

Provided for non-commercial research and education use.  
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at SciVerse ScienceDirect

## International Journal of Plasticity

journal homepage: [www.elsevier.com/locate/ijplas](http://www.elsevier.com/locate/ijplas)

# Thermodynamics and kinetics of nucleation of a spherical gas bubble inside an elastoplastic material due to sublimation

Valery I. Levitas<sup>a,\*</sup>, Nataliya Altukhova<sup>b</sup><sup>a</sup> Iowa State University, Departments of Aerospace Engineering, Mechanical Engineering, and Material Science and Engineering, Ames, IA 50011, USA<sup>b</sup> Iowa State University, Departments of Aerospace Engineering, Ames, IA 50011, USA

## ARTICLE INFO

## Article history:

Received 5 May 2011

Received in final revised form 23 November 2011

Available online 25 January 2012

## Keywords:

Sublimation

Spherical gas bubble

Elastoplastic materials

Thermodynamics and kinetics

Nucleation and growth

## ABSTRACT

General thermodynamic and kinetic approaches for sublimation inside an elastoplastic material developed in Levitas (2012) are applied to the problem of a nucleation of a spherical gas bubble inside an infinite elastoplastic sphere. A large-strain solution of the mechanical problem on a spherical void formation is generalized for the case with internal pressure and surface tension. Nucleation via homogeneous transformation in the nucleus of a fixed mass and nucleation via continuous interface propagation are studied in detail. For both paths, the explicit expressions for the thermodynamic driving forces and activation energies are derived. Using a kinetic nucleation criterion, the kinetic relationships between tensile sublimation pressure and temperature are derived. For both transformation paths, three different regions are present on the kinetic temperature–stress curve. For small stresses, elastic deformation of a sphere takes place, and the results for both paths coincide. For large stresses, nucleus size is equal to the minimum radius for which one still can distinguish between solid and gas, and for the intermediate stresses the radius of the critical nucleus maximizes the activation energy. For all cases with plastic expansion, nucleation via homogeneous transformation is more probable for small stresses and significantly more probable for large stresses. However, such a homogeneously transformed nucleus cannot grow. It is necessary to slightly increase temperature or tensile pressure (to a value well below that for nucleation via interface propagation) to cause growth. Below some critical temperature  $\theta_{in}$ , while the nucleus cannot grow because of solid–gas transformation, it expands like a balloon due to loss of mechanical stability. To our knowledge, this is the only known example of transformation of a subcritical nucleus into a supercritical one due to mechanical instability. The thermodynamics and the kinetics of evaporation are considered as well, and similar mechanical instability is found. Also, homogeneously transformed nucleus, while it starts to shrink, does not completely disappear; it represents a metastable rather than a critical nucleus. All of these results do not have counterparts in nucleation in elastic materials.

© 2012 Elsevier Ltd. All rights reserved.

## 1. Introduction

General thermodynamic and kinetic approaches for sublimation inside an elastoplastic material developed in Levitas (2012) are quite sophisticated and predict the potential for nontrivial nucleation scenarios. Here, we consider the simplest case of appearance of a spherical gas nucleus inside an infinite elastoplastic sphere that allows closed-form solution and explicitly demonstrates the nontrivial effects. Both scenarios described in Levitas (2012), namely nucleation via

\* Corresponding author.

E-mail address: [vlevitas@iastate.edu](mailto:vlevitas@iastate.edu) (V.I. Levitas).

homogeneous transformation in the nucleus of a fixed mass and nucleation via continuous interface propagation, are studied in the paper. We will consider small elastic strain but large plastic strains. In fact, for low temperatures and large tensile stresses, the volume of the void changes by a factor of 1000 due to plastic deformation. Essential simplifications for the spherical bubble are related to the following points.

1. A large-strain analytical solution of the mechanical problem on a spherical void formation (Hill, 1950) is slightly generalized here for the case with internal gas pressure and surface tension.
2. Based on this solution, an explicit expression for the mechanical work during nucleation via homogeneous transformation can be obtained even without knowledge of the equation of state of transformed material in the intermediate state between solid and gas.
3. There is no necessity to minimize an activation energy with respect to position and shape of the nucleus.

A priori, one would expect that the appearance of a nucleus by an interface propagation from zero or infinitesimal size up to the radius above which it grows by spontaneous sublimation, is the most natural definition of the critical nucleus because the statistical theory of appearance of a critical nucleus (Zeldovitch, 1943; Landau and Lifshitz, 1980) considers atom-by-atom nucleus growth. However, at large tensile pressures, when the critical nucleus consists of only a few molecules, nucleation via homogeneous transformation from solid to gas is more appropriate. We have defined a nucleus with the smallest radius of  $r_{min}$  in the reference (undeformed) configuration that consists of only a few molecules, for which one still distinguishes solid and gaseous phases. Then, due to path-dependence, nucleation via interface propagation includes homogeneous appearance of a nucleus of the smallest radius, followed by its growth up to critical size. Alternatively, we consider nucleation via homogeneous transformation in the nucleus of a fixed mass. For both paths, the explicit expressions for the thermodynamic driving forces, activation energies, and the kinetic relationships between tensile sublimation pressure and temperature are derived. For small stresses, a sphere deforms elastically and the solution of the elastic problem is utilized. For elastic deformations, the results for both transformation paths coincide, and simple analytical expression is obtained for the kinetic relationships between tensile sublimation pressure and temperature. Pressure-dependence of the sublimation temperature is weak for the elastic regime. For large stresses, nucleus size in the reference (undeformed) configuration is assumed to be equal to the minimum radius  $r_{min}$  because the radius obtained by maximization of the activation energy is smaller than  $r_{min}$ . Pressure-dependence of the sublimation temperature is very strong for this regime because nucleus volume grows drastically. We are not aware of research on nucleation that introduces  $r_{min}$  and treats the case with the minimum radius separately. For the intermediate stresses, the radius of the critical nucleus is determined from the condition of maximization of the activation energy; this is a transitional regime from the weak to strong pressure-dependence of the kinetic sublimation temperature.

Maximum pressure sensitivity corresponds to the radius of the critical nucleus in the reference configuration equal to  $r_{min}$ . For the last two cases, all equations are essentially simplified if the ratio of the volumes of a gas bubble and the corresponding solid nucleus are much greater than one. The following results are obtained for the energetic crystal HMX. For all cases that involve plastic deformation, the kinetic sublimation temperature–sublimation stress curve is lower for nucleation via homogeneous transformation, which means that it is more probable than the nucleation via interface propagation. For large stresses, the difference between these curves is significant. However, such a homogeneously transformed nucleus cannot grow, which means that it is still a subcritical nucleus. It is necessary to slightly increase temperature or tensile pressure (to a value well below that for nucleation via interface propagation) to cause growth. What is more important is that below some critical temperature  $\theta_{in}$ , while the nucleus cannot grow because of sublimation, it expands like a balloon due to loss of mechanical stability. That means that during fluctuational gas bubble expansion, the reduction in gas pressure is smaller than the reduction in resistance to expansion due to plastic flow and surface tension. To our knowledge, this is the only known example of transformation of a subcritical nucleus into a supercritical one due to mechanical instability. Also, using rough estimates we found that a homogeneously transformed nucleus, while it starts to shrink, does not completely disappear; it represents a metastable nucleus rather than the critical void. Thus, sublimation can be a mechanism of nucleation of a supercritical and metastable voids, alternative to fracture (atomic bond breaking). All these results do not have counterparts in nucleation in elastic materials or cavitation in liquid.

Thermodynamics and kinetics of evaporation is considered as well using classical nucleation theory supplemented by restriction of the smallest radius of nucleus. For large gas expansion (i.e. for large tensile stresses), the kinetic sublimation curve inside elastoplastic materials can be obtained from the kinetic evaporation curve when the external stress  $\sigma$  is substituted with  $\sigma - \sigma_c$ , where  $\sigma_c$  is the cavitation pressure for an elastoplastic solid defined below. We found that mechanical instability exists for evaporation as well, i.e. this is property of a gas bubble rather than an elastoplastic solid.

The paper is organized as follows. In Section 2 thermodynamics and kinetics of nucleation of a spherical gas bubble via homogeneous transformation inside nucleus of fixed mass is developed. In Section 3 finite strain analytical solution for deformation of an elastoplastic sphere with spherical cavity under external and internal pressure is presented and analyzed. Mechanical work is evaluated analytically. In Section 4 free energies and equations of state for gas and solid are given. Complete system of equations for nucleation via homogeneous transformation is summarized in Section 5. It includes four cases: (a) intermediate stresses; (b) large stresses and small radius of the critical nucleus  $r_{on} = r_{min}$ ; (c) small external stresses and sublimation in an elastic material, and (d) large plastic expansion  $a_n \gg 1$ . In Section 6 thermodynamics and kinetics of

nucleation via continuous interface propagation are developed. Complete system of equations for nucleation via interface propagation is summarized in Section 7 for the same four cases as for homogeneous transformation process. In Section 8 condition for the mechanical instability of the nucleus is derived. Algorithms for finding the critical nucleus for both nucleation scenarios and for all ranges of stresses and plastic expansions are presented in Section 9. In Section 10 numerical results for energetic crystal HMX are presented and analyzed. Calculations for sublimation from the plane external surface are in good agreement with published experimental data. Both scenarios are treated in detail, including finding mechanical instability conditions; the choice of the final critical nucleus is analyzed. In Section 11 appearance of the critical nucleus during the evaporation of liquid is considered. Section 12 contains concluding remarks. In Boxes 1–3, all equations are summarized for two sublimation scenarios and for evaporation. Some preliminary results for appearance of a spherical gas bubble were reported in a short letter (Levitas and Altukhova, 2008). In comparison with Levitas and Altukhova (2008), current paper contains detailed derivation of all equations (in most cases in more general form), formulations of algorithms, consideration of many more possible scenarios, and much more detailed study of sublimation.

## 2. Nucleation of a spherical gas bubble via homogeneous transformation inside nucleus of fixed mass

Let a small spherical region with a radius  $r_{0n}$  in undeformed reference configuration undergo transformation into gas, which occurs as a homogeneous process of changing of all properties of solid to the properties of gas. Mass of the transforming region  $m_n = \rho_s V_{0n}$ , where  $\rho_s$  is the density of solid in unloaded state and  $V_{0n} = 4/3\pi r_{0n}^3$  is the volume of a nucleus in undeformed configuration (Fig. 1).

Since elastic deformations are small, the radius of the region with mass  $m_n$  under pressure  $\sigma$  is approximately equal to  $r_{0n}$ . This process is accompanied by change in pressure within the region from the tensile pressure  $\sigma > 0$  to the compressive gas pressure  $p_g > 0$ , plastic expansion of the hole and appearance of the surface energy. In deformed configuration, the radius of the nucleus changes from  $r_{0n}$  to its final value  $r_n$  due to plastic deformation.

