crystals) in the activation energy of CN. In this case, the energy of CN drops below the energy of thermal fluctuations, which indicates a thermally activated...
PT. This is in consistence with experimental results reported in the literature.

In chapter 5, effect of elastic energy on the formation of a nanometer sized intermediate melt at the SS interface 120K below melting temperature. It was shown that although, presence of elastic energy slightly promotes the barrierless formation of IM, it drastically changes the activation energy and changes the nature of PT from a stable phase to a thermally activated PT. Furthermore, we could demonstrate the formation of a curved SS interface when the elastic energy was taken into account. This was due to the radially increasing contribution of transformation strain volume, and could not be captured by the classical sharp-interface models.

The phase-field model that was developed, can also be adjusted to study other problems, such as surface wetting, surface-induced PT, intergranular and interfacial phase diagrams, grains and grain boundaries, as well as amorphization.
Let us prove Eq. (3.45) using stationary 1D Eqs. (3.43) and (3.44). Since for the stationary solution $\Upsilon = \Upsilon(x)$ and $\vartheta = \vartheta(x)$, we can invert $x = x(\Upsilon)$ and $x = x(\vartheta)$, and can consider either $\Upsilon$ or $\vartheta$ as an independent variable, and also express $\Upsilon = \Upsilon(\vartheta)$ or $\vartheta = \vartheta(\Upsilon)$. This will be used in the transformations below. Thus, we evaluate in Eq. (3.43)

$$
\frac{d}{dx} \left( \beta^{SO}(\vartheta) \Upsilon_x \right) = \beta^{SO}(\vartheta) \frac{d\Upsilon_x}{dx} + \Upsilon_x \vartheta_x \frac{d \beta^{SO}(\vartheta)}{d\vartheta};
$$

(A.1)

$$
\beta^{SO}(\vartheta) \frac{d\Upsilon_x}{dx} = \beta^{SO}(\vartheta) \frac{d\Upsilon}{d\Upsilon_x} = 0.5 \beta^{SO}(\vartheta) \frac{d \Upsilon_x^2}{d\Upsilon} = \frac{d(0.5 \beta^{SO}(\vartheta) \Upsilon_x^2)}{d\Upsilon} - 0.5 \Upsilon_x \vartheta_x \frac{d \beta^{SO}(\vartheta)}{d\vartheta}.
$$

Consequently,

$$
\frac{d}{dx} \left( \beta^{SO}(\vartheta) \Upsilon_x \right) = \frac{d(0.5 \beta^{SO}(\vartheta) \Upsilon_x^2)}{d\Upsilon} + 0.5 \Upsilon_x \vartheta_x \frac{d \beta^{SO}(\vartheta)}{d\vartheta},
$$

(A.3)

and Eq. (46) transforms to

$$
\frac{\partial \psi}{\partial \Upsilon} = -0.5 \beta^{21} \vartheta_x^2 \frac{d \phi(\Upsilon)}{d\Upsilon} + \frac{d(0.5 \beta^{SO}(\vartheta) \Upsilon_x^2)}{d\Upsilon} + 0.5 \Upsilon_x \vartheta_x \frac{d \beta^{SO}(\vartheta)}{d\vartheta}.
$$

(A.4)

Similarly, Eq. (44) transforms to

$$
\frac{\partial \psi}{\partial \vartheta} = -0.5 \Upsilon_x^2 \frac{d \beta^{SO}(\vartheta)}{d\vartheta} + \frac{d(0.5 \beta^{21} \vartheta_x^2 \phi(\Upsilon))}{d\vartheta} + 0.5 \beta^{21} \Upsilon_x \vartheta_x \frac{d \phi(\Upsilon)}{d\Upsilon}.
$$

(A.5)

