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Sublimation, chemical decomposition, and melting inside an elastoplastic material: General continuum thermodynamic and kinetic theory

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ABSTRACT

General thermodynamic and kinetic approaches for sublimation inside an elastoplastic material are developed for large strains. Various conceptual problems related to the effect of irreversible plastic deformation and dissipation, path-dependence of the appearance of a critical nucleus, and the presence of large strains are considered. Two transformation paths are studied: nucleation via homogeneous transformation in the nucleus of fixed mass and nucleation via continuous interface propagation. For both paths, the expressions for the thermodynamic driving forces and activation energies are derived. The activation energy is equal to the negative driving force for the appearance of a nucleus maximized with respect to nucleus mass and minimized over the nucleus shape, transformation path, and position. This definition corresponds to the principle of the minimum of transformation time and reduces to the traditional one in the limit of elastic materials. An Arrhenius-type kinetic equation for nucleation time and kinetic nucleation criterion are formulated. Algorithms for the determination of the critical nucleus are suggested. After appearance of the nucleus via homogeneous transformation, the possibility of its growth should be checked. Growth may occur by further sublimation or by mechanical expansion without phase transformation due to mechanical instability. Because the driving force for forward and reverse transformations maybe different, several scenarios are possible. The nucleus can grow, disappear, or be arrested; in the last case, it represents a stable rather than a critical nucleus. It is demonstrated that with small modifications, our approach to sublimation can be applied to chemical decomposition and melting inside an elastoplastic material. In the accompanying paper (Levitas and Altukhova, 2012) we will apply the developed theory to nucleation of a spherical gas bubble inside an elastoplastic material.

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1. Introduction

Sublimation is a direct, first-order phase transformation from the solid to the gas phase. Sublimation always occurs from the free surface of the solid until partial gas pressure reaches an equilibrium value for a given temperature. Thermodynamic equilibrium between a gas and a free solid surface and sublimation from a free surface are problems from any advanced thermodynamics textbook (e.g., Moran and Shapiro, 2008). Evaporation within a liquid is a typical nucleation problem (formally completely similar to melting and solidification), see Landau and Lifshitz (1980) and Porter and Easterling (1992). Thus, the total Gibbs energy change of a system when a spherical nucleus of a radius r appears is $\Delta G = \Delta g \frac{4}{3} \pi r^3 - \Gamma 4 \pi r^2$, where Δg is the change of the local Gibbs energy and Γ is the surface energy of a nucleus. The plot of ΔG versus radius r is shown in Fig. 1. Note that the dissipation increment $X = -\Delta G$. Thus, for small radii, dissipation is negative and the nucleus is thermodynamically inadmissible – i.e., it can appear due to thermal fluctuation only.

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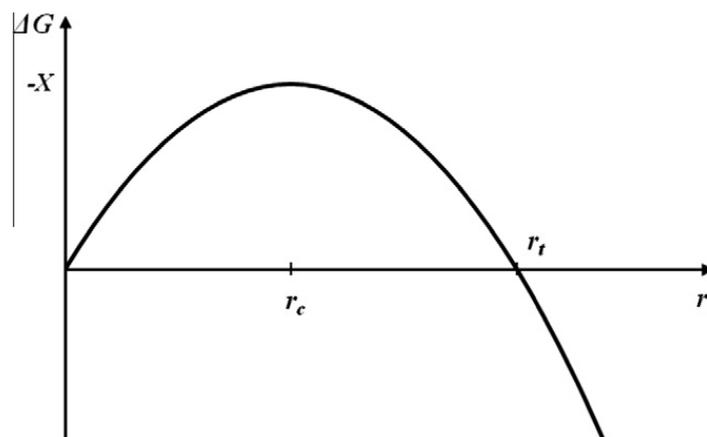


Fig. 1. Change in the Gibbs energy and energy dissipation versus nucleus radius; r_c is the radius of the critical nucleus, and r_t is the radius of the thermodynamically admissible nucleus. For the appearance of a nucleus with $r < r_t$, the dissipation increment X is negative and the nucleus is thermodynamically inadmissible – i.e., it can appear due to thermal fluctuation only.

For analysis of the possibility of growth of a nucleus that appeared as a result of thermal fluctuation, the crucial role is played by the concept of the critical radius r_c that corresponds to the maximum change in Gibbs energy ΔG . The dissipation rate for nucleus growth is $D = -\frac{dG}{dr} \dot{r}$. For a subcritical nucleus (i.e., for $r < r_c$), one has $\frac{dG}{dr} > 0$ and for $\dot{r} > 0$, one has $D < 0$. That means that after its appearance, its growth is thermodynamically inadmissible (i.e., it requires thermal fluctuations) but shrinkage ($\dot{r} < 0$) corresponds to the reduction of the Gibbs energy and the positive dissipation. If the nucleus of the supercritical radius $r > r_c$ appears due to thermal fluctuation, then $\frac{dG}{dr} < 0$ and for $\dot{r} > 0$, one has $D > 0$, i.e., its growth is accompanied by a reduction in the Gibbs energy (positive dissipation) and it is thermodynamically admissible. Consequently, the limiting event for nucleation is an appearance of the critical nucleus, which requires thermal fluctuation with the activation energy $Q = G_{max} = G(r_c)$; the main problem is to find the critical nucleus and to calculate Q .

Since the process of the appearance of the critical nucleus is not thermodynamically favorable and requires fluctuations, it cannot be described by classical thermodynamics. Indeed, thermodynamics operates with parameters that are averaged over characteristic time and spatial scales, and any fluctuations are filtered out. As a result of this, the nucleation process is generally described by statistical theories (see, e.g., Kashchiev, 2003), which will not be considered here. In thermodynamics, the critical nucleus is determined from the condition that it corresponds to the saddle point of the energy G , i.e., maximum with respect to size and minimum with respect to other parameters (such as shape and internal structure, see Lin et al. (1993), Porter and Easterling (1992), Olson and Roytburd (1995), Olson and Cohen (1986a) and Levitas et al. (2003)). Then this nucleus (including small perturbations) is introduced in a problem formulation as an initial condition and its further evolution is considered through solving thermodynamically consistent kinetic equations, such as the Ginzburg–Landau equation (Levitas et al., 2003; Ngan and Truskinovsky, 2002). However, again, the appearance of the critical nucleus cannot be described with the thermodynamically consistent kinetic equations. In the phase-field approach, a stochastic term is usually included in the Ginzburg–Landau equation to account for thermal fluctuations (see, e.g., Artemev et al., 2001).

As we will discuss below, for an elastoplastic material we cannot just search for a saddle point of the Gibbs energy. The whole process of the appearance of the critical nucleus must be considered. Then, in addition to the scientific problem, there is a psychological problem: continuum mechanics demands fulfillment of the second law of thermodynamics (see any book, e.g., by Grinfeld (1991), Ottosen and Ristinmaa (2005), Truesdell and Noll (1965) and Levitas (1996)), however, the appearance of the critical nucleus is accompanied by negative dissipation. There are very few works that state and address this issue explicitly. Lusk (1994), in his treatment of nucleation in nonlinear elastic materials, specifies that nucleation produces rather than dissipates energy and that the subcritical nuclei cannot grow due to the restriction produced by the dissipation inequality. Levitas (2000), after stating that the appearance of the critical nucleus is accompanied by a negative dissipation increment and that is why it requires thermal fluctuations, suggested the concept of the thermodynamically admissible nucleus. In particular, the nucleus of the radius r_t in Fig. 1 corresponds to $X = -\Delta G = 0$, i.e., it is thermodynamically admissible. However, such a treatment is not consistent with all existing textbook approaches on nucleation and this does not determine the activation energy explicitly. This method will not be pursued here. At the same time, the approach in Levitas (2000) illustrates that, in general, there is not anything unusual in the nucleation and that the second law is satisfied for the event averaged over the size $r > r_t$ or the corresponding time interval. The problem arises because we are interested in the event that occurs during the smaller time and it is not surprising that the second law of thermodynamics is not applicable for such a scale. The situation is the same for any thermally activated process such as diffusion, propagation of phase interfaces, grain boundaries, or dislocations. While for the averaging over a large enough spatial or temporal scale the second law of thermodynamics is fulfilled, for the ranges with increasing energy it is not; this is when the inclusion of thermal fluctuations is required.

Here, we consider sublimation inside an elastoplastic material, a problem which we are not aware of as having been studied before. We consider the homogeneous nucleation of a gas bubble inside an elastoplastic body – i.e., nucleation that is not

promoted by internal surfaces, defects, or stress singularities. There are several conceptual problems in treating sublimation inside the material, as follows.

1. During the transformation of a solid into a gas inside of a solid, a large volume increase (for example, by a factor of 10 to 1000) takes place, which generates high pressure inside the gas and causes large elastoplastic deformations of the solid around the bubble. Actual pressure inside the bubble is determined by resistance to plastic flow during sublimation and also the surface tension. Thus, nonlinear continuum mechanics should be employed. In contrast, pressure in gas does not change for sublimation from an external surface since it is equal to the fixed external pressure.
2. For phase transformations in reversible systems (when dissipation can be neglected), the driving force for phase transformation is the change in Gibbs (or chemical) potential of the system, see, for example, Grinfeld (1980, 1991). Because plastic dissipation occurs even at infinitesimally slow deformations, it cannot be neglected. Thus, a new driving force for sublimation in an elastoplastic material should be derived.
3. Because of plastic dissipation, the principle of minimum Gibbs energy cannot be applied for sublimation in elastoplastic materials either; a new extremum principle is required.
4. The kinetics of sublimation is determined by the activation energy of appearance of a critical nucleus. For phase transformations in reversible systems, the activation energy is equal to the Gibbs energy of a nucleus and the critical nucleus corresponds to the maximum of the Gibbs potential as a function of the nucleus volume. Since the Gibbs energy is not the driving force anymore, an alternative expression for activation energy should be found.
5. For systems with neglected dissipation due to deformation (we will call them conservative), activation energy is independent of the transformation path – i.e., it is independent of whether a nucleus appears as a result of: (1) homogeneous transformation from solid to gas within a critical nucleus, (2) nucleation by continuous interface propagation from zero size to a critical nucleus, or (3) by a complex heterogeneous process inside the critical nucleus. In contrast, due to the path-dependence of the solution of the elastoplastic problem, activation energy for sublimation in plastic material should be dependent of the transformation path. Thus, an “optimal” transformation path should be found.
6. For phase transformation in a conservative system, if the critical nucleus appears, it can grow in accordance with the second law of thermodynamics. For nucleation in plastic material, due to the path-dependence of a nucleation process, conditions for appearance of a nucleus and its growth could be different.