In the general theory (Levitas, 2012), we need to describe the transformation process by prescribing the constitutive properties of a transforming region in terms of the internal variable  $\xi$  that varies from zero (solid state) to 1 (gas), see Eqs. (79)–(81) in Levitas (2012). They include equation of state and surface energy. However, as we will show below, for the given simple problem one does not need such properties in the intermediate states. The thermodynamic driving force for sublimation (Levitas, 2012) is

$$X_{PT} = X_v V_{n0} - \Gamma \Sigma, \tag{1}$$

where

$$X_v = W - \rho_s (\psi_g - \psi_s) \tag{2}$$

is the volumetric driving force for sublimation per unit undeformed volume,  $\Sigma = 4\pi r_n^2$  is the nucleus surface in the deformed state,  $\Gamma$  is the surface energy per unit current area,  $W$  is the mechanical work of the pressure in solid at the solid–gas interface on the void expansion per unit undeformed volume, the mass density of solid  $\rho_s$  is considered as a constant, and  $\psi$  is the Helmholtz free energy per unit mass. Designating  $a_n = V_n/V_{0n} > 1$ , we obtain

$$r_n = \left( \frac{3}{4\pi} V_n \right)^{1/3} = \left( \frac{3}{4\pi} V_{0n} a_n \right)^{1/3}; \quad \Sigma = 4\pi \left( \frac{3}{4\pi} V_{0n} a_n \right)^{2/3}. \tag{3}$$

Substituting the expression for the surface  $\Sigma$  from Eq. (3) into Eq. (1), one obtains the driving force for phase transformation in terms of  $V_{n0}$

$$X_{PT} = X_v V_{n0} - (4\pi)^{1/3} 3^{2/3} \Gamma V_{n0}^{2/3} a_n^{2/3}. \tag{4}$$

The volume of the critical nucleus can be found by minimizing  $X_{PT}$  with respect to  $V_{n0}$ , which leads to

$$V_{0nc} = \frac{32\pi a_n^2 \Gamma^3}{3X_v^3}; \quad V_{nc} = \frac{32\pi a_n^3 \Gamma^3}{3X_v^3}. \tag{5}$$

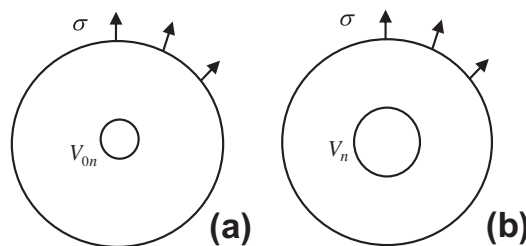


Fig. 1. Scheme of nucleation of a small spherical region  $V_{0n}$  (a) via homogeneous transformation into a gas  $V_n$  (b).

This is equivalent to the maximization of the Gibbs energy with respect to  $V_{n0}$ , see Levitas (2012). Note that  $X_v$  is the volumetric part of the thermodynamic driving force per unit undeformed volume, i.e. in reference configuration. If we introduce the volumetric thermodynamic driving force per unit deformed volume (i.e. in actual configuration),  $\bar{X}_v := X_v/a$ , then the second Eq. (5) looks like in the classical nucleation theory (see, e.g. Landau and Lifshitz (1980); Porter and Easterling (1992)):

$$V_{nc} = \frac{32\pi\Gamma^3}{3\bar{X}_v^3}. \quad (6)$$

The radii of the critical nucleus in reference and actual configurations are

$$r_{0nc} = \left(\frac{3V_{0nc}}{4\pi}\right)^{1/3} = \frac{2\Gamma a_n^{2/3}}{X_v}; \quad r_{nc} = r_{0nc} a_n^{1/3} = \frac{2\Gamma a_n}{X_v}. \quad (7)$$

Eq. (7) leads to the interesting expression for the surface tension for the critical nucleus

$$\frac{2\Gamma}{r_{nc}} = \frac{X_v}{a_n} = \bar{X}_v. \quad (8)$$

After substitution of the expression for  $V_{n0}$  from Eq. (5) into Eq. (4) and taking into account the definition of an activation energy, one obtains

$$Q = -X_{PT} = \frac{16\pi a_n^2 \Gamma^3}{3X_v^2}. \quad (9)$$

The kinetic nucleation criterion will be accepted in the form (Levitas, 2012; Porter and Easterling, 1992)

$$Q = 80k\theta, \quad (10)$$

where  $\theta$  is the temperature and  $k = 1.381 \cdot 10^{-23} J/K$  is the Boltzmann constant. We took the factor of 80, which is the upper value used in literature (Levitas, 2012; Porter and Easterling, 1992). In this way we take into account the minor pre-existing nucleation sites, like point defects.

### 3. Finite strain analytical solution for deformation of an elastoplastic sphere with spherical cavity under external and internal pressure

Consider an infinite sphere made of an elastoplastic material under prescribed tensile pressure  $\sigma$  at its surface with the spherical hole with the radius  $r_{0n}$ . Tensile stress  $\sigma_n > 0$  is applied to the solid at the surface of the hole, and it reduces from  $\sigma_{n0}$  to the current value of  $\sigma_n$  while hole expands up to the radius  $r$  (Fig. 2).

The stress  $\sigma_n$  resists to the hole expansion. Since there are only two parameters with dimension of length, solution should depend on  $r/r_{0n}$  or more convenient on  $a = V/V_{0n}$ , where  $V$  is the volume of the hole. In connection to sublimation problem,  $V$  varies between  $V_{0n}$  and the final volume of a nucleus  $V_n$  and  $a$  varies from 1 to  $a_n$ .

Solution of the large-strain elastoplastic problem for the volume change of the cavity was obtained in form

$$\frac{V_{0n}}{V} = \frac{1}{a} = 1 - \frac{\sigma_n}{K} - \frac{3(1-\nu)}{E} \sigma_y e^{-1 + \frac{3}{2\sigma_y}(\sigma - \sigma_n)}, \quad (11)$$

where  $\nu$  is the Poisson's ratio,  $K$  and  $E$  are the bulk and Young's moduli, respectively, and  $\sigma_y$  is the yield strength. This solution is based on von Mises plasticity condition,  $\sigma_\phi - \sigma_r = \sigma_y$ , where  $\sigma_\phi$  and  $\sigma_r$  are the circumferential (hoop) and radial stresses, respectively. When  $\sigma_n = 0$ , solution Eq. (11) coincides with the solution in Hill (1950). Similar problem was re-

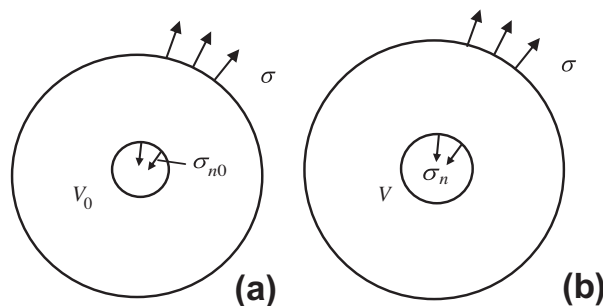


Fig. 2. Deformation of the elastoplastic material with spherical hole under external and internal tensile pressure; reference configuration (a) and actual configuration (b).

cently treated by Fischer and Antretter (2009) but for small strains. The equilibrium condition at the interface is Levitas (2012) (Fig. 3)

$$\sigma_n = -p(\xi) + 2\Gamma(\xi)/r, \tag{12}$$

where  $0 \leq \xi \leq 1$  is the internal variable,  $p(\xi) > 0$  is the pressure which varies from  $\sigma$  for  $\xi = 0$  to the value pressure in the gas  $p_g$  when  $\xi = 1$  and  $\Gamma(\xi)$  is the surface energy which varies from zero for  $\xi = 0$  to the value  $\Gamma$  for the solid–gas interface when  $\xi = 1$ . For simplicity, we assume the equality of surface energy and stresses (tension), see Fischer et al. (2008). The sign minus in Eq. (12) is because we consider compressive gas pressure as positive,  $p_g > 0$ .

For a final nucleus,  $\xi = 1$  and

$$\sigma_n = -p_g + 2\Gamma/r_n. \tag{13}$$

We need resolve Eq. (11) with respect to  $\sigma_n$  in order to calculate mechanical work  $W$ :

$$\sigma_n = K \left(1 - \frac{1}{a}\right) + \frac{2}{3} \sigma_y \text{ProductLog} \left[ \frac{9 \exp[-1 + \frac{3(K-ak+a\sigma)}{2a\sigma_y}] K(-1 + \nu)}{2E} \right],$$

where special function  $\text{ProductLog}[z]$  gives the principal solution for  $y$  in  $z = y e^y$  (Wolfram Research, 2005).

This expression, however, does not allow analytical evaluation of  $W$ . Then we neglect elastic strain  $\sigma_n/K$  in Eq. (11) and obtain from it

$$\sigma_n = \sigma - \frac{2}{3} \sigma_y \left(1 + \ln \left(\frac{\mu\alpha}{\sigma_y} \left(1 - \frac{1}{a}\right)\right)\right), \tag{14}$$

where  $\mu$  is the shear modulus,  $\alpha = \frac{2(1+\nu)}{3(1-\nu)}$  and relationship  $E = 2\mu(1 + \nu)$  was used. Putting in Eq. (14)  $\sigma_n = 0$  and  $a \rightarrow \infty$ , one obtains

$$\sigma = \sigma_c := \frac{2}{3} \sigma_y \left(1 + \ln \left(\frac{\mu\alpha}{\sigma_y}\right)\right), \tag{15}$$

where  $\sigma_c$  is often called the “cavitation pressure”, which is possible maximum value of tensile pressure that solid can sustain if surface energy is neglected. For typical values  $E/\sigma_y = 1000$  and  $\nu = 0.3$ , one obtains  $\sigma_c \simeq 4.5\sigma_y$ . Then

$$\sigma_n = \sigma - \sigma_c - \frac{2}{3} \sigma_y \ln \left(1 - \frac{1}{a}\right). \tag{16}$$

To evaluate mechanical work  $W$  per unit nucleus volume in the solid state in Eq. (2), we integrate (see Eq. (31) in Levitas (2012))

$$W = \int_{a_1}^{a_n} \sigma_n da = (\sigma - \sigma_c)(a_n - a_1) - \frac{2}{3} \sigma_y \ln \left(\frac{(a_n - 1)^{(a_n-1)} (a_1)^{a_1}}{(a_1 - 1)^{(a_1-1)} (a_n)^{a_n}}\right). \tag{17}$$

Indeed, according to Eq. (31) in Levitas (2012), mechanical work is produced by the stress in solid at the interface with gas, i.e. by stress  $\sigma_n$  rather than gas pressure  $p_g$ . Based on geometry change,  $a_1 = 1$ . However, since we neglected elastic strain, this leads to singularity in  $\sigma_n$  and  $W$ . To avoid the singularity, we determine  $a_1$  from the condition that before sublimation, when  $V_n \rightarrow 0$  and  $V_{0n} \rightarrow 0$ , in Eq. (14)  $\sigma_n = \sigma$ , i.e.

$$a_1 = \frac{1}{1 - \frac{\sigma_y}{e\mu\alpha}}. \tag{18}$$

There is an important consequence of the Eq. (17). The only term, where the constitutive equations for intermediate states for pressure  $p(\xi)$  and surface energy  $\Gamma(\xi)$  enter the general theory, is the mechanical work  $W$ . However, for a spherical

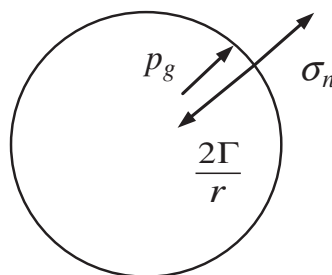


Fig. 3. The scheme illustrating the equilibrium condition at the interface and the choice of signs in Eq. (12).

problem, since solution for  $\sigma_n$  Eq. (14) is independent of  $\xi$  and so does Eq. (17) for mechanical work  $W$ , one does not need constitutive equations for an intermediate state.

