Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2016

Journal Name

ARTICLE TYPE

Cite this: DOI: 10.1039/xxxxxxxxxx

Phase-Field Approach to Nonequilibrium Phase Transformations in Elastic Solids via Intermediate Phase (Melt) Allowing for Interface Stresses

Kasra Momeni[a] and Valery I Levitas*[b]

Received Date
Accepted Date

DOI: 10.1039/xxxxxxxxxx

www.rsc.org/journalname

Electronic Supplementary Information

1 Applications of Virtual Melting

Pressure-induced crystal-crystal and crystal-amorphous PTs via the unstable virtual melt was discussed in[1] for materials with the negative derivative of the melting temperature with respect to pressure. They include geological materials (ice, $\alpha-$quartz, jadeite, and coesite), electronic materials (Si and Ge), and ceramics (graphite and boron nitride). For some cases, this was (and for other materials, it was not) related to the relaxation of internal stresses, and it included both nucleation and growth. Amorphization via virtual melting was observed during heating in experiments[2] for Avandia (Rosiglitazone), an anti-diabetic pharmaceutical. The important role of the virtual melting phenomena for the PT and plastic flow in various systems is discussed in[3]. The PT between square and triangular lattices of colloidal films of microspheres via the *IM* was in-situ observed in[4]. One should mention that the thermodynamic and kinetic interpretations of this phenomenon in[4] possess significant deficiencies. While it is explicitly stated that PT between two lattices occurs below the bulk melting temperature, the bulk driving force for melting is considered to be positive, which is possible above the bulk melting temperature only. In contrast to the statement in Ref. [4], crystal-crystal transformation via virtual and intermediate melting have been reported and analyzed for a decade, utilizing significantly more general thermodynamic and kinetic descriptions and far below the bulk melting temperature[1–3,5–10].

Crystal-crystal PTs via an intermediate *surface-induced virtual pre-melt and melt* were justified thermodynamically in[9]. Substituting the initial interface with interfaces of lower energy during the formation of melt provides a thermodynamic driving force in addition to (or instead of) relaxation of elastic energy. A similar approach was developed for crystal-crystal PT via virtual melting in bulk, which generalizes the approach developed in[7,8,11]. Including reduction in the interface energy lead to two important consequences. First, melt can be in thermodynamic equilibrium with an internally non-hydrostatically stressed solid below melting temperature. Thus it is not always a transitional state (virtual melt), but thermodynamically stable (i.e., *SS*-interface stabilized) intermediate melt (*IM*). The above theoretical estimates have been confirmed by direct experimental observation of the amorphous few-nanometer size region within the interface between pre-perovskite and perovskite phases in $PbTiO_3$ nanofibers, which represents quenched *IM*[9] (Fig. A.1).

Note that there are many phenomena unrelated to solid-solid PT via the *IM* which exhibit few-nanometers-size interfacial phases (*IPs*) within interface between two other phases. They include barrierless austenite nucleation at interfaces between two martensitic variants or twins[12–14], formation of intergranular and interface amorphous or crystalline phases (complexions)[15–24] in ceramic and metallic systems, and developing interfacial phase diagrams for them[17–19], which differ from the phase diagrams for bulk phases, pre-melting at grain boundaries[16,25], surface pre-melting and melting[26–29] at moving solid-melt-gas interfaces, surface-induced *SS* phase transformation[13,14,30], and

---

[a] Department of Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania 16802, U.S.A.
[b] Department of Aerospace Engineering; Department of Mechanical Engineering; Department of Material Science and Engineering; Iowa State University, Ames, Iowa 50011, U.S.A. E-mail: vlevitas@iastate.edu

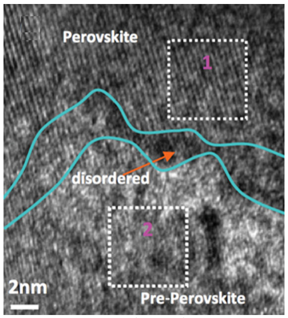

Fig. A.1 Experimental evidence of the formation of the quenched intermediate melt during the transformation from the metastable preperovskite to the stable perovskite phase in $PbTiO_3$ nanowire[9].

liquid-metal embrittlement[31]. Modeling the behavior of *IPs*, which are commonly nanometer-size phases, plays a key role in understanding the underlying physics, designing new nanodevices, and improving the current ones.