All of the above points demonstrate that sublimation inside an elastoplastic material is a nontrivial problem. In physical experiments, sublimation may be promoted by high tensile stresses and high temperature. Large dynamic tensile stresses appear, for example, in rarefaction waves during laser ablation (Zhigilei and Garrison, 2000; Ivanov and Zhigilei, 2003). According to the melt-dispersion mechanism of reaction of aluminum nanoparticles covered by an oxide shell (Levitas et al., 2007), high-rate heating of these particles causes fast melting of aluminum. The volume increase due to melting is of 6%, and it causes high compressive pressure (few GPa) inside aluminum and large tensile hoop stresses of 10 GPa in an aluminum oxide shell. After dynamic fracture and spallation of the shell, an unloading spherical wave creates large (4–9 GPa) tensile pressures that disperse molten aluminum and drastically accelerate its highly energetic oxidation. There is currently a search for ways to create tensile stresses and disperse solid energetic materials due to sublimation or cavitation; see Levitas et al. (2007, 2008). Initial compressive pressures can be generated, for example, due to solid–solid phase transformation in a particle within a strong shell, and, after fast fracture of the shell, an unloading wave will produce high tensile pressures, which promote sublimation. Alternatively, an unloading wave can be generated by dynamic or static compression and fast release of compressive pressure. High tensile pressure appears in a solid nucleus, the appearance of which inside the parent phase is accompanied by significant volume collapse.

During thermomechanical loading, high temperatures can be induced in local spots inside the material – for example, due to shear banding or void collapse (Tarver et al., 1996). Sublimation on hot spots followed by chemical reactions in the gas phase is one of the mechanisms of ignition of various explosives. Sublimation can also be a mechanism of void nucleation competing with fracture.

Chemical decomposition of the solid phase into a mixture of several gaseous phases may occur under conditions similar to those described above; its description has the same fundamental problems as sublimation. We will demonstrate that minor modifications are required to extend our theory for sublimation to the description of chemical decomposition.

For solid–solid phase transformations and chemical reactions in inelastic materials, a general thermodynamic and kinetic theory was developed in Levitas (1998, 2000) and references herein, they are summarized in Levitas (2004a). It was applied to find a number of analytical and numerical solutions that were used for interpretation of experiments. They, in particular, include phase transformation in ellipsoidal inclusion (Levitas, 2000) and phase transformation in spherical inclusion with application to graphite–diamond transformation (Levitas, 1997, 2000). A number of problems have been solved at finite strains: transformation in a thin layer in a rigid-plastic half-space, strain-induced nucleation at shear-band intersection in TRIP steel, chemical reactions in the shear band with revealing the reaction-induced plasticity phenomenon (Levitas et al., 1998; Levitas, 2000), appearance and growth of a temperature-induced martensitic plate in austenitic matrix with application to plate-path morphological transition in steel (Idesman et al., 1999, 2000), low pressure phase transformation from rhombohedral to superhard cubic BN and revealing phase transformation induced by rotational plastic instability phenomenon (Levitas and Shvedov, 2002), and description of high pressure mechanochemical phenomena in a rotational diamond anvil cell (Levitas, 2004b); see also review in Levitas (2004a). There are significant differences that do not allow

direct generalization of the theory for solid–solid phase transformation to solid–gas transformation. In particular, the concept of transformation strain that transforms the crystal lattice of the parent phase into the crystal lattice of the product phase does not have counterparts for solid–gas transformation. The kinetics of nucleation in Levitas (2000) differs significantly from what is usually used in material science and will not be applied here. Thus, in Levitas (2000), a thermodynamically admissible nucleus is considered (nucleus of the radius r_i in Fig. 1, corresponding to $\Delta G = 0$) – i.e., its appearance is accompanied by a non-negative dissipation increment. In contrast, appearance of the critical nucleus is accompanied by a negative dissipation increment; this is why it requires thermal fluctuations. Here, we will determine conditions for the appearance of the critical nucleus. However, one of the key points of the theory in Levitas (1998, 2000), that the driving force for the phase transition in plastic materials is equal to the dissipation due to the phase transformation only during the entire transformation in the nucleus, will be used here. Approach developed by Fischer's group is reviewed in Fischer et al. (2008).

Melting is also a first-order phase transformation that leads to complete relaxation of deviatoric stresses. The general theory for a solid–solid phase transformation in Levitas (1998, 2000) can be easily adapted (in fact, simplified) to describe melting, but it will possess the same drawbacks. Simplified theories have been developed for a spherical melt drop inside an infinite solid. Thus, a thermodynamic approach to the appearance of a spherical melt drop in elastoplastic materials with neglected surface energy was developed in Lifshitz and Gulida (1952) and Roitburd and Temkin (1986). The thermodynamics of growth of a spherical melt drop in an elastoplastic solid was analyzed in Kaganova and Roitburd (1987). A kinetic approach to nucleation of a spherical melt drop in an elastoplastic material was suggested in Levitas (2000) and was analyzed above. The kinetics of the appearance of a spherical melt drop is a typical nucleation problem (see, e.g., Porter and Easterling (1992)). An approach that allows elastic energy was considered in Lu and Li (1998) and Jin et al. (2001). Here, we will obtain the main equations of thermodynamics and kinetics of melt nucleation in an elastoplastic material as a slight modification of our sublimation theory.

This paper is organized as follows. In Section 2, the general thermodynamic approach to nucleation of a gas bubble within an elastoplastic solid is developed. The driving force for such a nucleation is derived as the dissipation increment due to phase transformation only during the entire nucleation process in the nucleus. However, we do not require that the dissipation increment be positive – i.e., the second law of thermodynamics is not satisfied for the critical nucleus. That is why thermal fluctuations are required, and this will lead us to formulation of nucleation kinetics. For nucleation in an elastic material, our driving force reduces to the change in the Gibbs energy of the entire system.

In Section 3, an Arrhenius-type kinetic equation for nucleation time is assumed, and the problem of formulating the proper expression for the activation energy is addressed. It is suggested that the activation energy is equal to the negative driving force for the appearance of a nucleus maximized with respect to nucleus mass (volume) and minimized over the nucleus shape, transformation path, and position. This definition transforms to the traditional one in the limit of elastic materials. It corresponds to the principle of the minimum transformation time, which was derived in Levitas (2000) using the postulate of realizability. This principle substitutes the principle of the minimum Gibbs energy, which is valid for thermodynamic equilibrium in the reversible systems. A kinetic nucleation criterion is formulated. Because the search for the “optimal” transformation path is quite a sophisticated problem, it is suggested to focus on the two simplest transformation paths.

The first one, called nucleation via homogeneous transformation, considers the homogeneous transformation process in the nucleus of the final mass. Then we introduce a nucleus of the minimal size, consisting of a few molecules, for which one can still distinguish solid and gaseous phases. The second path, called nucleation via interface propagation, consists of the homogeneous nucleation of the nucleus of a minimal mass followed by continuous interface propagation up to its critical size.

In Section 4, a system of equations for isotropic, large strain plasticity theory is summarized. In Section 5, nucleation via homogeneous transformation is treated in detail. Since the sequence in which shear moduli in each direction and yield strength reduces to zero is unknown, we choose the transformation path that leads to the simplest treatment. We assume that the shear moduli reduce to zero in the transformed volume before the bulk elastic modulus and the yield strength started changing; i.e., we neglect plastic dissipation within the nucleus. Choosing the simplest equation of state for intermediate states during the transformation process, we arrived at the simplest theory that in contrast to Levitas (1998, 2000) does not require lengthy derivation for a material point.

In Section 6, nucleation via interface propagation is studied. If plastic dissipation at the interface is neglected, there is no necessity to determine constitutive equations for intermediate states. For both transformation paths in Sections 5 and 6, the driving force for sublimation and the activation energy are determined. Algorithms for the determination of the critical nucleus are formulated.

In Section 7, some additional points for the determination of the critical nucleus related to the path-dependence of the solution for an elastoplastic problem are considered. After the appearance of the nucleus via homogeneous transformation, the possibility of its growth should be checked. Growth may occur by further sublimation or by mechanical expansion due to mechanical instability. Also, because the driving force for forward and reverse transformations may be different, several scenarios are possible. The nucleus can grow, disappear, or be arrested; in the latter case it represents a stable, rather than a critical, nucleus. Sections 8 and 9 describe the minor modifications that are necessary for applying the developed sublimation theory to chemical decomposition of solids into gas species and to melting; Section 10 contains concluding remarks. Some preliminary results for the appearance of a spherical gas bubble were reported in a short letter (Levitas and Altukhova, 2008).

Direct tensor notations are used throughout this paper. Tensors are denoted in boldface type; $\mathbf{A}:\mathbf{B}$ is the contraction of tensors over two indices, \mathbf{I} is the second-rank unit tensor, superscripts t and -1 denote transposition and inverse operation, $:=$ des-

ignates “equal by definition”, subscripts *sym* and *a* mean symmetric and skew-symmetric parts of the tensors, and subscripts 1 and 2 (or “s” and “g”) denote parameters before and after the sublimation, respectively.

2. Continuum thermodynamic treatment of sublimation in an inelastic material

2.1. Thermodynamics laws

Let the motion of an elastoplastic material with phase transformations be described by a vector function $\mathbf{r} = \mathbf{r}(\mathbf{r}_0, t)$, where \mathbf{r} and \mathbf{r}_0 are the positions of points in the actual (deformed) Ω and reference (undeformed) Ω_0 configurations, respectively. Consider a volume V of an elastoplastic material with a boundary S in the actual configuration and their mapping, V_0 and S_0 into the reference configuration. On one part of surface S_v , the particle velocity vector \mathbf{v} is prescribed, and on the other part S_p the traction vector \mathbf{p} is given; mixed boundary conditions on the same surface are also possible. Assume that in some volume V_n with a boundary Σ_n a gas bubble appears during the time t_n due to sublimation (Figs. 2 and 3). We consider the appearance of a critical gas nucleus, while several definitions of the critical nucleus will be given later.

As the starting point, we formulate the first law of thermodynamics (the energy balance equation) and the entropy balance equation for the entire volume V in the actual configuration:

$$\int_S (\mathbf{p} \cdot \mathbf{v} - \mathbf{h} \cdot \mathbf{n}) dS - \frac{d}{dt} \int_V \rho(u + 0.5 \mathbf{v} \cdot \mathbf{v}) dV - \frac{d}{dt} \int_{\Sigma_n} \Gamma d\Sigma_n + \int_V \rho(\mathbf{f} \cdot \mathbf{v} + q) dV = 0, \quad (1)$$

$$S_i := \frac{d}{dt} \int_V \rho s dV - \int_V \rho \frac{q}{\theta} dV + \int_S \frac{\mathbf{h}}{\theta} \cdot \mathbf{n} dS. \quad (2)$$

Here, \mathbf{h} is the heat flux, \mathbf{n} is the unit normal to Σ , ρ is the mass density, u and s are the specific (per unit mass) internal energy and entropy, \mathbf{f} and q are the body force and volumetric heat supply per unit mass, S_i is the total entropy production, $\theta \geq 0$ is the temperature, and Γ is the surface energy per unit current area.