For large  $a_n$ , when the expansion  $\ln(1 - \frac{1}{a}) \simeq -\frac{1}{a}$  is true, one obtains

$$\sigma_n = \sigma - \sigma_c + \frac{2\sigma_y}{3a} \quad (19)$$

and

$$W = \int_{a_1}^{a_n} \sigma_n da = (\sigma - \sigma_c)(a_n - a_1) + \frac{2}{3} \sigma_y \ln \frac{a_n}{a_1}. \quad (20)$$

For even larger  $a_n \gg 1$ , the last term in Eq. (16) disappears and  $\sigma_n$  is getting independent of  $a_n$ :

$$\sigma_n = \sigma - \sigma_c. \quad (21)$$

For this case

$$W = (\sigma - \sigma_c)(a_n - 1) \simeq (\sigma - \sigma_c)a_n. \quad (22)$$

#### 4. Free energies and equations of state for gas and solid

To complete the equations, we consider equation of state for an ideal gas

$$p_g = \frac{m_n R \theta}{M V} = \frac{\rho_s V_{0n} R \theta}{M V} = \frac{L \theta}{a}; \quad L = \frac{\rho_s R}{M} \quad (23)$$

and for solid

$$p_s = K(\varepsilon_0 - 1), \quad (24)$$

where  $M$  is the molecular mass,  $R = 8.3145$  J/K mole is the universal gas constant, and  $\varepsilon_0$  is the elastic volumetric strain in solids. Corresponding Helmholtz free energies per unit mass are

$$\psi_g = \psi_g^\theta - \frac{R\theta}{M} \ln \left( \frac{p_0}{p_g} \right) - \frac{R\theta}{M} \ln \left( \frac{\theta}{\theta_0} \right), \quad (25)$$

$$\psi_s = \psi_s^\theta + \frac{\sigma^2}{2K\rho_s}, \quad (26)$$

where  $p_0$  is the reference pressure and  $\psi^\theta$  is the thermal part of free energy per unit mass. We took into account that pressure in solid before sublimation is equal to  $\sigma$ . We assume that the jump in the thermal part of free energy

$$\Delta\psi^\theta = \psi_g^\theta - \psi_s^\theta = \Delta\psi_0^\theta - \Delta s(\theta - \theta_0), \quad (27)$$

where  $\theta_0$  is the reference temperature,  $\Delta\psi_0^\theta$  is the jump in the thermal part of free energy at reference temperature, and  $\Delta s$  is the jump in entropy.

#### 5. Complete system of equations for nucleation via homogeneous transformation

##### 5.1. General case

Substituting Eqs. (16), (23) and (8) in Eq. (13), one obtains

$$\sigma - \sigma_c - \frac{2}{3} \sigma_y \ln \left( 1 - \frac{1}{a_n} \right) = \frac{1}{a_n} (X_v - L\theta). \quad (28)$$

Substitution of Eqs. (17), (25), (26), (27) and (8) in Eq. (2) results in

$$X_v = (\sigma - \sigma_c)(a_n - a_1) - \frac{2}{3} \sigma_y \ln \left( \frac{(a_n - 1)^{(a_n-1)}}{(a_1 - 1)^{(a_1-1)}} \frac{(a_1)^{a_1}}{(a_n)^{a_n}} \right) - \rho_s (\Delta\psi_0^\theta - \Delta s(\theta - \theta_0)) + L\theta \ln \left( \frac{a_n p_0}{L\theta_0} \right) + \frac{\sigma^2}{2K}. \quad (29)$$

Then substituting  $X_v$  from Eq. (29) into Eq. (28) gives us a highly nonlinear algebraic equation for  $a_n$ . After solving this equation numerically, one can obtain function  $a_n(\theta, \sigma)$ . Inserting this function into Eq. (29), one can obtain  $X_v(\theta, \sigma)$ . Substituting  $a_n(\theta, \sigma)$  and  $X_v(\theta, \sigma)$  into kinetic criterion Eqs. (9) and (10)

$$Q = \frac{16\pi a_n(\theta, \sigma)^2 \Gamma^3}{3X_v(\theta, \sigma)^2} = 80k\theta, \quad (30)$$

one can solve it for  $\theta(\sigma)$ , which is the desired kinetic relationship between sublimation pressure  $\sigma$  and temperature  $\theta$ . In practise, one fixes arbitrary  $\theta$  and finds corresponding  $\sigma$  or vice versa. After this, the radii of critical nucleus in the reference and actual configurations can be found from Eq. (7).

5.2. Large plastic expansion  $a_n \gg 1$

In this case  $\sigma_n = \sigma - \sigma_c$  and  $W = (\sigma - \sigma_c)(a_n - 1) \simeq (\sigma - \sigma_c)a_n$  (see Eqs. (21) and (22)), which leads to a significant simplifications of Eqs. (28) and (29):

$$(\sigma - \sigma_c)a_n = X_v - L\theta, \tag{31}$$

$$X_v = (\sigma - \sigma_c)(a_n - 1) - \rho_s(\Delta\psi_0^\theta - \Delta s(\theta - \theta_0)) + L\theta \ln\left(\frac{a_n p_0}{L\theta_0}\right) + \frac{\sigma^2}{2K}. \tag{32}$$

Substitution of Eq. (32) into Eq. (31) results in equation

$$\sigma - \sigma_c + \rho_s(\Delta\psi_0^\theta - \Delta s(\theta - \theta_0)) - \frac{\sigma^2}{2K} + L\theta = L\theta \ln\left(\frac{a_n p_0}{L\theta_0}\right), \tag{33}$$

with the following solution for  $a_n$

$$a_n = \frac{L\theta_0}{p_0} \exp\left[\left(\rho_s(\Delta\psi_0^\theta - \Delta s(\theta - \theta_0)) + \sigma - \sigma_c - \frac{\sigma^2}{2K}\right)/(L\theta) + 1\right]. \tag{34}$$

Eqs. (30) and (7) should be used to determine kinetic relationship  $\theta(\sigma)$  and then the radii of critical nucleus in the reference and actual configurations.

5.3. Small radius of the critical nucleus  $r_{on} = r_{min}$

If for the general case the calculated radius of the critical nucleus  $r_{on}$  is smaller than the accepted minimum radius  $r_{min}$ , for which one still distinguishes solid and gaseous phases, we should put  $r_{on} = r_{min}$  and reconsider equations. Using corresponding minimal volume  $V_{min}$  in Eq. (4), the activation energy and kinetic sublimation criterion take the form

$$Q = -X_{PT} = (4\pi)^{1/3} 3^{2/3} \Gamma V_{min}^{2/3} a_n^{2/3} - X_v V_{min} = 80k\theta. \tag{35}$$

Equilibrium Eq. (13) at the interface simplifies as well

$$\sigma - \sigma_c - \frac{2}{3} \sigma_y \ln\left(1 - \frac{1}{a_n}\right) = \frac{2\Gamma}{r_{min} a_n^{1/3}} - \frac{L\theta}{a_n} \tag{36}$$

After substitution of  $a_n$  from Eq. (36) in Eq. (29) for  $X_v$ , and then  $X_v$  into kinetic criterion Eq. (35), the required kinetic relationship  $\theta(\sigma)$  can be obtained.

If for  $r_{on} = r_{min}$  and large  $a_n$  we simplify  $\ln\left(1 - \frac{1}{a_n}\right) \simeq -\frac{1}{a_n}$ , then equilibrium Eq. (36) at the interface simplifies to

$$\sigma - \sigma_c + \frac{2}{3} \frac{\sigma_y}{a_n} = \frac{2\Gamma}{r_{min} a_n^{1/3}} - \frac{L\theta}{a_n}, \tag{37}$$

an gives the following solution for  $a_n$

$$a_n = \left(\frac{(6\Gamma + A_2)^2 - 6\Gamma A_2}{9r(\sigma - \sigma_c)A_2}\right)^3, \tag{38}$$

where  $A_2 = 3\left[8\Gamma^3 + \frac{3}{2}\left(-3r_{min}^3(\sigma - \sigma_c)^2(3L\theta + 2\sigma_y) + A_1\right)\right]^{1/3}$  and

$$A_1 = \sqrt{r_{min}^3(\sigma - \sigma_y)^2(3L\theta + 2\sigma_y)\left(-32\Gamma^3 + 9r_{min}^3(\sigma - \sigma_c)^2(3L\theta + 2\sigma_y)\right)}.$$

This expression for  $a_n$  should be substituted in Eq. (32) for  $X_v$  and then substitution of  $X_v$  into kinetic criterion Eq. (35) will result in the kinetic relationship  $\theta(\sigma)$ .

It follows from Eq. (37), that for  $\theta = const$  increase in the tensile stress  $\sigma$  leads to reduction of expansion  $a_n$ , which from the mechanical point of view looks counterintuitive. It should be noted that Eq. (37) has to be considered together with kinetic criterion Eq. (35); then increase in  $\sigma$  reduces sublimation temperature  $\theta$ , so the conclusion about decrease in the expansion  $a_n$  is not straightforward. Numerical calculations (see Fig. 10), however, indeed demonstrate that for  $r_{on} = r_{min}$ , the expansion  $a_n$  reduces with increasing tensile stress  $\sigma$  along the kinetic sublimation curve. Since decrease in  $a_n$  for  $r_{on} = r_{min}$  with growing  $\sigma$  means decrease in the critical nucleus volume with increasing driving force, this is in accordance with the classical kinetic theory.