Next, let us evaluate with the help of Eqs. (A.4) and (A.5) for fixed temperature

$$
d\psi = \frac{\partial \psi}{\partial \Upsilon} d\Upsilon + \frac{\partial \psi}{\partial \vartheta} d\vartheta = d \left( 0.5 \beta^{SO}(\vartheta) \Upsilon_x^2 + 0.5 \beta^{21} \phi(\Upsilon) \vartheta_x^2 \right) +
0.5 \beta^{21} \vartheta_x \left( \frac{d \phi(\Upsilon)}{d\Upsilon} \Upsilon_x d\vartheta - \vartheta_x d \phi(\Upsilon) \right) + 0.5 \Upsilon_x \left( \frac{d \beta^{SO}(\vartheta)}{d\vartheta} \vartheta_x d\Upsilon - \Upsilon_x d \beta^{SO}(\vartheta) \right).
$$

(A.6)

Since in the second parenthesis in Eq. (A.6) one has $\Upsilon_x d\vartheta = d\vartheta \Upsilon_x$, it disappears. Similarly, since in the third parenthesis one has $\vartheta_x d\Upsilon = d\Upsilon \vartheta_x$, it disappears as well. Then Eq. (A.6)
results in

\[ d\psi^I(\theta, \Upsilon, \vartheta) = d\psi^\nabla. \]  

(A.7)
APPENDIX B. NUMERICAL MODEL

The following is a complete system of equations for the description of the PT comprised of kinematic relations Eqs. (5.1) and (5.37)-(5.38), momentum balance Eq. (5.6), elastic coefficients Eqs. (5.21)-(5.22), change in thermal energy Eq. (5.24), energy barrier Eq. (5.26), connecting functions and their derivatives Eqs. (5.29)-(5.34), GL Eqs. (5.47)-(5.48), elasticity rule Eq. (5.39), and boundary conditions Eq. (5.18).

Material properties — The energetic crystal cyclotetramethylene-tetranitramine ($C_4H_8N_8O_8$) (also known as 1,3,5,7-tetranitro-octahydro 1,3,5,7-tetrazocine), which is called HMX, is chosen as the model material for our simulations. Parameters of the developed model were calibrated by the thermodynamic properties of $\delta$- and $\beta$-HMX which are indicated by $S_1$ and $S_2$, respectively. Mechanical and thermophysical properties of HMX are extensively studied in Refs. (Levitas et al., 2007c,b, 2006b) and parameters for the PT kinetics are described in Ref. (Momeni and Levitas, 2014). Here, we will use an an isotropic approximation for thermal expansion $\alpha_i = \alpha I$ and for tensors of elastic moduli:

$$ C_i = K_i I + 2\mu_i D, \quad (B.1) $$

where $K_i$ and $\mu_i$ are the bulk and shear modulus of phase $i$; $I = \{\delta_{ij}\delta_{kl}\}$ is the volumetric and $\bar{D} = 0.5 \{\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} - 2/3 \delta_{ij}\delta_{kl}\}$ is the deviatoric part of the forth rank unit tensor (Landau and Lifshitz, 1970). Thermophysical properties of the homogeneous phases and interfaces between them are listed in Tables C.1 and C.2, respectively. We have assumed all $a = 3$, $A_e^{0} = -3\Delta s_{s0}$, $A_e^{21} = -3\Delta s_{21}$, and $\bar{A}^{21} = 0$, which results in temperature-independent interface energies and widths, which is assumed to avoid unnecessary complication of the model and analysis of the results. The large negative value of $\theta_e^{21}$ indicates high stability of $S_1$ at $\theta = \theta_e^{21} = 432K$ and loss of stability cannot occur in reality. Negative instability temperature has also been reported for the NiAl by fitting it to the MD simulations (Levitas and Preston,
Table B.1: Thermophysical properties of homogeneous HMX.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass (M)</td>
<td>0.296 kg/mol</td>
</tr>
<tr>
<td>Density (ρ)</td>
<td>1848.78 kg/m³</td>
</tr>
<tr>
<td>$K_0 = K_1 = K_2$</td>
<td>15 (GPa) (Sewell et al., 2003)</td>
</tr>
<tr>
<td>$\mu_0$</td>
<td>0 (GPa)</td>
</tr>
<tr>
<td>$\mu_1 = \mu_2$</td>
<td>7 (GPa) (Sewell et al., 2003)</td>
</tr>
</tbody>
</table>

Table B.2: Thermophysical properties of melt (phase 0), $\delta$ (phase 1), and $\beta$ (phase 2) HMX.