Usually, the second law of thermodynamics requires $S_i \geq 0$. However, for a thermally activated nucleation event this is not the case: for appearance of subcritical and critical nuclei it is always $S_i < 0$ (Landau and Lifshitz, 1980; Porter and Easterling, 1992). This is why thermally activated fluctuations are needed. While we cannot impose $S_i \geq 0$, we will work with the entropy production, dissipation rate, and dissipation in the same way as in traditional thermodynamic approaches.

To make our nucleation theory simple, the following assumptions will be made:

- (a) The temperature is stationary and homogeneous during the nucleation event.

Then one can introduce the total dissipation rate in the form

$$D := \theta S_i = \frac{d}{dt} \int_V \rho \theta s dV - \int_V \rho q dV + \int_S \mathbf{h} \cdot \mathbf{n} dS. \quad (3)$$

Alternatively, the dissipation rate defined in Eq. (3) can be considered as the primary thermodynamic function instead of the entropy production in Eq. (2). Then, the assumption about stationary and homogeneous temperature is not necessary. We believe that this approach is more productive, and we will use Eq. (3) without the assumption (a).

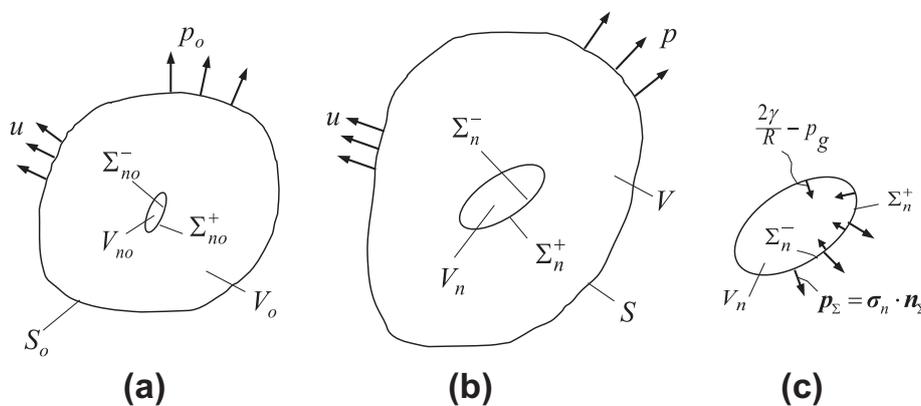


Fig. 2. Scheme of the elastoplastic body under the load with the gas nucleus that appears via homogeneous transformation in a fixed region in the reference configuration (a); the same process in the actual configuration (b). The scheme of the nucleus in the variable current configuration (c). Surfaces Σ_n^+ and Σ_n^- are infinitesimally close to the surface of the nucleus Σ_n from the solid state and gas state, respectively.

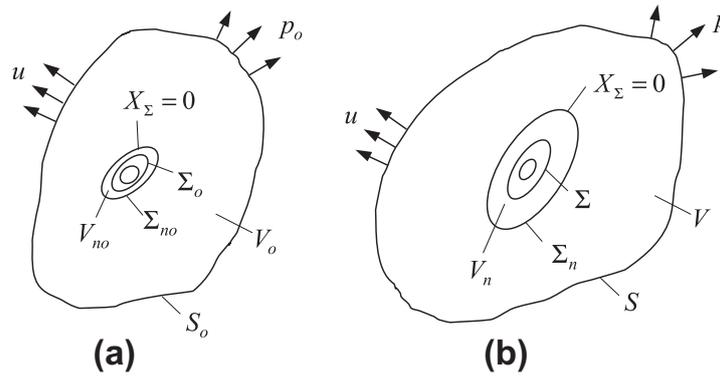


Fig. 3. Scheme of the elastoplastic body under the load with the gas nucleus that appears via continuous interface propagation. (a) The reference configuration; (b) the actual configuration.

(b) The body force and change in kinetic energy will be neglected.

Then, expressing terms related to heat flux and volumetric supply from Eq. (1) and substituting them into Eq. (3), one obtains

$$D = \int_S \mathbf{p} \cdot \mathbf{v} dS - \frac{d}{dt} \int_m \psi dm - \frac{d}{dt} \int_{\Sigma_n} \Gamma d\Sigma_n, \quad (4)$$

where the specific Helmholtz free energy $\psi = u - \theta s$ and mass $dm = \rho dV$ were introduced.

2.2. The driving force for nucleation in an elastoplastic material

It was demonstrated in Levitas (1998, 2000, 2002) that in order to define the driving force for the phase transformation:

- (a) The plastic dissipation rate should be excluded from the total dissipation rate in order to receive the dissipation rate due to phase transformation only.
- (b) The dissipation rate due to phase transformation only should be averaged over the nucleation process or time t_n .

We will perform similar steps here. Thus, the dissipation due to phase transformation only, D_{PT} , is

$$D_{PT} = D - D_p = \int_S \mathbf{p} \cdot \mathbf{v} dS - \frac{d}{dt} \int_m \psi dm - \int_m \mathbf{X}_p : \mathbf{d}_p dm - \frac{d}{dt} \int_{\Sigma_n} \Gamma d\Sigma_n, \quad (5)$$

where \mathbf{d}_p is the plastic deformation rate and \mathbf{X}_p is the conjugate dissipative stress. In the simplest case considered in Section 4, $\mathbf{X}_p = \frac{1}{\rho} \mathbf{T}$, where \mathbf{T} is the true Cauchy stress tensor. Then, we introduce the dissipation rate due to phase transformation averaged over the nucleation time:

$$\overline{D}_{PT} := \frac{1}{t_n} \int_0^{t_n} D_{PT} dt = \frac{X_{PT}}{t_n} = X_{PT} \dot{\chi}, \quad (6)$$

where

$$X_{PT} := \int_0^{t_n} \int_S \mathbf{p} \cdot \mathbf{v} dS dt - \int_m (\psi_2 - \psi_1) dm - \int_0^{t_n} \int_m \mathbf{X}_p : \mathbf{d}_p dm dt - \Delta \overline{\Gamma} \quad \text{and} \quad \dot{\chi} := \frac{1}{t_n} \quad (7)$$

are the dissipative (driving) force and rate for phase transformation, respectively. Also,

$$\Delta \overline{\Gamma} := \int_{\Sigma_{n2}} \Gamma_2 d\Sigma_n - \int_{\Sigma_{n1}} \Gamma_1 d\Sigma_n \quad (8)$$

is the change in surface energy of the nucleus during phase transformation.

The above expression for the driving force for phase transformation X_{PT} can be simplified. Since X_{PT} is the dissipation increment due to phase transformation only, integrals in Eq. (7) (excluding the integral over Σ_n) can be evaluated over an arbitrary material volume with the fixed mass and bounding surface that includes the nucleus. In particular, material volume and mass may coincide with the final volume V_{n2} and mass m_2 of the critical nucleus. This is because in the volume $V - V_{n2}$ the dissipation increment due to phase transformation only is zero because of the lack of phase transformations. Thus,

$$X_{PT} := \int_0^{t_n} \int_{\Sigma_{n2}^+} \mathbf{p} \cdot \mathbf{v} d\Sigma_n^+ dt - \int_{m_{n2}} (\psi_2 - \psi_1) dm_{n2} - \int_0^{t_n} \int_{m_{n2}} \mathbf{X}_p : \mathbf{d}_p dm_{n2} dt - \Delta \overline{\Gamma}, \quad (9)$$

where superscript + means the external part of the surface of the nucleus. Due to surface tension, there is discontinuity in traction across the interface.

2.3. Driving force for nucleation in elastic materials

Let us demonstrate that for elastic materials $X_{PT} = -\Delta G$, where G is the Gibbs potential for the entire body – i.e., X_{PT} reduces to the known driving force for a phase transformation. First, we introduce a traction vector \mathbf{p}_0 and a surface element dS_0 in the fixed reference (initial) configuration, $\mathbf{p}_0 dS_0 = \mathbf{p} dS$. For elastic materials, one has $\mathbf{d}_p = 0$. During the nucleation process, let the traction vector \mathbf{p}_0 be fixed on S_{p0} and the displacement vector \mathbf{u} be fixed on $S_{\nu 0}$. Then,

$$\int_0^{t_n} \int_S \mathbf{p} \cdot \mathbf{v} dS dt = \int_0^{t_n} \int_{S_0} \mathbf{p}_0 \cdot \mathbf{v} dS_0 dt = \int_0^{t_n} \int_{S_{p0}} \mathbf{p}_0 \cdot \mathbf{v} dS_{p0} dt = \int_{S_{p0}} \mathbf{p}_0 \cdot (\mathbf{u}_2 - \mathbf{u}_1) dS_{p0}. \quad (10)$$

Introducing the Gibbs potential,

$$G := \int_m \psi dm + \int_{\Sigma_n} \Gamma d\Sigma_n - \int_{S_{p0}} \mathbf{p}_0 \cdot \mathbf{u} dS_{p0}, \quad (11)$$

we obtain from Eqs. (7), (8), (10), and (11) that

$$X_{PT} = -\Delta G. \quad (12)$$

3. Kinetic relationship

As is usual in nonequilibrium thermodynamics, a relationship between the generalized thermodynamic force X_{PT} and the rate $1/t_n$ has to be postulated. For nucleation, the dissipation inequality is not met, but still we assume the existence of a kinetic relationship between X_{PT} and $1/t_n$. Here, we will consider thermally activated kinetics, based on classical nucleation theory (Fisher, 1948; Turnbull and Fisher, 1949; Hammes, 1978; Porter and Easterling, 1992). Our starting point is the equation for the rate of appearance of the number of critical nuclei n per unit volume of solid in the reference state V_0

$$\frac{dn}{dt} = fC \exp\left(\frac{-Q}{k\theta}\right), \quad (13)$$

where $k = 1.380 \cdot 10^{-23}$ J/K is the Boltzmann constant, C is the number of atoms per unit reference volume, and f is the frequency of adding one atom to the critical nucleus that will transform it to the supercritical one. Evidently that $C = N\rho_0/M$, where $N = 6.022 \cdot 10^{23}$ mol⁻¹ is Avogadro's constant, and M is the molecular mass. There are various expressions for f – e.g., in Fisher (1948) and Turnbull and Fisher (1949) – $f = \frac{k\theta}{h} \exp\left(\frac{-Q_d}{k\theta}\right)$, where $h = 6.626 \cdot 10^{-34}$ J s is Planck's constant, and Q_d is the activation energy for motion of the individual molecule, which is considered to be equal to the activation energy for diffusion or viscosity (Fisher, 1948); in Hammes (1978), $f = \frac{kZ\theta}{h}$, where Z is an equilibrium constant relating the concentrations of molecules in the activated transition state to those of the stable state; in Porter and Easterling (1992), f depends on the vibrational frequency of the atoms, the activation energy for diffusion, and the surface area of the critical nucleus.