#### 5.4. Small external stresses: sublimation in an elastic material $a_n \simeq 1$

For high temperatures and relatively small pressures, solution of the exact system of equations demonstrates very small change in volume and  $a_n \simeq 1$ . The value  $a_n = 1$  should be plugged in the general expressions for gas pressure, radius of the critical nucleus and expressions for free energy of the gas. For such  $a_n$ , elastic rather than large-plastic-strain solution should be used but it will give us even smaller strains. In this case  $W$  should be calculated for elastic small-strain solution and Eq. (29) for  $X_v$  transforms to

$$X_v = -\rho_s \Delta\psi_E = -\rho_s (\Delta\psi_0^\theta - \Delta s(\theta - \theta_0)) + L\theta \ln \left( \frac{p_0}{L\theta_0} \right) + \frac{3\sigma^2(1-2\nu)}{2E}. \quad (39)$$

The last term represents change in elastic energy for void appearance in elastic material and it is taken from Levitas (2000), that is why we use the subscript  $E$ . Substituting  $X_v$  into activation energy Eq. (9) and kinetic criterion Eq. (10),

$$Q = -X_{PT} = \frac{16\pi a_n^2 \Gamma^3}{3(\rho_s \Delta\psi_E)^2} = 80k\theta, \quad (40)$$

one obtains an explicit expression for kinetic sublimation criterion

$$\frac{3(1-2\nu)}{2E} \sigma^2 = \left( \frac{\pi \Gamma^3}{15k\theta} \right)^{1/2} + \rho_s (\Delta\psi_0^\theta - \Delta s(\theta - \theta_0)) - L\theta \ln \left( \frac{p_0}{L\theta_0} \right). \quad (41)$$

Note that since we neglected deviation of  $a_n$  from 1 in  $\ln \left( \frac{a_n p_0}{L\theta_0} \right)$  in Eq. (39), we have to check that the error in  $X_v$  is negligible in comparison with elastic energy  $\frac{3(1-2\nu)}{2E} \sigma^2$ . Otherwise, we have to use  $\ln \left( \frac{a_n p_0}{L\theta_0} \right) \simeq \ln \left( \frac{a_n p_0}{L\theta_0} \right) + a_n - 1$  and find  $a_n$  from equilibrium condition with  $\sigma_n$  from elastic solution. Final kinetic  $\theta - \sigma$  relationship is getting complicated in this case.

To find tensile pressure range for which elastic approximation is valid, we find intersection of kinetic curves based on Eqs. (30) and (41). Corresponding values will be designated as  $a_e$ ,  $\theta_e$ , and  $\sigma_e$ . Function  $\theta(\sigma)$  in this pressure range is weakly dependent of  $\sigma$  and connection of these curves is smooth (see Fig. 11). Also, one can put  $\sigma = 0$  in Eq. (41) to obtain an estimate for sublimation temperature in this pressure range.

## 6. Nucleation via continuous interface propagation

As the first step, a nucleus of a smallest radius in the reference configuration  $r_{min}$  appears via homogeneous transformation process (Fig. 4). Then this nucleus grows by the interface propagation until it reaches the critical size  $r_{0nc}$ . Critical size is determined by the condition  $X_\Sigma = 0$ , where  $X_\Sigma$  is the thermodynamic driving force for an interface propagation. For a subcritical nucleus,  $r_0 < r_{0nc}$  and  $X_\Sigma < 0$ , i.e. the growth of a nucleus occurs due to thermal fluctuations, because it is thermodynamically impossible. For the supercritical nucleus  $r_0 > r_{0nc}$ , the negative contribution due to surface energy reduces and  $X_\Sigma > 0$ , i.e. nucleus can thermodynamically grow. Such a definition coincides with the classical definition of the critical nucleus for phase transformation in liquid, gas and elastic solid. For a spherical nucleus, there is no need to use kinetic equation for subcritical nucleus (like Eq. (94) in Levitas (2012)), because the shape evolution of the nucleus is known.

### 6.1. Appearance of a nucleus of a smallest radius via homogeneous transformation process

This process was considered in Section 5.3. First, the expansion  $a_m$  (subscript  $m$  is for minimum, to distinguish from the nucleus of the final size, designated with the subscript  $n$ ) is to be found from the equilibrium condition at the interface (Eq. (28))

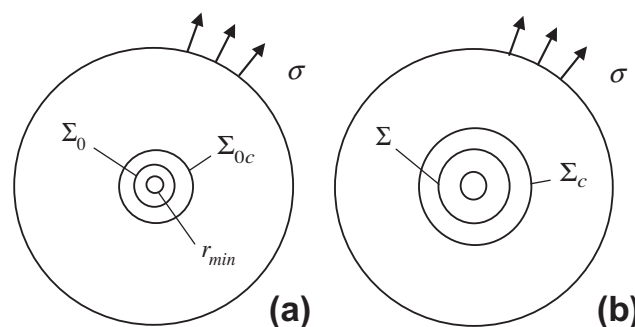


Fig. 4. Scheme of the appearance of gas nucleus via interface propagation in the reference (a) and deformed (b) configurations. Nucleus with the smallest radius  $r_{min}$  in the reference configuration appears via homogeneous transformation and grows to its critical size by continuous interface propagation.

$$\sigma - \sigma_c - \frac{2}{3} \sigma_y \ln \left( 1 - \frac{1}{a_m} \right) = \frac{2\Gamma}{r_{\min} a_m^{1/3}} - \frac{L\theta}{a_m} \quad (42)$$

and expression for  $X_v$  (Eq. (29))

$$X_v = (\sigma - \sigma_c)(a_m - a_1) - \frac{2}{3} \sigma_y \ln \left( \frac{(a_m - 1)^{(a_m-1)} (a_1)^{a_1}}{(a_1 - 1)^{(a_1-1)} (a_m)^{a_m}} \right) - \rho_s (\Delta\psi_0^\theta - \Delta s(\theta - \theta_0)) + L\theta \ln \left( \frac{a_m p_0}{L\theta_0} \right) + \frac{\sigma^2}{2K}. \quad (43)$$

This  $a_m$  is used to evaluate the activation energy (Eq. (35))

$$Q_0 = -X_{PT} = (4\pi)^{1/3} 3^{2/3} \Gamma V_{\min}^{2/3} a_m^{2/3} - X_v V_{\min}. \quad (44)$$

### 6.2. Thermodynamic driving force for interface propagation

We can use any of three Eqs. (89)–(91) from Levitas (2012)

$$X_\Sigma = - \left( \frac{p_g}{\rho_g} + \frac{\sigma_n}{\rho_s} \right) - \Delta\psi_p; \quad (45)$$

$$X_\Sigma = -p_g \left( \frac{1}{\rho_g} - \frac{1}{\rho_s} \right) - \Delta\psi_p - \frac{2\Gamma}{\rho_s r}; \quad (46)$$

$$X_\Sigma = \sigma_n \left( \frac{1}{\rho_g} - \frac{1}{\rho_s} \right) - \Delta\psi_p - \frac{2\Gamma}{\rho_g r}, \quad (47)$$

where the subscript “P” is for nucleation via interface propagation, in contrast to  $\Delta\psi$ , which is for nucleation via homogeneous transformation. Note that in these equations  $r$  is an arbitrary radius of a gas bubble in the actual configuration,  $r_{\min} a^{1/3} \leq r \leq r_{nc}$ , rather than the critical radius  $r_{nc}$ . The critical radius is determined from the condition

$$X_\Sigma = 0. \quad (48)$$

### 6.3. Activation energy and kinetic criterion

Activation energy is determined by Eq. (95) from Levitas (2012)

$$Q = Q_0 - \int_{m_m}^{m_c} X_\Sigma dm = 80k\theta, \quad (49)$$

where  $m$  is the mass of a nucleus of the radius  $r$  in the actual configuration (or the radius  $r_0$  in the reference configuration) that varies from the mass of nucleus of the minimal size  $m_m$  to the mass of the critical nucleus  $m_c$ . Since mass  $m = 4/3 \rho_s \pi r^3$ , then  $dm = 4\rho_s \pi r_0^2 dr_0$ . One can use  $m = 4/3 \rho_g \pi r^3$  but then  $\rho_g$  depends on  $r$ , which is less convenient. As soon as dependence  $X_\Sigma(r_0)$  is found, integral in Eq. (49) can be evaluated numerically.

### 6.4. Pressure in solid at the moving solid–gas interface

Consider an infinite sphere made of an elastoplastic material under prescribed tensile pressure  $\sigma$  at its surface with the spherical hole with the radius  $r_0$  in reference configuration. The difference between the problem formulation here and in Section 3 is that the radius of the hole varies not only in the actual configuration but also in the reference configuration. In general, it is quite a sophisticated problem, but due to simple geometry and the monotonous loading process in the remaining solid hollow sphere, its solution can be reduced to Eq. (16) with a proper definition of  $a$ .

Consider a hole of radius  $r$  in the actual configuration and a corresponding hole of radius  $r_0$  in the reference configuration for two cases. In the first one, this hole appeared as a result of the homogeneous sublimation process, and in the second one it appeared due to continuous interface growth. Since  $r$  and  $a = (r/r_0)^3$  for both cases the same, it follows from the equilibrium Eq. (13) at the interface that

$$\sigma_n = -L\theta/a + 2\Gamma/r \quad (50)$$

is the same for both cases as well. Solution Eq. (16) is based on the assumption that under fixed  $\sigma$  expansion  $a$  depends on the final value of  $\sigma_n$  and is independent of its history because the history of variation of  $\sigma_n$  is unknown. Keeping the same assumption here, we conclude that for each  $r_0$  Eq. (16) is valid – i.e.,

$$\sigma_n = \sigma - \sigma_c - \frac{2}{3} \sigma_y \ln \left( 1 - \frac{1}{a} \right). \quad (51)$$

The only difference is that  $a$  is calculated with respect to a different  $r_0$  for each interface position, because  $r_0$  in the reference configuration grows. Note that change in  $r_0$  in the reference configuration is due to sublimation, while change in radius  $r$  in the current configuration with respect to  $r_0$  is due to plastic expansion.