<table>
<thead>
<tr>
<th>$\Delta s$ (J/kg · K)</th>
<th>$\theta_e$ (K)</th>
<th>$L$ (μ · s/kg)</th>
<th>$\theta_c$ (K)</th>
<th>$\beta$ (nJ/m)</th>
<th>$\varepsilon_{0t}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta - \beta$ (1 – 2)</td>
<td>-76.62</td>
<td>432</td>
<td>1298.3</td>
<td>-16616</td>
<td>2.4845</td>
</tr>
<tr>
<td>$m - \delta$ (0 – 1)</td>
<td>-429.36</td>
<td>550</td>
<td>2596.5</td>
<td>$f(k_E, k_\delta)$</td>
<td>$g(k_E, k_\delta)$</td>
</tr>
<tr>
<td>$m - \beta$ (0 – 2)</td>
<td>-505.98</td>
<td>532.14</td>
<td>2596.5</td>
<td>$f(k_E, k_\delta)$</td>
<td>$g(k_E, k_\delta)$</td>
</tr>
</tbody>
</table>

$^a$ Values are obtained from (Henson et al., 2002; McCrone, 1950; Menikoff and Sewell, 2002).

Here, a systematic study is performed to investigate the effect of main material parameters on the formation and stability of the IP$\text{s}$. The time scale of the simulations is determined by $L_0/A^{21}$ and is on the order of magnitude of 1 ns. A time-dependent solver is utilized to study the evolution of microstructures by solving time-dependent GL equations. Time-dependent GL equations are integrated using an implicit time-stepping method, which uses variable-order variable-step-size backward differentiable formulas. An initial time step on the order of 1 ps and a relative tolerance of $10^{-4}$ are chosen. It worth noting that the integration time step will be chosen automatically during the simulations and it reaches larger values (e.g. 0.1 ns) when steady state interface motion is reached. A stationary solver is used for finding the CN associated with the maximum energy of the structure by solving stationary GL equations. The stationary solver uses a nonlinear solver that is an affine invariant form of the damped Newton method. Different initial guesses are utilized to initialize the problem and find a configuration close to CN so that the solution of the nonlinear solver converges and gives the final structure of CN. Details of the initialization process is described in the following for each study.
Sample sizes with dimensions at least an order of magnitude larger than the largest interface width are chosen and simulations are performed for different sample sizes to ensure size-independent results. For propagating interface studies, an even larger sample size of up to 50 times larger than the largest interface width is considered to get a steady interface velocity and profile. The GL evolution equations are solved for a rectangular sample of 40 nm height and 300 nm width with a roller boundary condition (i.e., zero normal displacement and zero shear stress) on the left side and fixed lower left point. Axis $x$ is along the width of the rectangular sample and perpendicular to the interface, axis $y$ is along the height of the sample, and axis $z$ is orthogonal to both of them. Plane strain conditions are imposed along the $z$-axis. Stresses at the faces orthogonal to the $x$- and $y$-axis are zero and stresses in the $z$-direction are due to confinement of the sample in this direction and transformation strains.

For the problem of finding the CN, an infinitely long axisymmetric sample with the radius of 20 nm with free boundaries is considered. We defined "perfectly matched" layers in COMSOL with height of 10 nm at both ends of the sample in the $z$-direction for mimicking the infinitely long sample. The interface is orthogonal to the axis of symmetry $z$. Gradient of the order parameters assumed to be zero at the boundaries, i.e., constant surface energy during PT.

The numerical model is implemented in the finite element commercial software package COMSOL. The standard PDE and Structural Mechanics modules are used for implementing the developed diffuse interface model. The relative calculation error is set to be $10^{-4}$ and $a_0$ values larger than this numerical zero ($a_0 = 0.01$ and $a_0 = 0.1$) are utilized in the simulations. A mapped mesh of quadratic Lagrange elements with five elements per $SS$ interface width is used to ensure a mesh-independent solution (Momeni and Levitas, 2014). Typical simulation times for the time-dependent solver for simulating up to 1 s is a few hours using a conventional desktop computer.