It follows from Eq. (13) that the number of nuclei that appear during time t in a volume V_0 for constant temperature and activation energy is

$$n = tV_0 fC \exp\left(\frac{-Q}{k\theta}\right). \quad (14)$$

Putting $n = 1$ and solving Eq. (14) for t , we obtain the Arrhenius-type equation for the nucleation time in a volume V_0 :

$$t_n = \frac{1}{V_0 fC} \exp\left(\frac{Q}{k\theta}\right). \quad (15)$$

Nucleation time is an inverse proportion to the sample volume.

3.1. Activation energy for phase transformation in elastic materials at small strains

For phase transformation in elastic materials, $X_{PT} = -\Delta G$ (Eq. (12)). The spherical critical nucleus in an elastic material corresponds to the maximum of ΔG with respect to the nucleus radius r (Fig. 1), and activation energy for the appearance of a nucleus is defined as $Q = \max_r \Delta G$. For a nucleus of an arbitrary shape, activation energy for elastic material is $Q = \max_{shape} \min_{shape} \Delta G$ (see, e.g., Lin et al., 1993) – i.e., the critical nucleus corresponds to the minimum value of ΔG with respect to the shape of the nucleus and the maximum value with respect to nucleus volume V (or characteristic size, or mass) – i.e., to a saddle point of the Gibbs energy.

3.2. Activation energy for phase transformation in an elastoplastic material

In elasticity, the transformation path along which the critical nucleus appears is irrelevant for determination of t_n because Q is path-independent. This is not the case for nucleation in an elastoplastic material, because stress variation depends on the entire transformation process. This means that the reasonable definition of the activation energy for an elastoplastic material is

$$Q = \max_{m_n} \min_{\text{shape}} \min_{\text{path}} \min_{\text{position}} (-X_{PT}); \quad (16)$$

i.e., activation energy is equal to the negative driving force for the appearance of a nucleus maximized over the mass of the nucleus and minimized over the shape, transformation path, and position of the nucleus (in case of heterogeneous initial fields). We maximize with respect to mass rather than volume because for large strain one has to distinguish between the volume of the nucleus in the reference and actual configurations. Phase transformation corresponds to a change in mass of the nucleus and consequently a change in volume V_{n0} in the reference state, while a change in actual volume includes deformation without phase transformation. This definition transforms to the classical one in the limit of elastic materials, small strains, and a homogeneous field before transformation. Note that minimization of the activation energy over the shape of the nucleus, transformation path, and maybe some other parameters corresponds to the principle of the minimum of transformation time (Levitas, 2000). This principle is derived in Levitas (2000) with the help of the postulate of realizability.

In elasticity, if a nucleus larger than critical (i.e., a supercritical nucleus) appears, it will grow, because the Gibbs potential reduces and dissipation rate is positive when the nucleus grows. However, while Eqs. (15) and (16) determine the nucleation time for the appearance of some nucleus, due to the path-dependence of plastic solutions, one cannot say whether it will grow, shrink, or remain unchanged after nucleation. Thus, an additional condition that should be checked is whether the nucleus can grow. As we will see, growth can be due to sublimation or to mechanical instability.

3.3. Kinetic nucleation criterion

There is significant indeterminacy in the frequency factor f . For example, in Henson et al. (2002) Z varies from 1 to $3 \cdot 10^{-10}$ depending on the order of the chemical reaction. However, despite this large discrepancy, because of the exponential function in Eq. (15), large variation in t_n corresponds to a very small variation of the driving force or the transformation stress. For example, a change in t_n by a factor of 10^{33} corresponds to a change in cavitation pressure by a factor of only 1.58 (Fisher, 1948). Thus, variations in V and f are not significant for the determination of the kinetic curve for sublimation temperature versus stress. That is why the usual way to determine a kinetic relationship between phase transformation parameters (e.g., pressure and temperature), is to use the kinetic nucleation criterion

$$Q = \beta k \theta, \quad \beta = (40 - 80), \quad (17)$$

which is determined from the condition that, for larger Q , the nucleation time exceeds any realistic time of observation for any V and C (Porter and Easterling, 1992; Lin et al., 1993; Levitas, 2004a).

3.4. Athermal interface friction

For solid–solid phase transformation, one usually introduces an athermal (threshold-type) resistance to the interface motion, which is caused by an interaction of the long-range stress field of defects with the interface (Olson and Cohen, 1986b; Ghosh and Olson, 1994; Levitas, 1994, 1998, 2000). In mechanical equilibrium, gas (as a hydrostatic medium) does not interact with the stress field of defects because the presence of a gas imposes a boundary condition for normal stress equal to gas pressure (minus capillary pressure) and zero shear stress, independent of the presence of defects. In dynamics, shear stress at the gas–solid boundary is determined by the friction law independent of the presence of defects. Thus, the athermal threshold is absent for the solid–gas (and solid–liquid) interfaces.

3.5. Transformation paths for appearance of a critical nucleus

The solution of a variational problem for finding the transformation path is in general quite complex. It can be solved in the framework of the phase field approach (Olson and Cohen, 1986a; Olson and Roytburd, 1995; Reid et al., 1998; Artemev et al., 2001; Levitas et al., 2003), but the solution will depend on a specific fluctuation, because a critical nucleus cannot appear without fluctuations. Also, here we would like to work with a sharp rather, than a finite-size interface. The simplest two paths will be considered. In the first one, which we call nucleation via homogeneous transformation, a critical nucleus appears as a result of the homogeneous transformation process from solid to gas within the entire nucleus—i.e., within a fixed mass. For this case, all material parameters inside the nucleus are changed from parameters of a solid to those of a gas.

We also define the smallest size of a nucleus in the reference configuration b_{min} that consists of only a few molecules, for which one still distinguishes the solid and gaseous phases. If, as a result of calculation, one obtains for the smallest size of a critical nucleus $b_c < b_{min}$, it will be used as $b_c = b_{min}$. While nucleation by interface propagation from zero size to a critical

nucleus looks a priori more probable, at large tensile pressures, when $b_c \simeq b_{min}$, homogeneous transformation from solid to gas is more appropriate. This also follows from the phase field approach (Levitas et al., 2006b). In addition, due to path-dependence, we cannot consider interface propagation from zero size. Thus, the second transformation path will consist of the homogeneous appearance of a subcritical nucleus with the minimum characteristic size b_{min} , followed by its growth to the critical size. This process will be called nucleation by interface propagation.

4. Equations for elastoplastic deformations at finite strains

For such a small scale, one has to apply dislocation plasticity. However, to make the problem treatable analytically, we will consider the simplest model for an isotropic, perfectly plastic material, which is described, for example, in Levitas (1996). Neglecting strain hardening is justified by high temperature. More complex models or single crystal plasticity models are broadly available in literature. The deformation gradient tensor, $\mathbf{F} = \partial \mathbf{r} / \partial \mathbf{r}_0$, can be multiplicatively decomposed into elastic and plastic parts, $\mathbf{F} = \mathbf{F}_e \cdot \bar{\mathbf{F}}_p = \mathbf{V}_e \cdot \mathbf{R} \cdot \bar{\mathbf{F}}_p = \mathbf{V}_e \cdot \mathbf{F}_p$, where \mathbf{R} is the rigid-body rotation tensor, $\mathbf{F}_p = \mathbf{R} \cdot \bar{\mathbf{F}}_p$, and \mathbf{V}_e is the symmetric elastic stretch tensor. We introduce elastic deformation measures $\mathbf{C}_e = \mathbf{V}_e \cdot \mathbf{V}_e$ and $\mathbf{B}_e = 0.5(\mathbf{C}_e - \mathbf{I})$ and plastic deformation rate $\mathbf{d}_p = (\dot{\bar{\mathbf{F}}}_p \cdot \mathbf{F}_p^{-1})_{sym}$. Then, the total system of equations includes (Levitas, 1996) the following relationships.

Decomposition of deformation rate into elastic and plastic parts:

$$\mathbf{d} = (\dot{\mathbf{F}} \cdot \mathbf{F}^{-1})_{sym} = \overset{\nabla}{\mathbf{B}}_e - 2(\mathbf{d} \cdot \mathbf{B}_e)_{sym} + \mathbf{C}_e \cdot \mathbf{d}_p; \quad (18)$$

Elasticity rule:

$$\mathbf{T} = \rho \mathbf{V}_e \cdot \frac{\partial \psi}{\partial \mathbf{B}_e} \cdot \mathbf{V}_e; \quad (19)$$

Yield condition and plastic flow rule:

$$\varphi(\mathbf{T}, \theta) \leq 0; \quad \mathbf{d}_p = \mathbf{f}(\mathbf{T}); \quad (20)$$

Equilibrium equation:

$$\nabla \cdot \mathbf{T} = 0. \quad (21)$$

Here, $\overset{\nabla}{\mathbf{B}}_e = \dot{\mathbf{B}}_e + 2(\mathbf{B}_e \cdot \mathbf{W})_{sym}$ is the Jaumann derivative, $\mathbf{W} = (\dot{\mathbf{F}} \cdot \mathbf{F}^{-1})_a$ is the spin tensor, and ∇ is the nabla operator. Because free energy is independent of the plastic deformation gradient, the plastic dissipation rate per unit mass is $D_p = \frac{1}{\rho} \mathbf{T} : \mathbf{d}_p > 0$, and consequently $\mathbf{X}_p = \frac{1}{\rho} \mathbf{T}$.

In most cases, elastic strains are small, but plastic strain and rotation are finite. Representing $\mathbf{V}_e = \mathbf{I} + \boldsymbol{\varepsilon}_e$ with small elastic strain $\boldsymbol{\varepsilon}_e \ll \mathbf{I}$, we present the simplest version of Eqs. (18)–(20), as follows:

Decomposition of the deformation rate into elastic and plastic parts:

$$\mathbf{d} = \overset{\nabla}{\boldsymbol{\varepsilon}}_e + \mathbf{d}_p; \quad (22)$$

Elastic Hooke's law:

$$\mathbf{T} = \mathbf{E} : \boldsymbol{\varepsilon}_e; \quad (23)$$

Von Mises yield condition and associated plastic flow rule:

$$\sigma_i \leq \sigma_y; \quad \mathbf{d}_p = \lambda \mathbf{s}. \quad (24)$$

Here, \mathbf{E} is the isotropic elastic moduli tensor, $\sigma_i = (3/2 \mathbf{s} : \mathbf{s})^{1/2}$ is the stress intensity, \mathbf{s} is the deviatoric Cauchy stress, σ_y is the yield strength, and the scalar $\lambda = 0$ for $\sigma_i < \sigma_y$ (elastic regime) or it is determined from the consistency condition $\dot{\sigma}_i = \dot{\sigma}_y$ for the plastic regime.