### 6.5. Elastic energy of solids

While the Helmholtz free energy of gas and  $\Delta\psi^\theta$  remain the same as in Eqs. (25) and (27), the elastic part of the free energy of solid changes because of different stress states at the moving interface. Elastic energy

$$\rho_s \psi_e = \frac{\sigma_0^2}{2K} + \frac{\sigma_i^2}{6\mu}, \quad (52)$$

where  $\sigma_0$  is the mean stress (hydrostatic pressure) and  $\sigma_i$  is the stress intensity. For the point of the interface, there are two equal hoop stresses  $\sigma_\phi$  and the radial stress  $\sigma_n$ . According to the von Mises plasticity condition,  $\sigma_i = \sigma_\phi - \sigma_n = \sigma_y$ . Then  $\sigma_\phi = \sigma_n + \sigma_y$ , the mean stress  $\sigma_0 = (2\sigma_\phi + \sigma_n)/3 = (3\sigma_n + 2\sigma_y)/3$ , and

$$\rho_s \psi_e = \frac{(3\sigma_n + 2\sigma_y)^2}{18K} + \frac{\sigma_y^2}{6\mu}. \quad (53)$$

Thus,

$$\rho_s \Delta\psi_p = \rho_s \Delta\psi^\theta - L\theta \ln\left(\frac{ap_0}{L\theta_0}\right) - \frac{(3\sigma_n + 2\sigma_y)^2}{18K} - \frac{\sigma_y^2}{6\mu}. \quad (54)$$

## 7. Complete system of equations for nucleation via interface propagation

### 7.1. General case

Combining Eqs. (13), (19), (28) and (51), we express the equilibrium equation for an interface in two forms

$$\sigma - \sigma_c - \frac{2}{3}\sigma_y \ln\left(1 - \frac{1}{a}\right) = \frac{2\Gamma}{r_0 a^{1/3}} - \frac{L\theta}{a} \quad (55)$$

and

$$\sigma - \sigma_c - \frac{2}{3}\sigma_y \ln\left(1 - \frac{1}{a}\right) = \frac{2\Gamma}{r} - \frac{L\theta}{a}, \quad (56)$$

one, in terms of  $r_0$ , and another in terms of  $r$ . Similarly, we express Eq. (47) for the driving force for an interface propagation:

$$X_\Sigma = \sigma_n \frac{a-1}{\rho_s} - \Delta\psi_p - \frac{2\Gamma a}{\rho_s r} \quad (57)$$

and

$$X_\Sigma = \sigma_n \frac{a-1}{\rho_s} - \Delta\psi_p - \frac{2\Gamma a^{2/3}}{\rho_s r_0}. \quad (58)$$

To find the radius of the critical nucleus, we first express  $\frac{2\Gamma}{r}$  from the condition  $X_\Sigma = 0$  in Eq. (57) and substitute it in Eq. (56). We derive that for the critical nucleus

$$\sigma_n = -\rho_s \Delta\psi_p - L\theta, \quad (59)$$

or, in detail,

$$\sigma - \sigma_c - \frac{2}{3}\sigma_y \ln\left(1 - \frac{1}{a}\right) = -\rho_s \Delta\psi^\theta + L\theta \left( \ln\left(\frac{ap_0}{L\theta_0}\right) - 1 \right) + \frac{[\sigma - \sigma_c - 2/3\sigma_y(\ln(1 - 1/a) - 1)]^2}{2K} + \frac{\sigma_y^2}{6\mu}. \quad (60)$$

One can solve algebraic Eq. (60) for  $a$ . Then from the condition  $X_\Sigma = 0$ , one finds from Eq. (57) the radius of the critical nucleus in the actual configuration

$$r_c = \frac{2\Gamma a}{\sigma_n(a-1) - \rho_s \Delta\psi_p}, \quad (61)$$

where  $a$  is determined from Eq. (60).

Since in Eq. (49) for the activation energy we integrate over volume in the reference configuration,  $X_\Sigma$  should be expressed in terms of  $r_0$ . Resolving Eq. (55) for  $a$  and substituting it into Eq. (58), we obtain the desired expression for

$X_{\Sigma}(r_0)$  for the prescribed  $\sigma$  and  $\theta$ . After numerical integration, Eq. (49) will give the desired kinetic relationship between sublimation temperature  $\theta$  and tensile stress  $\sigma$ .

### 7.2. Large plastic expansion $a_n \gg 1$

Eq. (60) significantly simplifies for  $a_n \gg 1$

$$\sigma - \sigma_c = -\rho_s \Delta\psi^\theta + L\theta \left( \ln \left( \frac{ap_0}{L\theta_0} \right) - 1 \right) + \frac{[\sigma - \sigma_c + 2/3\sigma_y]^2}{2K} + \frac{\sigma_y^2}{6\mu} \quad (62)$$

and can be solved explicitly:

$$a = \frac{L\theta_0}{p_0} \exp \left[ \left( \sigma - \sigma_c + \rho_s \Delta\psi^\theta - \frac{[\sigma - \sigma_c + 2/3\sigma_y]^2}{2K} - \frac{\sigma_y^2}{6\mu} \right) / L\theta + 1 \right]. \quad (63)$$

Eq. (61) for the radius of the critical nucleus simplifies as well:

$$r_c = \frac{2\Gamma a}{(\sigma - \sigma_c)a - \rho_s \Delta\psi_p} \quad (64)$$

and with Eq. (63) for  $a$  gives the explicit expression for  $r_c$ .

Eq. (63) transforms to the cubic equation for  $x = a^{1/3}$

$$\sigma - \sigma_c = \frac{2\Gamma}{r_0 x^{1/3}} - \frac{L\theta}{a} \quad (65)$$

and allows the following solution:

$$x = \frac{(2\Gamma + A_3)^2 - 2\Gamma A_3}{3r_0(\sigma - \sigma_c)A_3}, \quad (66)$$

where  $A_3 = 2^{-1/3} \left( 4\Gamma^3 - 27r_0^3 L\theta(\sigma - \sigma_c)^2 + 3\sqrt{3} \sqrt{r_0^3 L\theta(-32\Gamma^3 + 27r_0^3 L\theta(\sigma - \sigma_c)^2)(\sigma - \sigma_c)^2} \right)^{1/3}$ . This solution can be substituted into Eq. (57) for integration and determination of the kinetic relationship between sublimation temperature  $\theta$  and tensile stress  $\sigma$ .

### 7.3. Small external stresses: Sublimation in an elastic material $a \simeq 1$

In this case,  $X_v = -\rho_s \Delta\psi_E$ . Eq. (61) for the radius of the critical nucleus transforms to

$$r_c = -\frac{2\Gamma}{\rho_s \Delta\psi_E}, \quad (67)$$

with

$$\rho_s \Delta\psi_E = \rho_s (\Delta\psi_0^\theta - \Delta s(\theta - \theta_0)) - L\theta \ln \left( \frac{p_0}{L\theta_0} \right) - \frac{3\sigma^2(1 - \nu)}{4E} \quad (68)$$

from Eq. (39). The expression Eq. (57) for the driving force for an interface propagation is

$$X_{\Sigma} = -\Delta\psi_E - \frac{2\Gamma}{\rho_s r}. \quad (69)$$

Then

$$\int_{m_m}^{m_c} X_{\Sigma} dm = 4\rho_s \pi \int_{r_m}^{r_c} X_{\Sigma} r^2 dr = -4/3 \rho_s \pi \Delta\psi_E (r_c^3 - r_m^3) - 4\pi\Gamma (r_c^2 - r_m^2). \quad (70)$$

Substituting Eq. (67) for the critical radius into Eq. (70) and then Eq. (70) into Eq. (49), we obtain

$$Q = Q_0 + \frac{16\pi\Gamma^3}{3(\Delta\psi_E)^2} - 4/3 \rho_s \pi \Delta\psi_E r_m^3 - 4\pi\Gamma r_m^2. \quad (71)$$

Since according to Eq. (44)

$$Q_0 = 4\pi\Gamma r_m^2 + 4/3 \rho_s \pi \Delta\psi_E r_m^3, \quad (72)$$

then

$$Q = \frac{16\pi\Gamma^3}{3(\rho_s\Delta\psi_E)^2} = 80k\theta; \quad (73)$$

i.e., similar to the classical nucleation theory. Eq. (73) coincides with Eq. (40) for the homogeneous transformation process. As expected, activation energy for sublimation in elastic material is path-independent. The explicit kinetic sublimation criterion is also the same as in Eq. (41)

$$\frac{3(1-\nu)}{4E}\sigma^2 = \left(\frac{\pi\Gamma^3}{15k\theta}\right)^{1/2} + \rho_s(\Delta\psi_0^\theta - \Delta s(\theta - \theta_0)) - L\theta \ln\left(\frac{p_0}{L\theta_0}\right). \quad (74)$$

If in all of the above kinetic sublimation criteria we put  $\Gamma = 0$ , we obtain what one can call thermodynamic equilibrium condition for appearance of a nucleus of relatively large size, when surface energy is irrelevant.

We also introduce the thermodynamic equilibrium sublimation temperature  $\theta_t$  for appearance of a nucleus of relatively large size without stresses. It can be found from Eq. (74) for  $\Gamma = \sigma = 0$ :

$$\rho_s(\Delta\psi_0^\theta - \Delta s(\theta_t - \theta_0)) = L\theta_t \ln\left(\frac{p_0}{L\theta_0}\right); \quad (75)$$

i.e.,

$$\theta_t = \frac{\Delta\psi_0^\theta - \Delta s\theta_0}{\Delta s + \frac{L}{\rho_s} \ln\left(\frac{p_0}{L\theta_0}\right)}. \quad (76)$$

### 8. Mechanical instability of the nucleus

After solving the problem of finding the critical nucleus, one needs to check the stability of the mechanical equilibrium with respect to the spontaneous increase of its radius without phase transformation and under the same prescribed tensile pressure  $\sigma$  and temperature  $\theta$ . Thus, if at fixed radius of the critical nucleus  $r_{0nc}$

$$p_g(a_n + \delta) > \sigma_n(a_n + \delta) + \frac{2\Gamma}{r_{0nc}(a_n + \delta)^{1/3}} \quad \text{for } \delta > 0, \quad (77)$$

then mechanical instability occurs for given  $a_n$  (see geometric interpretation in Figs. 12 and 13). This means that a spontaneous increase in the bubble radius will lead to its unlimited expansion because gas pressure exceeds the resistance to plastic flow and surface tension. Substituting Eqs. (14) and (23) in Eq. (77), we obtain

$$\frac{L\theta}{a_n + \delta} > \sigma - \sigma_c - \frac{2}{3}\sigma_y \ln\left(1 - \frac{1}{a_n + \delta}\right) + \frac{2\Gamma}{r_{0nc}(a_n + \delta)^{1/3}} \quad \text{for } \delta > 0. \quad (78)$$

Expanding this expression into a series, taking into account that at  $\delta = 0$ , the equilibrium equation

$$\frac{L\theta}{a_n} = \sigma - \sigma_c - \frac{2}{3}\sigma_y \ln\left(1 - \frac{1}{a_n}\right) + \frac{2\Gamma}{r_{0nc}(a_n)^{1/3}} \quad (79)$$

is valid, and keeping the linear terms only, Eq. (78) can be presented in the form

$$\frac{L\theta}{a_n} < \frac{2}{3}\sigma_y \frac{1}{a_n - 1} + \frac{2\Gamma}{3r_{0nc}(a_n)^{1/3}}. \quad (80)$$

For  $a_n \gg 1$  inequality Eq. (80) can be solved for  $a_n$ :

$$a_n > \left(\frac{(3L\theta - 2\sigma_y)r_{0nc}}{2\Gamma}\right)^{3/2}. \quad (81)$$

It is difficult to analyze Eq. (81) because  $\theta$ ,  $r_{0nc}$ , and  $a_n$  are interrelated. It is only clear that mechanical instability may start above some critical value  $a_n$ . Determination of the instability point and its consequences for determination of the critical nucleus are discussed in Section 10.