When the numerical model was calibrated by the properties of austenite $\rightarrow$ martensite PT in NiAl, we could reproduce the results such as surface induced PT, which was reported in the literature (Levitas and Javanbakht, 2011b, 2010), indicating its correct implementation. Numerical simulations are also performed for the same problem without mechanics and calculated values of the interface energy, width, and velocity was compared with the analytical
solutions. The results from the numerical calculations perfectly matched the analytical solutions, which also verifies the numerical model. In the next two sections, we will give details of the initialization process for both phase evolution studies and finding the CN.

Initial conditions for a critical nucleus — The problem of finding CN corresponds to finding a saddle point of the energy functional. It is equivalent to the maximum of energy functional versus size for the given shape of the CN. Critical nucleus is a solution to stationary GL equations. However, it should be noted that solving time-dependent GL equations results in the solution corresponding to the minimum of the energy functional. Thus, time-independent GL equations need to be solved to find the solution corresponding to the saddle point of the free energy functional. We have used a modified Newtonian numerical technique (Deuflhard, 1974) to solve the stationary GL equations. A thermally activated IM formation is investigated by considering two CN of IM within $S_1S_2$ interface: (i) IM forms at $r = 0$, $CN_1$ and (ii) IM is located at the external surface, $CN_2$.

The convergence of a numerical algorithm is drastically affected by initial conditions. Therefore, choosing initial conditions close to the final morphology of the CN is a key step in this process and involves many iterations, which is explained in the following. To introduce $CN_1$ of melt with different widths determined by a free parameter $r_0$ within a $SS$ interface, the following function is used in the cylindrical coordinate system with the symmetry axis $z$ and radial coordinate $r$:

$$
\Upsilon_{CN_1}(r,z) = \left[\left\{(1 + \exp[-(z - z_0 - W/2)/\delta^{20}])^{-1} + (1 + \exp[(z + z_0 - W/2)/\delta^{10}])^{-1}\right\} \cdot H(r_0),\right.
$$

where $W$ is the width of the sample, the plane $SS$ interface is orthogonal to $z$, and $H$ is the smoothened Heaviside function. The degree of smoothness of the Heaviside function depends on the choice of system parameters and should be chosen to avoid numerical instabilities. The $CN_2$ can be obtained by defining $\Upsilon_{CN_2}(z,r) = 1 - \Upsilon_{CN_1}(z,r)$, with a large $z_0$ value – e.g., $z_0 = 8\delta^{21}$. To find the configuration of CN, different initial conditions with different widths need to be considered. It can be achieved by substituting different $z_0$ values. The chosen value of $z_0$ that results in the solution of CN strongly depends on the system parameters especially
$k_E$ and $k_\delta$. However, during the simulations we found out that an initial guess of $z_0 \sim 0.5 \delta^{21}$ commonly leads to a proper solution for CN$_1$. Furthermore, including mechanics makes the system of equations extremely sensitive to the chosen initial conditions. In this case, final configuration of CN cannot be found only by adjusting the $z_0$ and $r_0$ values and a tedious trial process of different initial conditions. Faster convergence to the final CN configuration can be achieved by first solving the system without mechanics and using this solution as the initial condition for the model with mechanics. During this process, gradually increasing the thermodynamic driving force (i.e., temperature) in order to equilibrate the contribution due to elastic energy might be necessary.

*Initial conditions for SS $\leftrightarrow$ SMS phase transformation* — Formation and stability of IM are studied using two different initial conditions: (i) a perturbed SS interface and (ii) a pre-existing melt confined between two SM interfaces. The final result is sensitive to the chosen initial conditions, because of the existence of three different stationary solutions. This is in contrast to previous models for multivariant martensitic PTs, for which the final results were not sensitive to the initial conditions. For perturbed SS interface, the order parameter $\Upsilon$ is initialized as 0.99 in the entire sample and the SS interface is modeled by a variation of $\vartheta$ according to Eq. (5.53) for a stationary interface with $v_{21} = 0$. Alternatively, using a step function for initializing $\vartheta$ in a SS interface is easy to implement and would not affect the final results for multivariant martensitic PTs. However, using this function leads to a large gradient energy at the interface and unphysical IM (i.e., IM which cannot appear barrierlessly from SS interface) forms in our simulations.