5. Nucleation via homogeneous transformation

5.1. Transformation process within a transforming points and plastic dissipation

A theory for the continuous phase transformation of one solid phase into another in a material point was developed in Levitas (1998, 2000), and it is quite a sophisticated one. In addition to approximations for thermodynamic functions in the intermediate states of the transformation process (similar to a phase field theory), it also requires an elastoplastic constitutive model for the intermediate states, which is unknown. For the solid–gas phase transformation that we develop in this section, we will use a much simpler approach: it will be based on the transformation process that leads to the simplest equations. In this approach, there is no need to develop the thermodynamic theory (for an isothermal case) and formulate an elastoplastic constitutive model for the intermediate states.

Under general nonhydrostatic loading of a solid, nonhydrostatic stress relaxation within the nucleus can occur due to the reduction of both the shear moduli and the yield strength. In the limit cases, when the shear moduli reduce much faster during the sublimation than the yield strength, stress relaxation will not cause plastic deformation and dissipation—i.e., $\mathbf{d}_p = 0$. In the opposite case, when the yield strength reduces instantaneously while the shear moduli reduce much slower during sublimation, plastic dissipation is maximum. Since the actual sequence is unknown, we will choose the transformation path that leads to the simplest treatment. We assume that under a prescribed load, the shear moduli reduce to zero in the transformed volume before the bulk elastic modulus and the yield strength start changing—i.e., we neglect plastic dissipation within the nucleus. Note that neglecting plastic deformation in the transforming volume does not reduce the problem to sublimation in an elastic material. Plastic deformation and related irreversibilities in the solid phase affect pressure history and mechanical work in the transforming nucleus. After the disappearance of the elastic shear moduli, the equation of state for the solid transforms in some way into the equation of state for the gas. We can introduce the internal variable (order parameter) that varies from zero to one during the phase transformation, which can be, for example, $\xi = (v - v_s)/(v_g - v_s)$, where v is the variable specific volume during the transformation. The equation of state during the transformation can be presented in the form

$$p = q(\xi)p_g(v) + (1 - q(\xi))p_s(v), \tag{25}$$

where $q(\xi)$ varies from zero to one when ξ varies from zero to one, and $p_g(v)$ and $p_s(v)$ are the isothermal equations of state for a gas and a solid. The change in yield strength is irrelevant, because a nucleus is already under hydrostatic conditions. In a similar way,

$$\Gamma(\xi) = q_1(\xi)\Gamma_2 + (1 - q_1(\xi))\Gamma_1, \tag{26}$$

where q_1 has the same properties as q . In the simplest case, $q = q_1 = \xi$. If there are no any initial inclusions possessing a surface energy, then $\Gamma_1 = 0$ and $\Gamma = q_1(\xi)\Gamma_2$.

The equilibrium condition at the interface is (see Fig. 4):

$$p_g = -\sigma_n + 2\Gamma(\xi)/R, \tag{27}$$

where σ_n is the normal stress in the solid at the interface, and $1/R$ is the mean curvature at the points of the interface. The sign minus in Eq. (27) is because tensile stress σ_n in solids and compressive pressure in gases p_g are considered positive.

5.2. Main relationships

As an initial state, we consider a solid under a prescribed load. Let us choose in the reference configuration a possible nucleus with the fixed mass m_n , volume V_{n0} , and bounding surface Σ_{n0} (Fig. 2). In the current configuration, this nucleus will have variable volume V and bounding surface Σ_n during the transformation process. Boundary conditions at the external surface of the body S are fixed during the transformation process.

We designate displacements at the external part Σ_n^+ of the nucleus surface as \mathbf{u}_1 before transformation, as $\bar{\mathbf{u}}$ after relaxation of the nonhydrostatic stresses under unchanged elastic bulk properties, and as \mathbf{u}_2 after complete transformation. For the stage between $\bar{\mathbf{u}}$ and \mathbf{u}_2 we have $\mathbf{p}_\Sigma = \sigma_n \mathbf{n}_\Sigma$, where \mathbf{n}_Σ is the outward unit normal to Σ_n , and $\mathbf{p}_\Sigma \cdot \mathbf{v} = \sigma_n v_n$, where v_n is the normal velocity of the points of the solid–gas interface in the actual configuration. Then, the work integral in Eq. (9) is

$$WV_{n0} := \int_0^{t_n} \int_{\Sigma_{n2}^+} \mathbf{p}_\Sigma \cdot \mathbf{v} d\Sigma_{n2}^+ dt = \int_{\mathbf{u}_1}^{\bar{\mathbf{u}}} \int_{\Sigma_{n2}^+} \mathbf{p}_\Sigma \cdot d\mathbf{u} d\Sigma_{n2}^+ + \int_{\bar{\mathbf{u}}_n}^{u_{n2}} \int_{\Sigma_{n2}^+} \sigma_n du_n d\Sigma_{n2}^+, \tag{28}$$

where W is the work per unit volume of the nucleus in the solid state in the reference configuration. The volume V_{n0} differs from the volume of the nucleus in the solid state before transformation V_1 because of elastic strain. Note, while pressure in gas is homogeneous, according to Eq. (27) the normal stress σ_n is not homogeneous for a non-spherical nucleus because the curvature $1/R$ is not homogeneous. Only if the nucleus is spherical in the actual configuration after relaxation of the nonhydrostatic stresses can the integration over the surface Σ_{n2}^+ be performed immediately, and

$$\int_{\bar{\mathbf{u}}_n}^{u_{n2}} \int_{\Sigma_{n2}^+} \sigma_n du_n d\Sigma_{n2}^+ = \int_{\bar{\mathbf{u}}_n}^{u_{n2}} \sigma_n \Sigma_{n2}^+ du_n = \int_{\bar{V}}^{V_2} \sigma_n dV, \tag{29}$$

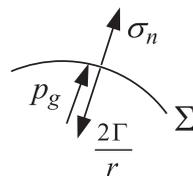


Fig. 4. Scheme for the choice of the signs for the equilibrium Eq. (27).

where \bar{V} is the volume of the nucleus after nonhydrostatic stress relaxation, both in actual configuration. If the initial stress state is hydrostatic, then

$$WV_{n0} = \int_{V_1}^{V_2} \sigma_n dV. \quad (30)$$

By introducing the volumetric deformation gradient $a = V/V_{n0}$, one obtains

$$W = \int_{a_1}^{a_2} \sigma_n da. \quad (31)$$

Since in the general case the numerical solution of the sublimation problem is possible only, we parameterize the geometry of a nucleus in the reference configuration in terms of V_{n0} and the set of volume-independent parameters χ_{0i} , which characterize, for example, the aspect ratios, position, and orientation of an ellipsoidal nucleus. The geometry of a nucleus in the current configuration after sublimation is characterized by the volume V_2 and the parameters χ_i . Surface energy will be assumed for simplicity to be isotropic and homogeneous; the methods of taking into account the anisotropy of the surface energy are well developed—e.g., in solidification theory. We present

$$\Sigma_n = zV^{2/3}\bar{f}(\chi_i) = zV_{n0}^{2/3}a^{2/3}f(\chi_{0i}), \quad (32)$$

where the dimensionless function $\bar{f}(\chi_i)$ can be easily found after the geometry of the nucleus in the current state is found with the help of the solution of the boundary-value problem, and the function f is obtained from $\bar{f}(\chi_i)$ by expressing χ_i in terms of χ_{0i} and geometric changes are found from the solution of the boundary-value problem. In Eq. (32), $z = (4\pi)^{1/3}3^{2/3}$ is the normalizing factor that gives $f = 1$ for a sphere. The integral is

$$\int_{m_{n2}} (\psi_2 - \psi_1) dm_{n2} = \rho_0 V_{n0} (\psi_2 - \langle \psi_1 \rangle), \quad (33)$$

where ρ_0 is the constant density of the solid in the reference state and $\langle \psi_1 \rangle$ is the free energy of the solid before transformation, averaged over the mass of the nucleus. It is taken into account that ψ_2 is homogeneous inside the gaseous nucleus.

Then, the driving force for phase transformation Eq. (7) takes the form

$$X_{PT} = X_v V_{n0} - \Gamma_2 V_{n0}^{2/3} a^{2/3} z f(\chi_{0i}); \quad X_v = W - \rho_0 (\psi_2 - \langle \psi_1 \rangle), \quad (34)$$

where X_v is the volumetric part of the driving force for phase transformation. The dependence of X_{PT} on V_{n0} is shown explicitly in Eq. (34). The volume of a critical nucleus can be found by minimizing X_{PT} with respect to V_{n0} , which leads to

$$V_{n0c} = \frac{32\pi a^2 \Gamma_2^3 f^3}{3X_v^3}. \quad (35)$$

Substituting the expression for V_{n0} from Eq. (35) into Eq. (34) and taking into account the definition of activation energy, Eq. (16), we obtain

$$Q = \frac{16\pi a^2 \Gamma_2^3 f^3}{3X_v^2}. \quad (36)$$

The activation energy Q is equal to 1/2 of the volumetric part of the driving force X_{PT} and 1/3 of the surface energy of the critical nucleus, as in classical nucleation theory. Eq. (36) formally looks like its counterpart in classical nucleation theory as well, with the exception of the factor a^2 and the fact that X_v and f depend on the entire transformation process.

The unknown parameters χ_{0i} are determined from the condition

$$X_{PT} \rightarrow \max_{\chi_{0i}} \Rightarrow \frac{\partial X_{PT}}{\partial \chi_{0i}} = 0, \quad (37)$$

where the second Eq. (37) is true if the maximum is analytical.

In addition to the above equations, one has to use the explicit form of the equation of state for a gas, expressions for the free energy of a gas and a solid, a full system of finite-strain elastoplastic constitutive equations for solid outside the nucleus, as well as all field equations (equilibrium equations and relationships between the displacements and the deformation gradient). The main equations are summarized in Box 1 at the end of the paper.

5.3. Algorithm for finding the critical nucleus for the homogeneous transformation path

The algorithm for determining the possibility of gas nucleation and the shape and position of the nucleus for the homogeneous nucleation path is as follows:

1. At time t , the geometry of the body (which may include already-transformed gas nuclei), boundary conditions, all fields (displacements, deformation gradient and its elastic and plastic components, possible internal variables, and a stress tensor), and temperature are known in both reference and current configurations. One has to find the temperature at which nucleation can occur, as well as the shape and position of a nucleus.
2. For a chosen position of a nucleus, with its volume and its shape in the reference configuration, characterized by parameters χ_{0i} , one first reduces all shear moduli to zero and then changes the parameter ξ from zero to one in the nucleus. By solving the boundary-value problem, one calculates the actual size and shape of nucleus and all fields in the actual configuration. Eqs. (79)–(82) should be satisfied for each calculation step. Functions $f(\chi_{0i})$ and $\bar{f}(\chi_i)$ can be found from Eq. (75), based on the calculated surface of the nucleus in the current configuration. If the smallest size of a critical nucleus is $b_c < b_{min}$, we put $b_c = b_{min}$ and change the other sizes proportionally.
3. Using Eqs. (28) and (33)–(36) or (71)–(76), one determines the driving force for the phase transformation and its volumetric and surface components, the volume of the critical nucleus in the reference configuration (different than the one that was assumed initially), and the corresponding activation energy.
4. Taking the new volume of a critical nucleus in the reference configuration, the different position of the nucleus, and its shape in the reference configuration, characterized by parameters χ_{0i} , one solves the same problem multiple times and finds parameters that satisfy the extremum principle (76) for the homogeneous nucleation process.
5. Then one can find the first approximation for the nucleation temperature from the kinetic nucleation criterion (78) with the specific chosen factor β . And then, the temperature at which the calculations were performed changes to the found temperature, and all previous calculations should be repeated and a second approximation for the nucleation temperature should be found. This process should be repeated until convergence, which will give the final position, volume, and shape of the critical nucleus and the nucleation temperature.