## 9. Algorithm for finding the critical nucleus

### 9.1. Nucleation via homogenous transformation

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

#### A. Finding nucleation condition

##### I. Intermediate stresses $\sigma$

##### 1. The mechanical equilibrium condition at the interface

###### 1.1. General condition

$$p_g = -\sigma_n + 2\Gamma/r_{nc} \quad (82)$$

###### 1.2. Ideal gas rule

$$p_g = L\theta/a \quad (83)$$

###### 1.3. Stress in solid

$$\sigma_n = \sigma - \sigma_c - \frac{2}{3}\sigma_y \ln\left(1 - \frac{1}{a}\right) \quad (84)$$

###### 1.4. Surface tension

$$\frac{2\Gamma}{r_{nc}} = \frac{X_v}{a_n} \quad (85)$$

###### 1.5. Final mechanical equilibrium equation at the interface

$$\sigma - \sigma_c - \frac{2}{3}\sigma_y \ln\left(1 - \frac{1}{a_n}\right) = \frac{1}{a_n}(X_v - L\theta) \quad (86)$$

##### 2. Volumetric driving force for sublimation

$$X_v = W - \rho_s \Delta\psi \quad \text{with} \quad (87)$$

###### 2.1. Mechanical work

$$W = (\sigma - \sigma_c)(a_n - a_1) - \frac{2}{3}\sigma_y \ln\left(\frac{(a_n - 1)^{(a_n-1)} (a_1)^{a_1}}{(a_1 - 1)^{(a_1-1)} (a_n)^{a_n}}\right) \quad (88)$$

###### 2.2. Change in free energy

$$\rho_s \Delta\psi = \rho_s (\Delta\psi_0^\theta - \Delta s(\theta - \theta_0)) - L\theta \ln\left(\frac{a_n p_0}{L\theta_0}\right) - \frac{\sigma^2}{2K} \quad (89)$$

##### 3. Nucleus critical volume and radii in the reference and actual configurations

$$V_{n0c} = \frac{32\pi a^2 \Gamma^3}{3X_v^3}; \quad r_{0nc} = \left(\frac{3V_{0nc}}{4\pi}\right)^{1/3} = \frac{2\Gamma a_n^{2/3}}{X_v}; \quad r_{nc} = r_{0nc} a_n^{1/3} = \frac{2\Gamma a_n}{X_v}. \quad (90)$$

##### 4. Activation energy and kinetic nucleation criterion

$$Q = \frac{16\pi a^2 \Gamma^3}{9X_v^2} = 80k\theta. \quad (91)$$

## II. Large stresses $\sigma$ and minimal radius of the critical nucleus $r_{0n} = r_{min}$

### 1. The mechanical equilibrium condition at the interface

$$\sigma - \sigma_c - \frac{2}{3} \sigma_y \ln \left( 1 - \frac{1}{a_n} \right) = \frac{2\Gamma}{r_{min} a_n^{1/3}} - \frac{L\theta}{a_n}. \quad (92)$$

### 2. Volumetric driving force for sublimation

$$X_v = (\sigma - \sigma_c)(a_n - a_1) - \frac{2}{3} \sigma_y \ln \left( \frac{(a_n - 1)^{(a_n - 1)} (a_1)^{a_1}}{(a_1 - 1)^{(a_1 - 1)} (a_n)^{a_n}} \right) - \rho_s (\Delta\psi_0^\theta - \Delta s(\theta - \theta_0)) + L\theta \ln \left( \frac{a_n p_0}{L\theta_0} \right) + \frac{\sigma^2}{2K}. \quad (93)$$

### 3. Activation energy and kinetic nucleation criterion

$$Q = -X_{PT} = (4\pi)^{1/3} 3^{2/3} \Gamma V_{min}^{2/3} a_n^{2/3} - X_v V_{min} = 80k\theta. \quad (94)$$

## III. Small stresses $\sigma$ and $a_n < a_e$ : sublimation in an elastic material, $a_n \simeq 1$

### 1. Volumetric driving force for sublimation

$$X_v = -\rho_s \Delta\psi_E = -\rho_s (\Delta\psi_0^\theta - \Delta s(\theta - \theta_0)) + L\theta \ln \left( \frac{p_0}{L\theta_0} \right) + \frac{3\sigma^2(1 - \nu)}{4E}. \quad (95)$$

### 2. Radius of the critical nucleus

$$r_c = -\frac{2\Gamma}{\rho_s \Delta\psi_E}. \quad (96)$$

### 3. Kinetic nucleation criterion

$$\frac{3(1 - \nu)}{4E} \sigma^2 = \left( \frac{\pi\Gamma^3}{15k\theta} \right)^{1/2} + \rho_s (\Delta\psi_0^\theta - \Delta s(\theta - \theta_0)) - L\theta \ln \left( \frac{p_0}{L\theta_0} \right). \quad (97)$$

## B. Growth conditions

### 1. By mechanical instability

$$p_g(a_n + \delta) > \sigma_n(a_n + \delta) + \frac{2\Gamma}{r_{0nc}(a_n + \delta)^{1/3}} \quad \text{for } \delta > 0. \quad (98)$$

### 2. By further sublimation

$$X_\Sigma^f > 0 \quad \text{and} \quad X_\Sigma^r < 0 \quad \Rightarrow \quad \text{growth}. \quad (99)$$

Main equations for this case are summarized in Box 1. To find the kinetic tensile stress  $\sigma$ –temperature  $\theta$  relationships for sublimation, the following steps are taken.

1. For prescribed  $\theta$  and a number of values of  $\sigma$ , the volume expansion  $a_n$  can be found numerically from the equilibrium condition at the interface Eq. (86) after substituting the volumetric driving force  $X_v$  (see Eqs. (87)–(89)), which are equivalent to Eq. (93).
2. Inserting these values  $a_n(\theta, \sigma)$  into Eq. (93), one can obtain  $X_v(\theta, \sigma)$ .
3. Substituting  $a_n(\theta, \sigma)$  and  $X_v(\theta, \sigma)$  into kinetic criterion Eq. (91)

$$Q = \frac{16\pi a_n(\theta, \sigma)^2 \Gamma^3}{3X_v(\theta, \sigma)^2} = 80k\theta, \quad (100)$$

we can solve it numerically for  $\sigma$  for each prescribed  $\theta$ , which is the desired kinetic relationship between tensile sublimation pressure  $\sigma$  and temperature  $\theta$ .

4. The radii of the critical nucleus in the reference and actual configurations can be found from Eq. (7) for obtained stress  $\sigma$  and corresponding  $a_n(\theta, \sigma)$  and  $X_i(\theta, \sigma)$ .

If obtained radius  $r_{0n} > r_{min}$  and  $a_n > a_e$ , then go to step 7. If  $r_{0n} < r_{min}$ , then go to step 5. If  $a_n < a_e$ , then go to step 6.

5. If obtained radius  $r_{0n} < r_{min}$ , then we put  $r_{0n} = r_{min}$  and switch to equations from Section II of Box 1.

5a. The parameter  $a_n(\theta, \sigma)$  can be found by solving Eq. (92).

5b. Inserting these values  $a_n(\theta, \sigma)$  into Eq. (93), we can obtain  $X_i(\theta, \sigma)$ .

5c. Substitution of the obtained values of  $a_n(\theta, \sigma)$  and  $X_i(\theta, \sigma)$  into kinetic criterion Eq. (94), and its numerical solution for  $\sigma$  for each prescribed  $\theta$  will lead to the desired kinetic relationship between tensile sublimation pressure  $\sigma$  and temperature  $\theta$ .

6. If obtained  $a_n < a_e$ , then one has to work with equations from Section III of Box 1.

6a. Kinetic nucleation criterion Eq. (97) can be found immediately.

6b. Nucleus volume

$$V_{n0c} = \frac{32\pi\Gamma^3}{3\left[-\rho_s(\Delta\psi_0^\theta - \Delta s(\theta - \theta_0)) + L\theta \ln\left(\frac{p_0}{L\theta_0}\right) + \frac{3\sigma^2(1-\nu)}{4E}\right]^3} \quad (101)$$

can be found after substitution of Eq. (95) into Eq. (96). Since  $a_e$  is unknown a priori, one has to find the intersection of the kinetic  $\theta$ - $\sigma$  curves based on Eqs. (100) and (97).

7. Using Eq. (102) and substituting in it the found parameters for critical nucleus  $\theta$ ,  $\sigma$ ,  $a_n$ , and  $r_{cn}$ , check whether the thermodynamic driving force for the interface propagation is

$$\rho_s X_\Sigma = \sigma_n(a - 1) - \rho_s(\Delta\psi_0^\theta - \Delta s(\theta - \theta_0)) + L\theta \ln\left(\frac{ap_0}{L\theta_0}\right) + \frac{(3\sigma_n + 2\sigma_y)^2}{18K} + \frac{\sigma_y^2}{6\mu} - \frac{2\Gamma a^{2/3}}{r_0} > 0. \quad (102)$$

If  $X_\Sigma < 0$ , then the nucleus can appear but cannot grow – i.e., it is not a critical nucleus. It should be also checked whether it will not transformed back.

8. If inequality in Eq. (98) (or in Eq. (80)) is met, then the nucleus is mechanically unstable and it can expand like a balloon and exceed the critical size, after which it can grow due to sublimation as well.

## 9.2. Nucleation via interface propagation

### Box 2. Equations for a spherical gas bubble nucleation via interface propagation

#### I. Appearance of a nucleus of minimum possible radius $r_{0n} = r_{min}$

##### 1.1. The mechanical equilibrium condition at the interface

$$\sigma - \sigma_c - \frac{2}{3}\sigma_y \ln\left(1 - \frac{1}{a_m}\right) = \frac{2\Gamma}{r_{min}a_m^{1/3}} - \frac{L\theta}{a_m} \quad (103)$$

##### 1.2. Volumetric driving force for sublimation

$$X_v = (\sigma - \sigma_c)(a_m - a_1) - \frac{2}{3}\sigma_y \ln\left(\frac{(a_m - 1)^{(a_m-1)} (a_1)^{a_1}}{(a_1 - 1)^{(a_1-1)} (a_m)^{a_m}}\right) - \rho_s(\Delta\psi_0^\theta - \Delta s(\theta - \theta_0)) + L\theta \ln\left(\frac{a_m p_0}{L\theta_0}\right) + \frac{\sigma^2}{2K} \quad (104)$$

##### 1.3. Activation energy

$$Q_0 = (4\pi)^{1/3} 3^{2/3} \Gamma V_{min}^{2/3} a_m^{2/3} - X_v V_{min} \quad (105)$$

#### II. Interface propagation: intermediate and large stresses $\sigma$

##### 1. Mechanical equilibrium condition at the interface

###### 1.1. General condition

$$p_g = -\sigma_n + 2\Gamma/r \quad (106)$$

###### 1.2. Ideal gas rule

$$p_g = L\theta/a \quad (107)$$

###### 1.3. Stress in solid

$$\sigma_n = \sigma - \sigma_c - \frac{2}{3}\sigma_y \ln\left(1 - \frac{1}{a}\right). \quad (108)$$



**1.4. Final mechanical equilibrium equation at the interface**

$$\sigma_n = \sigma - \sigma_c - \frac{2}{3}\sigma_y \ln\left(1 - \frac{1}{a}\right) = \frac{2\Gamma}{r} - \frac{L\theta}{a}. \quad (109)$$