To study the stability of IM during the solidification process, we need to initialize the system with a pre-existing melt, which can be treated as a specific form of $S_1MS_2$ CN in the $S_1S_2$ interface. Thus, we can use a specific form of the CN initializing function $\Upsilon_{1CN}(r, z)$, Eq. (B.2), as an initial condition. In this case, we choose a large value for $z_0$—e.g. $z_0 = 10\delta^{21}$ and substitute the Heaviside function $H$ with 1. For the plane strain problem and the rectangular sample, where $x$ and $y$ axes are respectively along the width and height of the sample, we need to substitute $r$ with $y$ and $z$ with $x$ in Eq. (B.2).
APPENDIX C. SUPPORTING INFORMATION

Mechanics equations — The relationship between the strain tensor $\varepsilon$, displacement vector $u$, and the decomposition of strain into elastic $\varepsilon_{el}$ and transformational $\varepsilon_t$ parts are:

$$\varepsilon = 1/3 \varepsilon_0 I + e; \quad \varepsilon = (\nabla u)_{sym}; \quad \varepsilon = \varepsilon_{el} + \varepsilon_t, \quad (C.1)$$

where $\varepsilon_0$ and $e$ are the volumetric and deviatoric contributions to strain tensor; $I$ is the unit tensor, $\nabla$ is the gradient operator, and subscript $sym$ means symmetrization. The equilibrium equation is

$$\nabla \cdot \sigma = 0, \quad (C.2)$$

where $\sigma$ is the stress tensor. The elasticity rule is

$$\sigma = \frac{\partial \psi}{\partial \varepsilon} = \frac{\partial \psi^e}{\partial \varepsilon_{el}} = K(\Upsilon, \vartheta) \varepsilon_{0el} I + 2\mu(\Upsilon, \vartheta) e_{el}, \quad (C.3)$$

where $K$ is the bulk modulus and $\mu$ is the shear modulus, which both are functions of polar order parameters $\Upsilon$ and $\vartheta$ (see Eqs. (C.12)-(C.15)), $\psi$ and $\psi^e$ are the total and elastic Helmholtz energies that are calculated using Eqs. (C.4) and (C.5), respectively.

Thermodynamic functions — The Helmholtz energy per unit volume consists of elastic $\psi^e$, thermal $\psi^\theta$, and gradient $\psi^\nabla$ parts, and the term $\tilde{\psi}^\theta$ describing double-well barriers between phases:

$$\psi = \psi^e + \psi^\theta + \psi^\nabla; \quad \psi^\theta = \Delta G^\theta(\theta, \vartheta) q(\Upsilon, 0); \quad (C.4)$$

$$\psi^e = 0.5 \left( K(\Upsilon, \vartheta) \varepsilon_{0el}^2 + 2\mu(\Upsilon, \vartheta) |e_{el}|^2 \right) ; \quad (C.5)$$

$$\psi^\nabla = 0.5 \left[ \beta^{30}(\vartheta) |\nabla \Upsilon|^2 + \beta^{21}(\Upsilon, a_\varphi, a_0) |\nabla \vartheta|^2 \right] ; \quad (C.6)$$

$$\tilde{\psi}^\theta = A^{30}(\theta, \vartheta) \Upsilon^2 (1 - \Upsilon)^2 + A^{21}(\theta) \vartheta^2 (1 - \vartheta)^2 q(\Upsilon, a_A); \quad (C.7)$$