2 Phase Field Approach

The structural changes are introduced with the help of the order parameters, which describe them and associated material instabilities in a continuous manner. The number of minima of the thermodynamic potential in the order parameters' space is equal to the number of considered phases or structural states. They are separated by energy barriers. Also, the potential depends on the gradients of the order parameters, which are localized within a finite-width interface, penalize interface energy, and determine the interface width. A linear relationship between the time derivative of order parameters and conjugate thermodynamic forces results in Ginzburg-Landau equations, which describe structural evolution, along with evolving stresses, temperature, and other coupled fields. This is a minimum physics that allows one to describe evolution of multiphase systems with bulk phases separated by finite-width interfaces. Additional important requirements are related to a conceptually correct description of the effect of stress tensors and equilibrium stress-strain curves, consistency with thermodynamic equilibrium and instability conditions have been formulated and satisfied for multivariant martensitic PTs for small[32–34] and large[35] strains, which resulted in more sophisticated expressions for thermodynamic potentials and transformation strains. Still, these theories have a significant drawback: while each austenite-martensitic variant PT is described with a help of a single order parameter, variant-variant transformation (twinnig) is described utilizing two order parameters. This does not allow one to obtain an analytical solution for the moving interface and ensure the chosen (experimentally determined) interface energy, width, and velocity by proper calibration of the material parameters of the model. The trajectory of the solution in the plane of two order parameters cannot be properly controlled.

An alternative approach developed by a different research community for multiphase PTs, including melting, is based on utilizing the constraint that the sum of all order parameters is equal to unity[36–45], like the concentration of phases. One of the main goals is to constrain a trajectory in the order parameter space for PT between any two phases to the straight line, which then can be parameterized with a single order parameter. This eliminates the problem mentioned above, but has two consequences. (1) Such a constraining comes with the price of some limitations or oversimplifications of models, see critical review in[46]. (2) This automatically excludes the third phase within interface between two other phases and does not allow one to consider *IM*. Note that most of these works do not involve stresses, and the requirement that PT criteria should follow from the thermodynamic instability conditions accepted in[32–34] was never applied in them. A more advanced approach to multiphase systems, which includes mechanics and all requirements from[32–34], as well as allow one to achieve the description of PT between any two phases with the help of a single order parameter, is presented in[47]. It is based on a new penalizing term and was applied to stress-induced martensitic PTs and twinning, when the third phase is excluded from the interface between two other phases.

3 Analytical relations for interface profile, energy, width, and velocity

The GL equation for PT between two phases without mechanics has an analytical solution[48], which lead to the following relations for the interface profile, energy E, width δ, and velocity v:

$$\vartheta(x) = 1/\left[1+e^{-p(x-v_{21}t)/\delta^{21}}\right]; \quad \Upsilon(x) = 1/\left[1+e^{-p(x-v_{s0}t)/\delta^{s0}}\right]; \tag{A.1}$$

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

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

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

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

$$v_{21} = 6L_{21}\delta^{21}\Delta G^{\theta}_{21}(\theta)/p; \quad v_{s0} = 6L_{s0}\delta^{s0}\Delta G^{\theta}_{s0}(\theta)/p, \tag{A.4}$$

with $p = 2.415$[32,49,50]. The thermodynamics and kinetics of the *IM* is determined (among others) by two main parameters – namely, k_E and k_δ. Using Eqs. (A.2)-(A.3) and assuming the interface energy and width of each phase to be independent of

Table A.1 Thermomechanical properties of HMX.