**2. Driving force for interface propagation**

$$X_\Sigma = \sigma_n \frac{a-1}{\rho_s} - \Delta\psi_p - \frac{2\Gamma a}{\rho_s \Gamma}. \quad (110)$$

**3. Condition at the interface of the critical nucleus**

$$X_\Sigma = 0 \rightarrow \sigma_n = -\rho_s \Delta\psi_p - L\theta. \quad (111)$$

**4. Radiuses of the critical nucleus in the current and reference configurations**

$$r_c = \frac{2\Gamma a_n}{\sigma_n(a_n - 1) - \rho_s \Delta\psi_p}; \quad r_{0c} = r_c a_n^{-1/3}. \quad (112)$$

**5. Change in Helmholtz free energies**

$$\rho_s \Delta\psi_p = \rho_s (\Delta\psi_0^\theta - \Delta s(\theta - \theta_0)) - L\theta \ln\left(\frac{ap_0}{L\theta_0}\right) - \frac{(3\sigma_n + 2\sigma_y)^2}{18K} - \frac{\sigma_y^2}{6\mu}. \quad (113)$$

**6. Activation energy and kinetic sublimation criterion**

$$Q = Q_0 - 4\rho_s \pi \int_{r_m}^{r_{0c}} X_\Sigma r_0^2 dr_0 = 80k\theta. \quad (114)$$

**III. Small stresses  $\sigma$  and  $a_n < a_e$ : sublimation in an elastic material,  $a_n \simeq 1$ .**

**1. Volumetric driving force for sublimation**

$$X_v = -\rho_s \Delta\psi_E = -\rho_s (\Delta\psi_0^\theta - \Delta s(\theta - \theta_0)) + L\theta \ln\left(\frac{p_0}{L\theta_0}\right) + \frac{3\sigma^2(1-\nu)}{4E}. \quad (115)$$

**2. Radius of the critical nucleus**

$$r_c = -\frac{2\Gamma}{\rho_s \Delta\psi_E}; \quad r_{0c} = r_c a_n^{-1/3}. \quad (116)$$

**3. Kinetic nucleation criterion**

$$\frac{3(1-\nu)}{4E} \sigma^2 = \left(\frac{\pi\Gamma^3}{15k\theta}\right)^{1/2} + \rho_s (\Delta\psi_0^\theta - \Delta s(\theta - \theta_0)) - L\theta \ln\left(\frac{p_0}{L\theta_0}\right). \quad (117)$$

The main equations for nucleation via interface propagation are summarized in Box 2. To find the kinetic tensile stress  $\sigma$ –temperature  $\theta$  relationships for sublimation, the following steps are taken for prescribed  $\theta$  and a number of values of  $\sigma$ .

1. Finding a nucleus of the minimum possible radius  $r_0 = r_{min}$ .

1a. The volumetric expansion  $a_m(\theta, \sigma)$  can be found from the mechanical equilibrium condition at the interface Eq. (103).

1b. After substitution of  $X_v$  from Eq. (104) into Eq. (105), one calculates the activation energy

$$Q_0 = (4\pi)^{1/3} 3^{2/3} \Gamma V_{min}^{2/3} a_m^{2/3} - \left( (\sigma - \sigma_c)(a_m - a_1) - \frac{2}{3}\sigma_y \ln\left(\frac{(a_m - 1)^{(a_m-1)} (a_1)^{a_1}}{(a_1 - 1)^{(a_1-1)} (a_m)^{a_m}}\right) \right) V_{min} - \left( \rho_s (\Delta\psi_0^\theta - \Delta s(\theta - \theta_0)) + L\theta \ln\left(\frac{a_m p_0}{L\theta_0}\right) + \frac{\sigma^2}{2K} \right) V_{min}, \quad (118)$$

with  $a_n(\theta, \sigma)$  from Eq. (103).

2. Finding the radius of the critical nucleus.

2a. The volumetric expansion  $a_n(\theta, \sigma)$  can be found from Eq. (111) after substitution of Eq. (108) for  $\sigma_n$  and Eq. (113) for  $\rho_s \Delta \psi_P$

$$\sigma_n := \sigma - \sigma_c - \frac{2}{3} \sigma_y \ln \left( 1 - \frac{1}{a_n} \right) = -\rho_s \Delta \psi^\theta + L\theta \left( \ln \left( \frac{a_n p_0}{L\theta_0} \right) - 1 \right) + \frac{[\sigma - \sigma_c - 2/3 \sigma_y (\ln(1 - 1/a_n) - 1)]^2}{2K} + \frac{\sigma_y^2}{6\mu}. \quad (119)$$

2b. Radius of the critical nucleus in the deformed configuration can be found from Eq. (112) after substitution of  $\rho_s \Delta \psi_P$  from Eq. (113):

$$r_c = \frac{2\Gamma a_n}{\sigma_n(a_n - 1) - \rho_s(\Delta \psi_0^\theta - \Delta s(\theta - \theta_0)) + L\theta \ln \left( \frac{a_n p_0}{L\theta_0} \right) + \frac{(3\sigma_n + 2\sigma_y)^2}{18K} - \frac{\sigma_y^2}{6\mu}}. \quad (120)$$

Note that the values  $a_n(\theta, \sigma)$  and corresponding  $\sigma_n$  should be taken from Eq. (119). Then the radius of the critical nucleus in the reference configuration is determined by Eq. (116).

2c. If  $r_{min} \geq r_{0c}$ , then the desired relationship between sublimation tensile pressure and temperature can be found from the kinetic criterion

$$Q_0 = 80k\theta. \quad (121)$$

Otherwise, one has to go to step 3.

3. Determination of the kinetic nucleation criterion

3.1. From the mechanical equilibrium condition at the interface Eq. (109) we find function  $a(\theta, \sigma_n, r_0)$  for each radius in the reference configuration  $r_0$  in the range  $r_{min} \leq r_0 \leq r_{0c}$ . The radius  $r_0$  is an integration variable in the expression for the activation energy Eq. (114).

3.2. Expression  $a(\theta, \sigma_n, r_0)$  and corresponding  $\sigma_n$  from Eq. (109) should be substituted into the expression for the thermodynamic driving force for an interface propagation:

$$\rho_s X_\Sigma = \sigma_n(a - 1) - \rho_s(\Delta \psi_0^\theta - \Delta s(\theta - \theta_0)) + L\theta \ln \left( \frac{ap_0}{L\theta_0} \right) + \frac{(3\sigma_n + 2\sigma_y)^2}{18K} + \frac{\sigma_y^2}{6\mu} - \frac{2\Gamma a^{2/3}}{r_0}. \quad (122)$$

3.3. Substituting  $X_\Sigma(\theta, \sigma_n, r_0)$  into the expression for the activation energy and kinetic sublimation criterion Eq. (114) and performing numerical integration, we obtain the desired relationship between sublimation tensile pressure and temperature.

If obtained  $a_n > a_e$ , go to step 5.

4. If obtained  $a_n < a_e$ , then one has to work with the equations from Section III of Box 2. These equations and the corresponding algorithm are identical to the case of nucleation via homogeneous transformation.

4a. Kinetic nucleation criterion Eq. (117) can be found immediately.

4b. Nucleus volume can be found from Eq. (101).

5. In contrast to the nucleation via homogeneous transformation, there is no necessity to check condition  $X_\Sigma > 0$  for  $r$  slightly greater than  $r_c$  because based on the procedure of finding the critical nucleus it is always the case, and the nucleus can grow. If the inequality in Eq. (98) (or in Eq. (80)) is met, then the nucleus is mechanically unstable and it can both expand like a balloon and/or grow due to sublimation.

10. Numerical results for energetic crystal HMX

Calculations were produced for the material parameters listed in Table 1, which are close to the data for the high-temperature  $\delta$  phase of the organic nitramine octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) energetic crystal, if known.

The molar entropy change for sublimation of HMX is  $\Delta S = S_g - S_s$ , where  $S_g, S_s$  is an entropy of gas, and solid states are given by equations

$$S_g = R \left( a_1 \ln \theta + a_2 \theta + \frac{a_3}{2} \theta^2 + \frac{a_4}{3} \theta^3 + \frac{a_5}{4} \theta^4 + a_7 \right), \quad (123)$$

$$S_s = R \left( b_1 \ln \theta + b_2 \theta + \frac{b_3}{2} \theta^2 + \frac{b_4}{3} \theta^3 + \frac{b_5}{4} \theta^4 + b_7 \right). \quad (124)$$

Here,  $a_i$  are the ideal gas coefficients for HMX, and  $b_i$  are the  $\delta$ -HMX coefficients given in Tables 2 and 3 (Lyman et al., 2002). Since the change in entropy weakly depends on temperature in the range of interest, for convenience we will use constant value  $\Delta S = 257.972$  J/K mole, which results in  $\Delta s = \Delta S/M = 1.031$  J/K kg, shown in Table 1.

Table 1  
Materials properties used in calculation.

$\theta_0$	$p_0$	$\Delta_s$	$\Delta \psi_0^\theta$	$\rho_s$	$M$	$K$	$\sigma_y^m$	$\sigma_y^r$	$\nu$	$\theta_m$	$r_m$
K	bar	J/kg	J/g	g/cm <sup>3</sup>	g/mole	GPa	MPa	MPa	-	K	nm
298.15	1	1.031	379.515	1.71	250.151	15	2.6	37	0.3	550	0.3

**Table 2**  
HMX ideal gas coefficients in Eq. (105).

$a_1$	7.97867853E+00
$a_2$	7.10845227E-02
$a_3$	7.78579787E-05
$a_4$	-1.61080531E-07
$a_5$	7.08780862E-11
$a_7$	7.29783372E-01

**Table 3**  
8-HMX coefficients in Eq. (106).

$b_1$	1.82078760E-05
$b_2$	1.40744490E-01
$b_3$	-1.52499203E-04
$b_4$	1.82841750E-07
$b_5$	-1.25215957E-10
$b_7$	1.98461992E+00

To take into account the temperature-dependence of the mechanical properties in an approximate way, we will proceed as follows. Temperature dependence of  $\sigma_y$  is scaled by the temperature dependence of  $\mu$  – i.e.,  $\mu/\sigma_y$ , as well as Poisson's ratio, and consequently  $\alpha$  are weakly temperature dependent. Below, we will use simple approximation  $\sigma_y = \sigma_y^r + (\sigma_y^m - \sigma_y^r) (\theta - \theta_r)/(\theta_m - \theta_r)$  for  $\theta < \theta_m$  and  $\sigma_y = \sigma_y^m$  for  $\theta > \theta_m$ , where  $\theta_m$  and  $\theta_r$  are the melting and room temperatures and  $\sigma_y^m$  and  $\sigma_y^r$  are the yield strengths at these temperatures. At very fast heating and/or loading, when material still remains solid above the melting temperature during time exceeding the gas bubble nucleation time, we will use  $\bar{\sigma}_y = \sigma_y^m$ ; at slow heating  $\bar{\sigma}_y = 0$ . In the latter case, one has to take into account pressure dependence of the melting temperature,  $\theta_m(\sigma)$ . In the former case, taking into account indeterminacy in melting temperature at very high heating rates and in the value  $\bar{\sigma}_y$ , pressure dependence of the melting temperature can be neglected. We will focus on fast heating and use  $\bar{\sigma}_y = \sigma_y^m$ . For simplicity and to obtain generic equations, we neglect strain-rate dependence of the yield strength. It is unknown in most cases under such extreme regimes and its inclusion unreasonably complicates the solution of the problem.