A similar procedure should be implemented when temperature is prescribed and one parameter that characterizes mechanical loading (e.g., magnitude of the traction or displacement field at the external surface) can be found from the kinetic nucleation criterion (78). The case with variable temperature during the phase transformation (which can be determined from the thermal conductivity equation) can be treated similarly.

6. Nucleation via interface propagation

In this scenario, as the first step, a nucleus of a smallest minimal size b_{min} and optimal shape, which appears via the homogeneous transformation process, is found using the procedure of Section 5. Then, it grows due to interface propagation until it reaches the equilibrium condition $X_\Sigma = 0$ (Fig. 3), with X_Σ being the driving force for interface propagation.

6.1. Driving force for interface propagation in an elastoplastic material

For the points of a moving interface, the mass conservation condition reads

$$dm = \rho_g(c - v_{ng})d\Sigma dt = \rho_s(c - v_{ns})d\Sigma dt \quad \text{or} \quad \bar{m} := \rho_g(c - v_{ng}) = \rho_s(c - v_{ns}), \quad (38)$$

where c is the normal interface velocity, v_{ng} and v_{ns} are normal to the interface components of the gas and solid particles, dm is the mass element covered by a moving interface $d\Sigma$ during time dt , and \bar{m} is the mass flux at the points of interface. The equilibrium condition at the interface is (Fig. 4):

$$p_g = -\sigma_n + 2\Gamma/R, \quad (39)$$

where σ_n is the normal stress in the solid at the interface, and $1/R$ is the mean curvature at the points of the interface.

We start with Eq. (9) and assume that phase transformation (nucleation) occurs in a volume with the mass element dm covered by a moving interface $d\Sigma$ during time dt (Levitas, 1998, 2000, 2002). For this case, Eq. (9) can be presented in the form

$$dX_\Sigma^{PT} = -[\mathbf{p}_\Sigma \cdot \mathbf{v}]d\Sigma dt - [\psi]dm - \frac{2\Gamma c d\Sigma dt}{R} - X_\Sigma^p dm, \quad (40)$$

where $[A] = A_g - A_s$ means the difference between the parameter in gas and solid phases across the interface, and $X_\Sigma^p = \int_0^{t_n} \mathbf{X}_p : \mathbf{d}_p dt$ is the plastic dissipation per unit mass at the moving interface. The first, second, and fourth terms in Eq. (40) are the same as in Levitas (1998). The third term comes from

$$\Delta \bar{\Gamma} = \frac{d}{dt} \int_{\Sigma_n} \Gamma d\Sigma dt = \int_{\Sigma} \left(\dot{\Gamma} + \frac{2\Gamma}{R} c \right) d\Sigma dt, \quad (41)$$

where the transport theorem for moving nonmaterial surfaces was used (see, e.g., Grinfeld (1991) and Cermelli et al. (2005)) and $\dot{\Gamma}$ is the normal time derivative. The assumption that $\Gamma = const$ leads to $\dot{\Gamma} = 0$. Introducing the dissipation rate due to phase transformation only per unit interface area, we obtain

$$D_\Sigma := dX_\Sigma^{PT} / (d\Sigma dt) = -[\mathbf{p}_\Sigma \cdot \mathbf{v}] - [\psi]\bar{m} - \frac{2\Gamma c}{R} - X_\Sigma^p \bar{m}. \quad (42)$$

We decompose the traction vectors

$$\mathbf{p}_g = -p_g \mathbf{n} + \boldsymbol{\tau}, \quad \mathbf{p}_s = \sigma_n \mathbf{n} + \boldsymbol{\tau} \quad (43)$$

and particle velocities

$$\mathbf{v}_g = v_{ng} \mathbf{n} + \mathbf{v}_\tau^g, \quad \mathbf{v}_s = v_{ns} \mathbf{n} + \mathbf{v}_\tau^s, \quad (44)$$

where $\boldsymbol{\tau}$ are the shear stresses at the interface, same in gas and solid, and \mathbf{v}_τ^g and \mathbf{v}_τ^s are the tangential to the interface components of material velocities for the gas and solid particles, respectively. The minus sign in front of p_g is used to keep the pressure in gas positive and make it consistent with Eq. (39). Then,

$$[\mathbf{p}_\Sigma \cdot \mathbf{v}] = -p_g v_{ng} - \sigma_n v_{ns} + \boldsymbol{\tau} \cdot (\mathbf{v}_\tau^g - \mathbf{v}_\tau^s). \quad (45)$$

Note that the term $-\boldsymbol{\tau} \cdot (\mathbf{v}_\tau^g - \mathbf{v}_\tau^s) \geq 0$ is the dissipation rate due to relative sliding at the moving interface, which is independent of phase transformation (Levitas, 1998). This is why it should be non-negative and should be excluded from the dissipation rate due to the phase transformation D_Σ , similar to the plastic dissipation rate $X_\Sigma^p \bar{m}$:

$$D_\Sigma = -[\mathbf{p}_\Sigma \cdot \mathbf{v}] - [\psi] \bar{m} - \frac{2\Gamma c}{R} - X_\Sigma^p \bar{m} + \boldsymbol{\tau} \cdot (\mathbf{v}_\tau^g - \mathbf{v}_\tau^s) = p_g v_{ng} + \sigma_n v_{ns} - [\psi] \bar{m} - \frac{2\Gamma c}{R} - X_\Sigma^p \bar{m}, \quad (46)$$

where we did not change the designation for the dissipation rate due to phase transformation. Let us transform

$$p_g v_{ng} + \sigma_n v_{ns} = -\frac{p_g}{\rho_g} \rho_g (c - v_{ng}) - \frac{\sigma_n}{\rho_s} \rho_s (c - v_{ns}) + (p_g + \sigma_n) c = -\left(\frac{\sigma_n}{\rho_s} + \frac{p_g}{\rho_g}\right) \bar{m} + \frac{2\Gamma c}{R}, \quad (47)$$

where Eqs. (38) and (39) have been used. Then, substituting Eq. (47) into Eq. (46), one obtains

$$D_\Sigma = X_\Sigma \bar{m}, \quad (48)$$

where

$$X_\Sigma = -\left(\frac{p_g}{\rho_g} + \frac{\sigma_n}{\rho_s}\right) - [\psi] - X_\Sigma^p \quad (49)$$

is the driving force for interface propagation per unit mass, which is the same in the reference and actual configurations. Using Eq. (39), we can present alternative expressions for X_Σ :

$$X_\Sigma = -p_g \left(\frac{1}{\rho_g} - \frac{1}{\rho_s}\right) - [\psi] - \frac{2\Gamma}{\rho_s R} - X_\Sigma^p, \quad (50)$$

$$X_\Sigma = \sigma_n \left(\frac{1}{\rho_g} - \frac{1}{\rho_s}\right) - [\psi] - \frac{2\Gamma}{\rho_g R} - X_\Sigma^p. \quad (51)$$

Similar to the case of homogeneous nucleation, we will neglect plastic dissipation at the moving interface, $X_\Sigma^p = 0$. Otherwise, the problem becomes as sophisticated as for phase transformations in solids (Levitas, 1998, 2000). However, plastic deformation and related irreversibilities in the solid phase essentially affect phase transformation through the σ_n field, which is different for forward and reverse transformations.

6.2. Activation energy and kinetic criterion

As an initial stage, a nucleus of a smallest minimal size b_{min} and optimal shape, which appears via the homogeneous transformation process, should be found. Assume that for each point of nucleus interface Σ , one has $X_\Sigma < 0$. This means that the growth of a nucleus is thermodynamically impossible and can occur only due to thermal fluctuations—i.e., it is a subcritical nucleus. Let this nucleus grow until for each point of its interface one has $X_\Sigma = 0$ —i.e., it is in thermodynamic equilibrium. With further nucleus growth, the negative contribution due to surface energy reduces, $X_\Sigma > 0$, and the nucleus can thermodynamically grow (i.e., it is a supercritical nucleus). Thus, the nucleus, for which for each point of its interface $X_\Sigma = 0$, can be called the critical nucleus. This definition coincides with the classical definition of a critical nucleus for phase transformation in conservative systems; such as for phase transformation in liquid, gas, and elastic solid. Then, the dissipation due to phase transformation for the appearance of critical nucleus is

$$X_\Sigma^{PT} = X_0^{PT} + X_G^{PT} = X_0^{PT} + \int_{m_m}^{m_c} X_\Sigma dm = X_0^{PT} + \int_{t_m}^{t_c} \int_\Sigma X_\Sigma \rho_s (c - v_{ns}) d\Sigma dt, \quad (52)$$

where X_0^{PT} and X_G^{PT} are the dissipation increments for the appearance of the smallest nucleus of an optimal shape and smallest size b_m (or mass m_m) and the dissipation increment during the growth of this nucleus until it reaches the critical size, respectively; m_c is the mass of the critical nucleus; and t_m and t_c are times for appearance of the smallest mass and critical nuclei, respectively.

Similar to the case of nucleation via homogeneous transformation, we define the activation energy for nucleation via interface propagation in an elastoplastic material as

$$Q = \min_{\text{shape}} \min_{\text{path}} \min_{\text{position}} \left(-X_{\Sigma}^{PT} \right) = \min_{\text{shape}} \min_{\text{position}} \left(-X_0^{PT} \right) + \min_{\text{path}} \min_{\text{position}} \left(-X_G^{PT} \right). \quad (53)$$

The term related to X_0^{PT} is treated in the same way as for nucleation via homogeneous transformation in Section 5. The path-dependence of the term related to X_G^{PT} appears because of path-dependence of the solution of the plastic boundary-value problem. For example, for an ellipsoidal nucleus X_G^{PT} , the final shape and volume of the critical nucleus depend on the history of variation of the aspect ratios during the nucleus growth between m_m and m_c .