Property	Value
Molar mass (M)	$0.296\,kg/mol$
Density (ρ_0) *	$1611.84\,kg/m^3$
$K_0 = K_1 = K_2$	$15\ (GPa)$ [53]
μ_0	$0\ (GPa)$
$\mu_1 = \mu_2$	$7\ (GPa)$ [53]

[1] Calculated for melt at $\theta = \theta_e^{21}$.

temperature, which can be achieved by $A_c^{ij} = -3\Delta s_{ij}$, we have [5,6]

$$k_E = \frac{E^{21}}{E^{s0}} = \sqrt{\frac{\beta^{21}}{\beta^{s0}}\ \frac{\Delta s_{21}(\theta_c^{21}-\theta_e^{21})}{\Delta s_{s0}(\theta_c^{s0}-\theta_e^{s0})}};$$

$$k_\delta = \frac{\delta^{21}}{\delta^{s0}} = \sqrt{\frac{\beta^{21}}{\beta^{s0}}\ \frac{\Delta s_{s0}(\theta_c^{s0}-\theta_e^{s0})}{\Delta s_{21}(\theta_c^{21}-\theta_e^{21})}}. \qquad (A.5)$$

The energy of the *SMS* interface is measured with respect to corresponding solid phases from each side of the interface [5,6,51]

$$E^* = \int_{-\infty}^{x_{\vartheta=0.5}} (\psi - \psi_{s1})dx + \int_{x_{\vartheta=0.5}}^{\infty} (\psi - \psi_{s2})dx, \qquad (A.6)$$

where $x_{\vartheta=0.5}$ is the chosen location the Gibbs dividing interface, at which $\vartheta = 0.5$. For the 2-3-4 potential and two-phase interface without any *IM*, the Gibbs dividing plane is proved to be located at $x_\vartheta = 0.5$ [50]. Here, we have assumed the same location for the dividing surface for *SMS* interface. A strict solution for determining the location of dividing surface in presence of *IM*, based on approach similar to one in [50,52], is left for future.

4 Thermomechanical properties of HMX

Thermomechanical properties of the model material, HMX, is presented in Table A.2.

5 Initial conditions

The *SS* diffuse interface $\vartheta(x)$ or $\vartheta(r)$ for initial conditions is obtained first by using either a sharp interface or the static analytical solution $(A.1)_1$.

Critical nuclei — In order to obtain solutions for CN_1 and CN_2 of the *IM* by using a solver for a stationary solution, initial conditions should be as close as possible to the final solutions shown in Figs. (12) and (13) of the main text. To address this problem, the following initial conditions for Υ_1^{CN} for CN_1,

$$\Upsilon_1^{CN} = \Big[\Big\{1+exp\Big[-(z-z_0-W/2)/\delta^{20}\Big]\Big\}^{-1} + \Big\{1+exp\Big[(z+z_0-W/2)/\delta^{10}\Big]\Big\}^{-1}\Big]\,H(r_0), \qquad (A.7)$$

is superposed on *SS* interface in a box of radius r_0. Here W is the length of the sample in z direction, H is the Heaviside step function, and z_0 is a parameter determining width of CN_1. Although appropriate value of z_0 that gives the CN is a strong function of the system parameters k_E and k_δ, we found that an initial guess of $z_0 \sim 0.5\,\delta^{21}$ is an appropriate choice. The Heaviside function H is smoothened to avoid numerical instabilities, and this smoothness depends on the chosen material parameters. For the models with mechanics and interfacial tension solution for the CN can converged much faster by solving first the problem without mechanics and use this solution as the initial condition for the complete model. Gradual increasing of the thermodynamic driving forces corresponding to the elastic energy might be necessary to avoid diverging of the numerical solution. For CN_2 we can use a modified version of Eq. (A.7) as $\Upsilon_2^{CN}(z,r) = 1 - \Upsilon_1^{CN}(z,r)$, with a large z_0 value – e.g., $z_0 = 8\,\delta^{21}$.

IM in rectangular sample — Eq. (A.7) can be used for initializing S_1MS_2 interface in the rectangular sample, if we substitute z with x and eliminate the Heaviside function. One has to use large z_0 – e.g. $x \sim 10\,\delta^{21}$. Formation of *IM* within *SS* interface was studied by assigning $\Upsilon = 0.99$ and ϑ to the analytical solution of order parameters for GL equations with $\psi^e = 0$, –i.e., Eq. $(A.1)_1$ with $\nu_{21} = 0$.