$$\varepsilon_t = [\varepsilon_{t1} + (\varepsilon_{t2} - \varepsilon_{t1}) q(\vartheta, a_{t\vartheta})] q(\Upsilon, a_{t\Upsilon}). \quad (C.8)$$
Here, sub- and superscripts 0 are for melt $M$ and 1 or 2 for solids $S_1$ or $S_2$; $\beta^{s0}$ and $\beta^{21}$ are $SM$ and $S_1S_2$ gradient energy coefficients, respectively; $\Delta G^\theta$ and $A^{s0}$ are the difference in thermal energy and energy barrier between $M$ and $S_s$ ($s = 1$ or 2); $A^{21}$ is the $S_1S_2$ energy barrier; function $q(x, a) = ax^2 - 2(a - 2)x^3 + (a - 3)x^4$, which varies between 0 and 1 when $x$ varies between 0 and 1 and has zero $x$-derivative at $x = 0$ and $x = 1$, smoothly interpolates properties of three phases; $a$ is a parameter in the range $0 \leq a \leq 6$; if unknown, $a = 3$ is accepted (see ref (Levitas et al., 2003)); the function $\phi(\Upsilon, a, a_0) = a_0 \Upsilon^2 - 2(a_0 - 2(1 - a_0))\Upsilon^3 + (a_0 - 3(1 - a_0))\Upsilon^4 + a_0$ differs from $q$ in that it is equal to $a_0$ (rather than 0) at $\Upsilon = 0$. Below we present the difference between the thermal energy of the solids and the melt

$$\Delta G^\theta(\vartheta) = \Delta G^\theta_{10} + (\Delta G^\theta_{20} - \Delta G^\theta_{10})q(\vartheta, a_{\vartheta G}),$$  \hspace{0.5cm} (C.9)

the barrier between solid and melt

$$A^{s0}(\theta, \vartheta) = A^{10}(\theta) + (A^{20}(\theta) - A^{10}(\theta)) q(\vartheta, a_\vartheta),$$  \hspace{0.5cm} (C.10)

the gradient energy coefficient

$$\beta^{ms}(\vartheta) = \beta^{s1-m} + (\beta^{s2-m} - \beta^{s1-m}) q(\vartheta, a_{ms}),$$  \hspace{0.5cm} (C.11)

the bulk moduli

$$K(\Upsilon, \vartheta) = K_0 + (K_s(\vartheta) - K_0) q(\Upsilon, a_K),$$  \hspace{0.5cm} (C.12)

$$K_s(\vartheta) = K_{s1} + (K_{s2} - K_{s1}) q(\vartheta, a_{ks}),$$  \hspace{0.5cm} (C.13)

and the shear moduli

$$\mu(\Upsilon, \vartheta) = \mu_0 + (\mu_s(\vartheta) - \mu_0) q(\Upsilon, a_\mu),$$  \hspace{0.5cm} (C.14)

$$\mu_s(\vartheta) = \mu_{s1} + (\mu_{s2} - \mu_{s1}) q(\vartheta, a_{\mu s}).$$  \hspace{0.5cm} (C.15)

The difference between the thermal energy of $S_s$ and $M$ is

$$\Delta G^\theta_{s0} = -\Delta s_{s0}(\theta - \theta_{e0}^s); \hspace{0.5cm} (s = 1, 2),$$  \hspace{0.5cm} (C.16)

where $\theta_{e0}^s$ is the equilibrium temperature between the solid phase $S_s$ and $M$, and $\Delta s_{s0}$ is the jump in entropy between $S_s$ and $M$. 
Ginzburg-Landau equations — Applying the first and second laws of thermodynamics to the system with a non-local free energy, and assuming a linear relationship between thermodynamic forces and fluxes, we obtain the Ginzburg-Landau equations (Levitas and Momeni, 2014):

\begin{align}
\dot{\Upsilon} &= L_\Upsilon \left( -\frac{\partial \psi}{\partial \Upsilon} + \frac{\beta^{21}}{2} \frac{\partial \phi(\Upsilon, a_\phi, a_0)}{\partial \Upsilon} |\nabla \phi|^2 + \nabla \cdot \left( \beta^0 \nabla \Upsilon \right) \right); \quad (C.17) \\
\dot{\vartheta} &= L_{\vartheta} \left( -\frac{\partial \psi}{\partial \vartheta} + \nabla \cdot \left( \beta^{21} \phi(\Upsilon, a_\phi, a_0) \nabla \vartheta \right) \right), \quad (C.18)
\end{align}

where \( L_\Upsilon \) and \( L_{\vartheta} \) are the kinetic coefficients and derivatives of \( \psi \), evaluated at \( \varepsilon = \text{const} \).