6.3. Algorithm for finding the critical nucleus for nucleation via interface propagation

For a supercritical nucleus, the kinetic relationship $\bar{m}(X_{\Sigma})$ between the interface velocity and the driving force for interface motion is postulated to satisfy the second law of thermodynamics. For a subcritical nucleus, the second law of thermodynamics is not satisfied, and such a relationship does not have a physical sense because the growth occurs by thermal fluctuations. However, to find an approximate growth path and a critical nucleus, we assume the existence of the monotonously growing relationship $\bar{m}(-X_{\Sigma})$ —e.g.,

$$\rho_s(c - v_{ns}) = -\lambda X_{\Sigma}, \quad (54)$$

where λ is the “mobility” of the interface. The motivation for such a relationship is as follows: for each given geometry of a subcritical nucleus, the larger deviation of X_{Σ} at the given interface point from zero (that corresponds to a critical nucleus), the larger should be the displacement of this point with respect to others toward reaching a critical nucleus. The specific value λ is not important, because Eq. (54) is used to determine the relative change in the shape of the nucleus rather than the time of its appearance. Then the expression for the activation energy Eq. (53) simplifies to

$$Q = \min_{\text{shape}} \min_{\text{position}} \left(-X_{\Sigma}^{PT} \right) = \min_{\text{shape}} \min_{\text{position}} \left(-X_0^{PT} \right) + \min_{\text{position}} \left(-X_G^{PT} \right). \quad (55)$$

The main equations for nucleation via interface propagation are summarized in Box 2 at the end of the paper.

The algorithm for the determination of the possibility of gas nucleation according to the interface propagation mechanism and the shape and position of the nucleus for a homogeneous nucleation path is as follows.

1. At time t , the geometry of the body (which may include already-transformed gas nuclei), boundary conditions, all fields (displacements, deformation gradient and its elastic and plastic components, possible internal variables, and stress tensor), and the temperature are known in both the reference and current configurations. One has to find the temperature at which nucleation can occur, as well as the shape and position of the nucleus.
2. For the chosen position of the nucleus, one has to repeat the procedure from Section 5.3 to find the nucleus of smallest size and optimal shape that appears via the homogeneous nucleation process, as well as to calculate the corresponding dissipation increment X_0^{PT} . If for some points of the interface of this nucleus $X_{\Sigma} > 0$ and the nucleus can grow, then $X_G^{PT} = 0$ and one can calculate the activation energy Q (Eq. (55)) and move to step 4. Otherwise, one has to consider step 3.
3. Using the kinetic Eq. (54) with one of the expressions for X_{Σ} from Eqs. (49)–(51), the traction continuity condition Eq. (98), the total system of equations for an elastoplastic material in solid and for gas in nucleus, the initial interface position at time \tilde{t} , and solving the boundary-value problem, one can find the interface position at time $\tilde{t} + \Delta\tilde{t}$ and all corresponding fields. Here, \tilde{t} and $\Delta\tilde{t}$ are an internal, time-like parameter and its increment that just designates the sequence of events, without specific relation to actual time t . Nucleation time t_n will be determined using the kinetic Eq. (96). For nucleation via interface propagation, one does not need to consider the intermediate state between solid and gas parameterized by ξ (as in Eqs. (25) and (26)). In the equation of state for gas, the mass of the gas should be updated. The same procedure has to be repeated for subsequent time increments $\Delta\tilde{t}$ and for the advancing interface position until the interface equilibrium condition $X_{\Sigma} = 0$ is satisfied for each interface point, with some small offset. The dissipation increment X_G^{PT} and activation energy Q can be calculated using Eq. (55).
4. Varying the position of the nucleus and repeating steps 1–3, one can find the position that minimizes activation energy Q in Eq. (55).
5. The nucleation temperature can be found in the first approximation from the kinetic nucleation criterion (97) with the specific chosen factor β . Then, the temperature at which calculations were performed should be changed to the found temperature, and all previous calculations should be repeated, giving the second approximation for nucleation temperature. This process should be repeated until convergence, which will give the final position, volume, and shape of the critical nucleus and nucleation temperature.

A similar procedure can be implemented when the temperature is prescribed and one parameter that characterizes mechanical loading (e.g., magnitude of the traction or displacement field at the external surface) can be found from the kinetic nucleation criterion (97).

7. Final choice of the critical nucleus

7.1. Growth of the homogeneously transformed nucleus: phase transformation and mechanical instabilities

While the procedure in Section 5 allows us to determine under which condition a nucleus can appear via the homogeneous transformation process, due to path-dependence of plastic solutions one cannot say whether this nucleus will grow, shrink, or remain unchanged after nucleation. Thus, an additional condition should be checked: whether the nucleus can grow. There are two possibilities for the nucleus to grow.

1. By further sublimation. This is possible if the driving force for interface propagation X_Σ is greater than zero.
2. By mechanical instability. There is no further solid–gas phase transformation (i.e., the mass of the gas does not change), but the gas bubble expands like a balloon, because during such an expansion the internal pressure exceeds surface tension plus the resistance to plastic flow—i.e., $p_g > \sigma_n + 2\Gamma/R$. After some expansion stage, the driving force for interface propagation X_Σ may become greater than zero, and growth due to sublimation will contribute as well. The mechanical stability condition should be checked also for a nucleus that appears via continuous interface propagation. It will be shown in Levitas and Altukhova (2012) that mechanical instability is an important growth mode for a spherical nucleus.

Due to the path-dependence of the solution of the elastoplastic problem, the driving force for interface propagation for forward X_Σ^f and reverse X_Σ^r phase transformation can be different. Independent of the transformation path for the appearance of a nucleus, the following cases are possible.

1. Let $X_\Sigma^f > 0$ and $X_\Sigma^r < 0$ or $X_\Sigma^f < 0$ and $X_\Sigma^r > 0$ (to avoid $X_\Sigma = 0$, we consider slightly supercritical and subcritical nuclei). These cases are similar to phase transformation in elastic materials, and the nucleus will grow in the first case and shrink in the second. If the nucleus appeared via homogeneous transformation and the $X_\Sigma^f < 0$ and $X_\Sigma^r > 0$, it will disappear—i.e. it cannot be considered as a critical nucleus.
2. Simultaneously, $X_\Sigma^f \geq 0$ and $X_\Sigma^r \geq 0$. This case does not have the counterparts for phase transformation in elastic materials, because of $X_\Sigma^r = X_\Sigma^f$. The evolution of the nucleus is determined by the sign of the resultant interface velocity:

$$v_{res} = (c - v_{ns})^f - (c - v_{ns})^r = f^f(X_\Sigma^f) - f^r(X_\Sigma^r), \quad (56)$$

where f^f and f^r are kinetic functions for forward and reverse phase transformation.

3. Simultaneously, $X_\Sigma^f \leq 0$ and $X_\Sigma^r \leq 0$. This case also does not have the counterparts for phase transformation in elastic materials. An obtained nucleus is not an unstable critical nucleus but the stable one, and it cannot grow or shrink at the prescribed temperature and external stresses.

It is also possible that case 1 is initially valid, but after some progress of forward or reverse transformation, case 2 or 3 will take place. For example, after the appearance of a nucleus via homogeneous transformation, it shrinks to some size, and then reverse transformation is arrested and one has $X_\Sigma^f \leq 0$ and $X_\Sigma^r \leq 0$.

After determination of the nucleation temperature–mechanical loading parameter (for example, tensile pressure) for both transformation paths, we have to choose the path that corresponds to smaller temperature or mechanical loading. If the smaller temperature corresponds to a continuous growth path, then this is the final choice. If it corresponds to the homogeneous transformation process, then one needs to check whether this nucleus can grow by further sublimation or loss of mechanical stability. One also needs to check whether alternative phase transformations are possible at lower temperature—for example, melting (Levitas and Altukhova, 2009).

8. Application to chemical decomposition of solid into gas species

A gas bubble may appear as a result of the chemical decomposition of a solid S into a mixture of the gaseous species A_i , $i = 1, 2, \dots, k$, which can be described by the following chemical reaction:



where v_S and v_i are the stoichiometric coefficients. For this reaction, the change in the number of moles of each components are related by the equation (Moran and Shapiro, 2008):

$$-\frac{dn_S}{v_S} = \frac{dn_1}{v_1} = \frac{dn_2}{v_2} = \dots = \frac{dn_n}{v_k}, \quad (58)$$

where $n_i = \frac{m_i}{M_i}$ is the number of moles of the i – th component, and m_i and M_i are the mass and molecular mass of the i th component, respectively. Applying Eq. (58) to the case when the number of moles of the solid reduces from v_S to zero and the number of moles of the gaseous species increases from zero to v_i , we obtain

$$\frac{n_S}{v_S} = \frac{n_1}{v_1} = \frac{n_2}{v_2} = \dots = \frac{n_n}{v_k} \quad (59)$$

and for each i

$$n_i = v_i \frac{n_S}{v_S}. \quad (60)$$

There are minor changes that should be made to the above sublimation theory to describe chemical decomposition. For simplicity, we assume that each of the gas species is described by the ideal gas rule

$$p_i V = n_i R \theta = \frac{m_i}{M_i} R \theta, \quad (61)$$

where p_i is the partial pressure of the i -th component and V is the gas volume. Utilizing the Dalton model (Moran and Shapiro, 2008) $p = \sum_{i=1}^k p_i$, one obtains

$$pV = \sum_{i=1}^k n_i R \theta = \sum_{i=1}^k v_i \frac{n_S}{v_S} R \theta = \sum_{i=1}^k v_i \frac{m_S}{M_S v_S} R \theta. \quad (62)$$

Because for sublimation the number of moles of solid and gas is the same, one obtains

$$pV = \frac{m_S}{M_S} R \theta, \quad (63)$$

i.e., the chemical reaction changes the product pV by a factor of $\frac{1}{v_S} \sum_{i=1}^k v_i$. Assuming additivity of the Helmholtz free energy, one obtains

$$\psi = \frac{\bar{\psi}}{M}, \quad (64)$$

where

$$\bar{\psi} = \sum_{i=1}^k y_i \bar{\psi}_i; \quad M = \sum_{i=1}^k y_i M_i \quad (65)$$

are the free energy per mole and molecular mass of the gas mixture, respectively, $y_i = n_i/n$ is the molar fraction of the i -th component in the gas mixture, and $n = \sum_{i=1}^k n_i$ is the total number of moles in the mixture. Then, with accounting for Eq. (59), we derive

$$\psi = \frac{\sum_{i=1}^k n_i \bar{\psi}_i}{\sum_{i=1}^k n_i M_i} = \frac{\sum_{i=1}^k v_i \bar{\psi}_i}{\sum_{i=1}^k v_i M_i}. \quad (66)$$

Note that $\bar{\psi}_i$ is a function of the partial pressure p_i and temperature. Thus, for chemical decomposition, one has to use the gas rule in Eq. (62) and the free energy in Eq. (66), plus all of the above equations for sublimation. If decomposition occurs in several stages, then one should use the chemical reaction in Eq. (57) to determine the composition of the critical nucleus rather than the final products.