Model verification — To verify the implemented numerical model, simulations are performed for cases in which the model reduces to the one with analytical solution and also cases with previously reported fields. Our numerical simulation results for a two-phase interface without mechanics and *IPs* at different temperatures coincide with the analytical solutions, Eqs. (A.1)-(A.4), and the values reported in Ref. [5].

References

1 V. I. Levitas, *Phys. Rev. Lett.*, 2005, **95**, 075701.

2 S. L. Randzio and A. Kutner, *J. Phys. Chem. B*, 2008, **112**, 1435–1444.

3 P. Ball, *Nat. Mater.*, 2012, **11**, 747–747.

4 Y. Peng, F. Wang, Z. Wang, A. M. Alsayed, Z. Zhang, A. G. Yodh and Y. Han, *Nat. Mater.*, 2015, **14**, 101–108.

5 K. Momeni and V. I. Levitas, *Phys. Rev. B*, 2014, **89**, 184102.

6 V. I. Levitas and K. Momeni, *Acta Mater.*, 2014, **65**, 125–132.

7 V. I. Levitas, B. F. Henson, L. B. Smilowitz and B. W. Asay, *Phys. Rev. Lett.*, 2004, **92**, 235702.

8 V. I. Levitas, B. F. Henson, L. B. Smilowitz and B. W. Asay, *J. Phys. Chem. B*, 2006, **110**, 10105–10119.

9 V. I. Levitas, Z. Ren, Y. Zeng, Z. Zhang and G. Han, *Phys. Rev. B*, 2012, **85**, 220104.

10 V. I. Levitas and R. Ravelo, *Proc. Natl. Acad. Sci. U.S.A.*, 2012, **109**, 13204–13207.

11 V. I. Levitas, L. B. Smilowitz, B. F. Henson and B. W. Asay, *J.*

Table A.2 Thermodynamic and kinetic properties of phase transformations between β, δ, and liquid phases of HMX.

	Δs $(kJ/m^3 \cdot K)$[54]	θ_e (K)[54]	L $(\mu \cdot s/kg)$	θ_c (K)	β (nJ/m)	ε_{0t}[54]
$\delta-\beta$	-141.66	432	1298.3	-16616 [1]	2.4845[1]	-0.08
$m-\delta$	-793.79	550	2596.5	$f(k_E,k_\delta)$	$g(k_E,k_\delta)$	-0.067
$m-\beta$	-935.45	532.14	2596.5	$f(k_E,k_\delta)$	$g(k_E,k_\delta)$	-0.147

[1] This value was calculated using Eqs. (A.2)-(A.3), assuming $E^{21} = 1.07\ J/m^2$ and $\delta^{21} = 1.07\ nm$, which are in the range of typical interface energy and width values[55].

Chem. Phys., 2006, **124**, 026101.

12 H. Xu, S. Tan and I. Müller, *Zeitschrift fur Metallkunde(Germany)*, 1998, **89**, 59–64.

13 V. I. Levitas and M. Javanbakht, *Phys. Rev. Lett.*, 2010, **105**, 165701.

14 V. I. Levitas and M. Javanbakht, *Phys. Rev. Lett.*, 2011, **107**, 175701.

15 A. E. Lobkovsky and J. A. Warren, *Physica D: Nonlinear Phenomena*, 2002, **164**, 202–212.

16 M. Tang, W. Carter and R. Cannon, *Phys. Rev. B*, 2006, **73**, 024102.

17 J. Luo, *Crc. Cr. Rev. Sol. State*, 2007, **32**, 67–109.

18 J. Luo and Y.-M. Chiang, *Annu. Rev. Mater. Res.*, 2008, **38**, 227–249.

19 J. Luo, *J. Am. Ceram. Soc.*, 2012, **95**, 2358–2371.

20 M. Baram, D. Chatain and W. D. Kaplan, *Science*, 2011, **332**, 206–209.

21 J. Luo and Y. M. Chiang, *Acta Mater.*, 2000, **48**, 4501–4515.

22 A. Avishai and W. D. Kaplan, *Acta Mater.*, 2005, **53**, 1571–1581.

23 S. Ma, P. R. Cantwell, T. J. Pennycook, N. Zhou, M. P. Oxley, D. N. Leonard, S. J. Pennycook, J. Luo and M. P. Harmer, *Acta Mater.*, 2013, **61**, 1691–1704.