Analytical solutions. One of the advantages of the Eqs. (C.4)-(C.16) is that, in contrast to multiphase models in Refs. (Tiaden et al., 1998; Levitas et al., 2003), each of three PTs is described by a single order parameter, without additional constraints on the order parameters. An analytical solution for each interface between \( i \) and \( j \) phases, propagating along \( y \)-direction is (Levitas and Momeni, 2014)

\begin{align}
\eta_{ij} &= \frac{1}{1 + e^{-p(y-v_{ij}t)/\delta_{ij}}}; \quad \delta_{ij} = p \sqrt{\beta^{ij} \left[ 2 \left( A^{ij}(\theta) - 3 \Delta G_{ij}^\theta(\theta) \right) \right]}; \\
v_{ij} &= 6L_{ij} \delta_{ij} \Delta G_{ij}^\theta(\theta)/p; \quad E^{ij} = \sqrt{2\beta^{ij} \left( A^{ij}(\theta) - 3 \Delta G_{ij}^\theta(\theta) \right)}/6, \quad (C.19)
\end{align}

where \( p = 2.415 \) (Levitas et al., 2003), \( \eta_{10} = \Upsilon \) at \( \vartheta = 0; \eta_{20} = \Upsilon \) at \( \vartheta = 1, \) and \( \eta_{21} = \vartheta \) at \( \Upsilon = 1; \) \( v_{ij} \) is the interface velocity. These equations allow us to calibrate the material parameters \( \beta^{ij}, A^{ij}, \theta_{c}^{ij}, \) and \( L_{ij} \) when the temperature dependence of the interface energy, width, and velocity are specified.

Using the Eq. (C.19), we defined two dimensionless parameters, \( k_E \) and \( k_\delta \), that characterize the energy and width ratios of \( SS \) to \( SM \) interfaces. We also assumed that energy and width of interfaces are temperature independent, which can be achieved by substituting \( A_{c}^{ij} = -3\Delta s_{ij} \). Then we have

\begin{align}
k_E &= \frac{E^{21}}{E^{00}} = \sqrt{\frac{\beta^{21} \Delta s_{21}(\theta_{c}^{21} - \theta_{c}^{21})}{\beta^{00} \Delta s_{21}(\theta_{c}^{00} - \theta_{c}^{00})}}; \quad k_\delta = \frac{\delta^{21}}{\delta^{00}} = \sqrt{\frac{\beta^{21} \Delta s_{21}(\theta_{c}^{21} - \theta_{c}^{21})}{\beta^{00} \Delta s_{21}(\theta_{c}^{00} - \theta_{c}^{00})}}; \quad (C.20)
\end{align}

where in the presented simulations, the energy and width of \( SS \) interface are considered to be fixed, \( E^{21} = 1 \, J/m^2 \) and \( \delta^{21} = 1 \, \text{nm} \). Energy and width of \( SM \) interface will be determined by changing the \( k_E \) and \( k_\delta \).
Table C.1: Elastic properties of HMX crystal.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_0 = K_1 = K_2$</td>
<td>15 (GPa)</td>
</tr>
<tr>
<td>$\mu_0$</td>
<td>$0$ (GPa)</td>
</tr>
<tr>
<td>$\mu_1 = \mu_2$</td>
<td>7 (GPa)</td>
</tr>
</tbody>
</table>

$^a$ Calculated for $\beta$-HMX at $\theta = \theta_e^{21}$ and considered as a constant within small-strain approximations.

$^b$ Values are obtained from (Sewell et al., 2003).

Material properties. For simplicity, we assume all transformation strains are purely volumetric. Properties of the melt, $\delta$ phase ($S_1$) and $\beta$ phase ($S_2$) of energetic material HMX ($C_4H_8N_8O_8$) are used (Table C.1). It is assumed that for all subscripts $a = 3$ except $a_A = 0$; $A_{ij} = -3\Delta s_{ij}$ (such a choice corresponds to the temperature-independent interface energies and widths (Levitas, 2013a)); $\theta_{ij}^{c} = \theta_{ij}^{e} + p E_{ij}^{e} / \Delta s_{ij}$ and $\beta_{ij} = 6 E_{ij}^{e} \delta_{ij}^{e} / p$ (Levitas et al., 2003); $E_{21}^{e} = 1 J/m^2$ and $\delta_{21}^{e} = 1 nm$. We have also assumed $\delta_{10}^{e} = \delta_{20}^{e}$ for simplicity.