9. Application to melting inside an elastoplastic solid

Melting is also a first-order phase transformation that leads to complete relaxation of deviatoric stresses, and plastic deformation in the transforming zone can be neglected in the first approximation. This is why our sublimation theory can be easily adapted to melting. In fact, because change in volume during melting usually does not exceed 10%, the small strain approximation can be used. The main difference is related to the equation of state of the melt, which can be presented in a form similar to that for a solid:

$$p_m = K(\varepsilon_0 - \varepsilon_{0t}), \quad (67)$$

where K is the bulk modulus, p is the hydrostatic pressure, ε_0 is the volumetric strain, and ε_{0t} is the transformation volumetric strain during melting. Then, instead of Eq. (25), one can suggest the following equation of state for the intermediate state between solid and melt:

$$p = K(\xi)(\varepsilon_0 - \varepsilon_{0t}\xi), \quad (68)$$

where $K(\xi)$ varies between the bulk modulus of the solid and liquid when ξ varies from 0 to 1. Note that to write down a single equation of state for the intermediate state between solid and melt, we accept that $p > 0$ for tensile pressures. Also, we do not expect that mechanical instability of a subcritical nucleus plays any significant role for melting.

10. Concluding remarks

In this paper, general thermodynamic and kinetic approaches for the initiation of sublimation inside an elastoplastic material are developed, and a number of conceptual problems are resolved. While we consider homogeneous nucleation in defect-free nanovolumes of material, the effect of defects, internal surfaces, and stress singularities can be taken into account in a standard way as the next approximation. Operating with thermodynamic functions far from equilibrium and using continuum mechanical concepts at the nanoscale are not strictly justified. However, the classical nucleation theory routinely utilizes these assumptions, and our goal is to conceptually advance this theory for processes with plastic deformation, irreversibility, and dissipation in the simplest way possible. Because the results of the application of classical nucleation theory are broadly used for analysis of nucleation at the nanoscale (e.g., for melting in Lu and Li (1998) and Jin et al. (2001)) and are in good correspondence with experiments involving the defect-free materials (e.g., for martensitic phase transformations in Lin et al. (1993) and cavitation in Zheng et al. (1991)), we anticipate that our generalization of this theory will be a reasonably good idealization of reality as well. The continuum thermodynamic approach also works surprisingly well even beyond its expected limit of small-scale applicability in many other cases. In the accompanying paper (Levitas and Altukhova, submitted for publication), we will apply the developed theory to the nucleation of a spherical bubble inside an elastoplastic material.

Note that the alternative processes leading to a gas bubble formation should be compared with the suggested scenarios. For example, crack or void formation followed by sublimation from their new surfaces is possible. An alternative two-stage process may include appearance of the virtual melt drop, which immediately evaporates (Levitas and Altukhova, 2009). Also, diffusion-induced void nucleation by the Kirkendall effect (Yin et al., 2004; Svoboda et al., 2009) is possible.

Box 1. Equations for a gas bubble nucleation via homogeneous transformation inside nucleus of fixed mass.

1. Dissipation rate due to phase transformation averaged over the nucleation time:

$$\overline{\mathcal{D}}_{PT} := \frac{1}{t_n} \int_0^{t_n} \mathcal{D}_{PT} dt = \frac{X_{PT}}{t_n} \quad (69)$$

2. Driving force for sublimation

$$X_{PT} := \int_0^{t_n} \int_S \mathbf{p} \cdot \mathbf{v} dS dt - \int_m (\psi_2 - \psi_1) dm - \int_0^{t_n} \int_m \mathbf{X}_p : \mathbf{d}_p dm dt - \int_{\Sigma_{n2}} \Gamma_2 d\Sigma_n + \int_{\Sigma_{n1}} \Gamma_1 d\Sigma_n \quad (70)$$

3. Driving force for sublimation: simplified expression

$$X_{PT} = X_v V_{n0} - \Gamma_2 \Sigma \quad (71)$$

3.1. Volumetric driving force for sublimation

$$X_v = W - \rho_0 (\psi_2 - \langle \psi_1 \rangle) \quad (72)$$

3.2. Mechanical work

$$WV_{n0} := \int_{\mathbf{u}_1}^{\mathbf{u}} \int_{\Sigma_{n2}^+} \mathbf{p}_\Sigma \cdot \mathbf{d}\mathbf{u} d\Sigma_{n2}^+ + \int_{\mathbf{u}_n}^{\mathbf{u}_{n2}} \int_{\Sigma_{n2}^+} \sigma_n du_n d\Sigma_{n2}^+ \quad (73)$$

3.3. Nucleus volume in the reference configuration

$$V_{n0c} = \frac{32\pi a^2 \Gamma_2^3 f^3}{3X_v^3} \quad (74)$$

3.4. Nucleus surface in the actual configuration

$$\Sigma_n = zV^{2/3} \bar{f}(\chi_i) = zV_{n0}^{2/3} a^{2/3} f(\chi_{0i}) \quad (75)$$

4. Activation energy

$$Q = \min_{shape} \min_{position} \left(\frac{16\pi a^2 \Gamma_2^3 f^3}{3X_v^2} \right) \quad (76)$$

5. Arrhenius-type relationship for nucleation time

$$t_n = t_0 \exp\left(\frac{Q}{k\theta}\right) \quad (77)$$

6. Kinetic nucleation criterion

$$Q = \beta k\theta; \quad \beta = 40 - 80 \quad (78)$$

7. Constitutive equations for the transforming nucleus

7.1. Internal variable (order parameter)

$$\xi = (v - v_s)/(v_g - v_s); \quad 0 \leq \xi \leq 1 \quad (79)$$

7.2. Equation of state during the phase transformation

$$p = q(\xi)p_g(v) + (1 - q(\xi))p_s(v); \quad 0 \leq q(\xi) \leq 1 \quad (80)$$

7.3. Equation for variable surface energy during the phase transformation

$$\Gamma(\xi) = q_1(\xi)\Gamma_2 + (1 - q_1(\xi))\Gamma_1; \quad 0 \leq q_1(\xi) \leq 1 \quad (81)$$

8. The mechanical equilibrium condition at the interface

$$p_g = -\sigma_n + 2\Gamma(\xi)/R \quad (82)$$

9. Large-strain elastoplastic constitutive equations (21)–(24)

10. Growth conditions

10.1. bf By mechanical instability

$$p_g > -\sigma_n + 2\Gamma_2/R \quad \text{for } V > V_c \quad (83)$$

10.2. By further sublimation

$$10.2.1. X_\Sigma^f > 0 \quad \text{and} \quad X_\Sigma^r < 0 \quad \Rightarrow \quad \text{growth} \quad (84)$$

$$10.2.2. X_\Sigma^f \geq 0 \quad \text{and} \quad X_\Sigma^r \geq 0 \Rightarrow v_{res} = (c - v_{ns})^f - (c - v_{ns})^r = f^f(X_\Sigma^f) - f^r(X_\Sigma^r) \quad (85)$$

$$10.2.3. X_\Sigma^f \leq 0 \quad \text{and} \quad X_\Sigma^r \leq 0 \quad \Rightarrow \quad \text{stable (rather than critical) nucleus} \quad (86)$$

Box 2. Equations for gas bubble nucleation via interface propagation.

1. Mass conservation

$$\bar{m} := \rho_g(c - v_{ng}) = \rho_s(c - v_{ns}) \quad (87)$$

2. Dissipation rate due to sublimation only per unit interface area

$$D_\Sigma = X_\Sigma \bar{m} \quad (88)$$

3. Driving force for interface propagation

$$X_\Sigma = -\left(\frac{p_g}{\rho_g} + \frac{\sigma_n}{\rho_s}\right) - [\psi] - X_\Sigma^p \quad (89)$$

$$X_\Sigma = -p_g \left(\frac{1}{\rho_g} - \frac{1}{\rho_s}\right) - [\psi] - \frac{2\Gamma}{\rho_s R} - X_\Sigma^p \quad (90)$$

$$X_\Sigma = \sigma_n \left(\frac{1}{\rho_g} - \frac{1}{\rho_s}\right) - [\psi] - \frac{2\Gamma}{\rho_g R} - X_\Sigma^p; \quad X_\Sigma^p = 0 \quad (91)$$

4. Condition at the interface of the critical nucleus

$$X_{\Sigma} = 0 \tag{92}$$

5. Dissipation due to sublimation only for the appearance of critical nucleus

$$X_{\Sigma}^{PT} = X_0^{PT} + X_G^{PT} = X_0^{PT} + \int_{t_m}^{t_c} \int_{\Sigma} X_{\Sigma} \bar{m} d\Sigma dt \tag{93}$$

6. Interface kinetics for a subcritical nucleus

$$\bar{m} = -\lambda X_{\Sigma} \tag{94}$$

7. Activation energy

$$Q = \min_{shape} \min_{position} (-X_{\Sigma}^{PT}) = \min_{shape} \min_{position} (-X_0^{PT}) + \min_{position} (-X_G^{PT}) \tag{95}$$

8. Arrhenius-type relationship for nucleation time

$$t_n = t_0 \exp\left(\frac{Q}{k\theta}\right) \tag{96}$$

9. Kinetic nucleation criterion

$$Q = \beta k\theta; \quad \beta = 40 - 80 \tag{97}$$

10. The mechanical equilibrium condition at the interface

$$p_g = -\sigma_n + 2\Gamma_2/R \tag{98}$$

11. Large-strain elastoplastic constitutive equations (21)–(24)

12. Growth conditions

12.1. By mechanical instability

$$p_g > -\sigma_n + 2\Gamma_2/R \quad \text{for } V > V_c \tag{99}$$

12.2. By further sublimation

$$12.2.1. X_{\Sigma}^f > 0 \quad \text{and} \quad X_{\Sigma}^r < 0 \quad \Rightarrow \quad \text{growth} \tag{100}$$

$$12.2.2. X_{\Sigma}^f \geq 0 \quad \text{and} \quad X_{\Sigma}^r \geq 0 \quad \Rightarrow \quad v_{res} = (c - v_{ns})^f - (c - v_{ns})^r = f^f(X_{\Sigma}^f) - f^r(X_{\Sigma}^r) \tag{101}$$

$$12.2.3. X_{\Sigma}^f \leq 0 \quad \text{and} \quad X_{\Sigma}^r \leq 0 \quad \Rightarrow \quad \text{stable (rather than critical) nucleus} \tag{102}$$

Typical of the considered processes (sublimation, chemical decomposition into the gas phase, and melting) is that they lead to complete relaxation of nonhydrostatic stresses. This property is considered as an important step for various scenarios of crystal-crystal and crystal-amorphous phase transformations via the virtual melting (Levitas, 2005; Levitas et al., 2006a) and for very high strain rate plastic deformation via virtual melting. It may be that sublimation and chemical decomposition (in addition to melting) could serve as intermediate (virtual) states for the same processes.

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