24 H. Qian, J. Luo and Y.-M. Chiang, *Acta Mater.*, 2008, **56**, 862–873.

25 A. E. Lobkovsky and J. A. Warren, *Physica D*, 2002, **164**, 202–212.

26 R. Lipowsky, *Phys. Rev. Lett.*, 1982, **49**, 1575–1578.

27 K. Koga, T. Ikeshoji and K.-i. Sugawara, *Phys. Rev. Lett.*, 2004, **92**, 115507.

28 V. I. Levitas and K. Samani, *Phys. Rev. B*, 2011, **84**, 140103(R).

29 V. I. Levitas and K. Samani, *Nat. Commun.*, 2011, **2**, 284.

30 J. Diao, K. Gall and M. L. Dunn, *Nat. Mater.*, 2003, **2**, 656–660.

31 J. Luo, H. Cheng, K. M. Asl, C. J. Kiely and M. P. Harmer, *Science*, 2011, **333**, 1730–1733.

32 V. Levitas, D. Preston and D.-W. Lee, *Phys. Rev. B*, 2003, **68**, 134201.

33 V. Levitas and D. Preston, *Phys. Rev. B*, 2002, **66**, 134206.

34 V. I. Levitas and D. L. Preston, *Phys. Rev. B*, 2002, **66**, 134207.

35 V. I. Levitas, *International Journal of Plasticity*, 2013, **49**, 85–118.

36 J. Tiaden, B. Nestler, H. J. Diepers and I. Steinbach, *Physica D: Nonlinear Phenomena*, 1998, **115**, 73–86.

37 B. Nestler and A. A. Wheeler, *Phys. Rev. E*, 1998, **57**, 2602–2609.

38 R. Kobayashi and J. A. Warren, *Physica A: Statistical Mechanics and its Applications*, 2005, **356**, 127–132.

39 G. I. Tóth, J. R. Morris and L. Gránásy, *Phys. Rev. Lett.*, 2011, **106**, 045701.

40 G. I. Tóth, T. Pusztai, G. Tegze, G. Tóth and L. Gránásy, *Phys. Rev. Lett.*, 2011, **107**, 175702.

41 Y. Mishin, W. J. Boettinger, J. A. Warren and G. B. McFadden, *Acta Mater.*, 2009, **57**, 3771–3785.

42 R. Folch and M. Plapp, *Phys. Rev. E*, 2003, **68**, 010602.

43 R. Folch and M. Plapp, *Phys. Rev. E*, 2005, **72**, 011602.

44 I. Steinbach, *Model Simul Mater Sc*, 2009, **17**, 073001.

45 P. C. Bollada, P. K. Jimack and A. M. Mullis, *Physica D: Nonlinear Phenomena*, 2012, **241**, 816–829.

46 G. I. Tóth and B. Kvamme, *Phys. Rev. E*, 2015, **91**, 032404.

47 V. I. Levitas and A. M. Roy, *Phys. Rev. B*, 2015, **91**, 174109.

48 V. I. Levitas, D.-W. Lee and D. L. Preston, *Int J Plasticity*, 2010, **26**, 395–422.

49 V. I. Levitas, *Acta Mater.*, 2013, **61**, 4305–4319.

50 V. I. Levitas, *Phys. Rev. B*, 2014, **89**, 094107.

51 K. Momeni and V. I. Levitas, *International Journal of Solids and Structures*, 2015, **71**, 39–56.

52 V. I. Levitas, *J. Mech. Phys. Solids*, 2014, **70**, 154–189.

53 T. D. Sewell, R. Menikoff, D. Bedrov and G. D. Smith, *J. Chem. Phys.*, 2003, **119**, 7417–7426.

54 V. I. Levitas, B. F. Henson, L. B. Smilowitz, D. K. Zerkle and B. W. Asay, *J. Appl. Phys.*, 2007, **102**, 113520.

55 D. Porter, *Phase Transformation in Metals and Alloys*, Van Nostrand Reinhold, 1981.