Table C.2: Thermophysical properties of melt (phase 0), $\delta$ (phase 1), and $\beta$ (phase 2) HMX.

<table>
<thead>
<tr>
<th>$\Delta s$ (kPa/K)</th>
<th>$\theta_e$ (K)</th>
<th>$L$ (mm²/N·s)</th>
<th>$\theta_c$ (K)</th>
<th>$\beta$ (nJ/m)</th>
<th>$\varepsilon_{0t}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta - \beta$ (1 - 2)</td>
<td>-141.654</td>
<td>432</td>
<td>1298.3</td>
<td>-16616 $^a$</td>
<td>2.4845 $^a$</td>
</tr>
<tr>
<td>$m - \delta$ (0 - 1)</td>
<td>-793.792</td>
<td>550</td>
<td>2596.5</td>
<td>$f(k_E, k_b)$</td>
<td>$g(k_E, k_b)$</td>
</tr>
<tr>
<td>$m - \beta$ (0 - 2)</td>
<td>-935.446</td>
<td>532.14</td>
<td>2596.5</td>
<td>$f(k_E, k_b)$</td>
<td>$g(k_E, k_b)$</td>
</tr>
</tbody>
</table>

$^a$ This value was calculated using Eq. (C.19), assuming $E_{21}^{e} = 1 J/m^2$ and $\delta_{21}^{e} = 1 nm$ (Porter, 1981).

$^b$ Values are adapted from (Henson et al., 2002; McCrone, 1950; Menikoff and Sewell, 2002)

Finding the Critical Nucleus. To find the structure of the critical nucleus (CN), the stationary Ginzburg-Landau equations must be solved using proper initial conditions for a distribution of the order parameters close to the final configuration of the CN. In this process, the order parameter associated with the phase transformation between two solid phases, $\varphi$, is initialized using Eq. (C.19). The other order parameter, describing the solid-melt phase
transformation, $\Upsilon$, is initialized for the CN1 at the sample center as

$$
\Upsilon_1(r, z) = \left[ \left\{ 1 + \exp \left[ - \frac{(z - z_0 - W/2)}{\delta^{20}} \right] \right\}^{-1} + \left\{ 1 + \exp \left[ \frac{(z + z_0 - W/2)}{\delta^{10}} \right] \right\}^{-1} \right] H(r_0),
$$

where $z_0$ determines the width of $IM$, and $W$ is the length of the simulation domain (excluding perfectly matched layers), $H$ is the Heaviside function, and $\delta^{10} = \delta^{20}$ are the widths of $S_1M$ and $S_2M$ respectively. Different widths and radii of the initial CN configuration is modeled by substituting different $z_0$ and $r_0$ values in Eq. (C.21). Based on a trial process, we found reasonable initial conditions using $z_0 = 0.5 \delta^{21}$ for modeling CN of $IM$ within the $S_1S_2$ interface. The initial conditions for the CN2, for which the $IM$ is located at the surface of $S_1S_2$ interface within a pre-existing interfacial melt, can be determined using $\Upsilon_2(z, r) = 1 - \Upsilon_1(z, r)$, and choosing a large $z_0$ value (e.g., $z_0 = 8 \delta^{10} k_d$). For the model with mechanics, a two-step process is pursued for finding the configuration of the CN. In the first step, we found the CN for the sample without mechanics. Then in the second step, we used the solution obtained for order parameters in previous step to initialize the system of equations for the sample with mechanics.
APPENDIX D. COPY RIGHT AGREEMENTS

Title: Solid−Solid Phase Transformation via Internal Stress-induced Virtual Melting, Significantly below the Melting Temperature. Application to HMX Energetic Crystal

Author: Valery I. Levitas, Bryan F. Henson, Laura B. Smilowitz, et al

Publication: The Journal of Physical Chemistry B

Publisher: American Chemical Society

Date: May 1, 2006

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Author Valery I. Levitas, Laura B. Smilowitz, Bryan F. Henson, et al.
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