Solution depends on the following dimensionless parameters. For the intermediate stresses, they are

$$\frac{\sigma}{\sigma_y^r}; \frac{\theta}{\theta_0}; \frac{\theta_m}{\theta_0}; \frac{\sigma_y^m}{\sigma_y^r}; \frac{\mu}{\sigma_y^r}; \frac{p_0}{\sigma_y^r}; \nu; \frac{\rho_s \Delta s \theta_0}{\sigma_y^r}; \frac{\rho_s \Delta \psi \theta_0}{\sigma_y^r}; \frac{L \theta_0}{\sigma_y^r} = \frac{\rho_s R \theta_0}{M \sigma_y^r}; \quad (125)$$

$$\frac{\Gamma}{\left( (\sigma_y^r)^2 k \theta_0 \right)^{1/3}}. \quad (126)$$

The last term in Eq. (125) characterizes the dimensionless gas pressure when volume during sublimation does not change. Eq. (126) is the ratio of two parameters with dimension of the length:  $\Gamma/\sigma_y^r$  and  $(k\theta/\sigma_y^r)^{1/3}$ .

For small stresses, the yield strength is not a parameter and the list of dimensionless parameters is as follows:

$$\frac{\sigma}{E}; \frac{\theta}{\theta_0}; \frac{p_0}{E}; \nu; \frac{\rho_s \Delta s \theta_0}{E}; \frac{\rho_s \Delta \psi \theta_0}{E}; \frac{L \theta_0}{E} = \frac{\rho_s R \theta_0}{ME}; \frac{\Gamma}{(E^2 k \theta_0)^{1/3}}. \quad (127)$$

For large stresses, parameters in Eq. (125) are valid, but the additional length  $r_{min}$  appears. Thus, instead of Eq. (126) we obtain two dimensionless lengths:

$$\frac{\Gamma}{r_{min} \sigma_y^r}; \frac{k \theta_0}{r_{min}^3 \sigma_y^r}. \quad (128)$$

### 10.1. Sublimation from the plane external surface

To check the validity of the thermodynamic data that we use, we consider the simplest case of sublimation from the plane external surface under constant gas pressure  $p_g$ . We can neglect elastic energy and use the thermodynamic driving force for interface propagation from Eq. (46) for an infinite radius of a sphere:

$$X_\Sigma = -p_g \left( \frac{1}{a} - 1 \right) - \rho_s (\Delta \psi_0^\theta - \Delta s (\theta - \theta_0)) + L \theta \ln \left( \frac{p_0}{p_g} \right) + L \theta \ln \left( \frac{\theta}{\theta_0} \right). \quad (129)$$

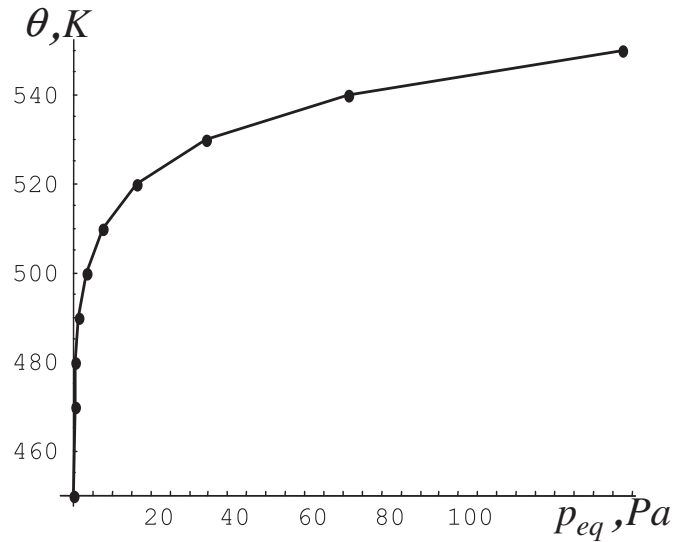


Fig. 5. Dependence of the equilibrium sublimation pressure on temperature for the plane surface for energetic crystal HMX. Curve corresponds to Eq. (130) and dots are experimental points collected in Lyman et al. (2002).

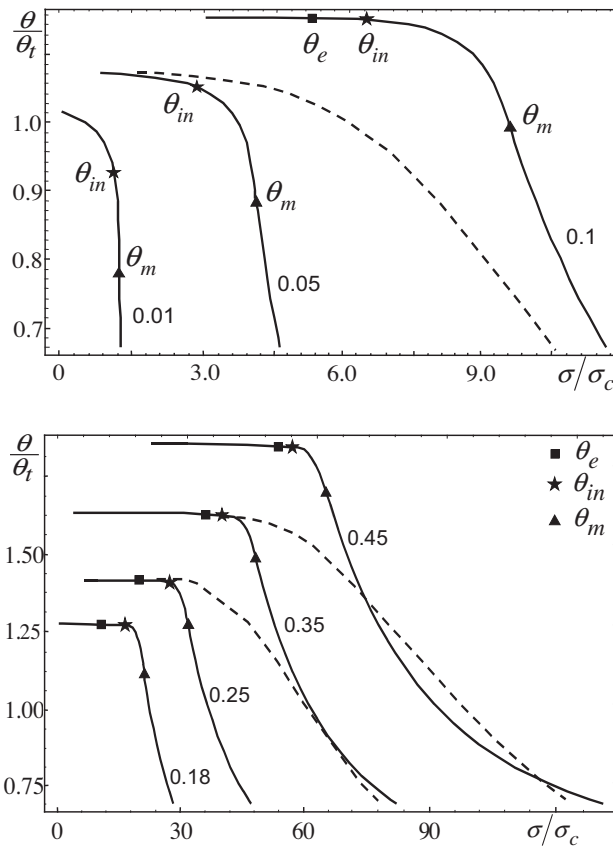


Fig. 6. Relationships between sublimation temperature and tensile pressure for nucleation via homogenous transformation for various surface energies (shown near curves). Below temperature  $\theta_m$ , radius of nucleus  $r_{sc} = r_{min}$ . Below temperature  $\theta_m$ , the nucleus is mechanically unstable and expands spontaneously. Above temperature  $\theta_e$ , deformation of the nucleus is elastic. Dashed lines are for nucleation via interface propagation.

Surface energy disappeared from the expression for  $X_\Sigma$ . Since gas pressure is low, the first term representing mechanical work can be neglected. Because interface exists initially, there is no necessity in the critical nucleus, and we can find the condition for solid–gas thermodynamic equilibrium from equation  $X_\Sigma = 0$ ; i.e.,

$$L\theta \ln \left( \frac{p_0}{p_g} \right) = \Delta\psi_0^\theta - \Delta s(\theta - \theta_0). \tag{130}$$

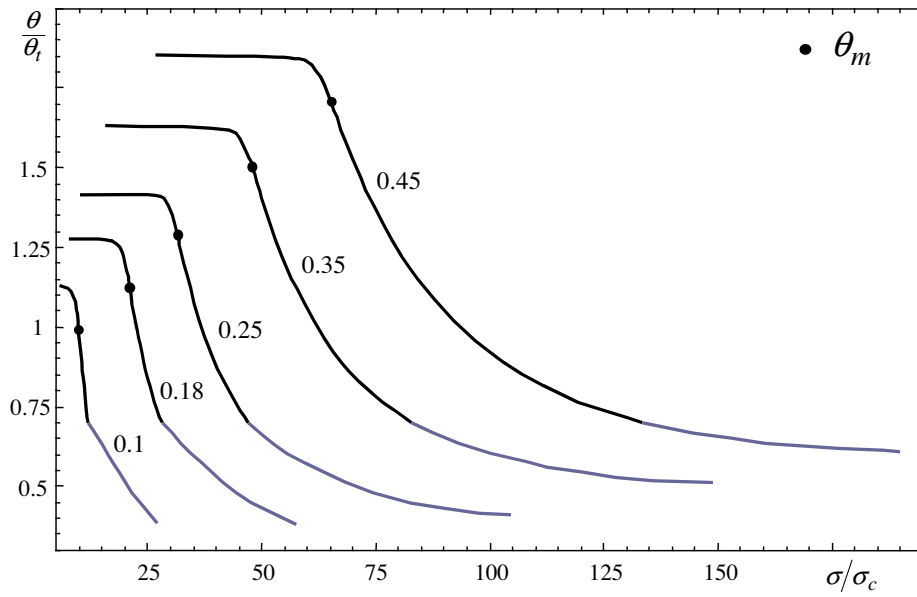


Fig. 7. Relationships between sublimation temperature and tensile pressure for nucleation via homogenous transformation for various surface energies (shown near curves) with temperature dependent  $\sigma_y$ .

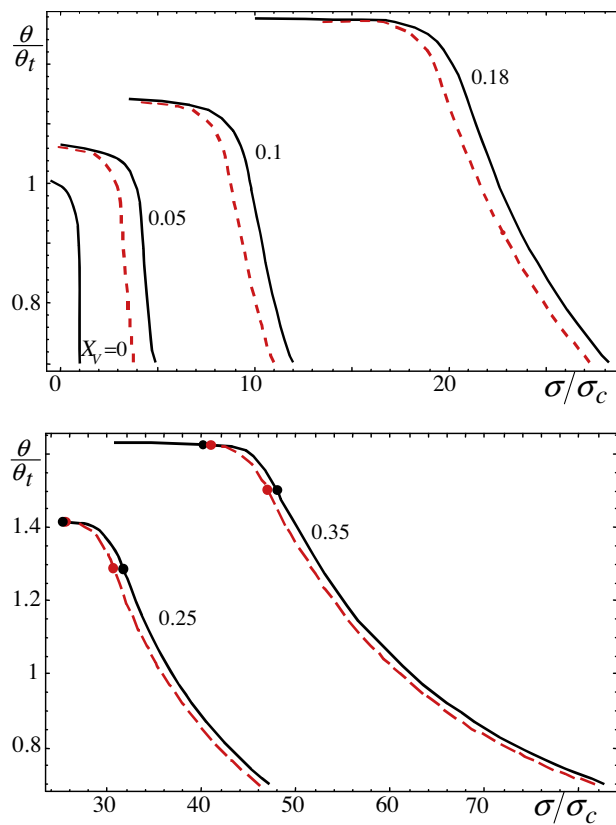
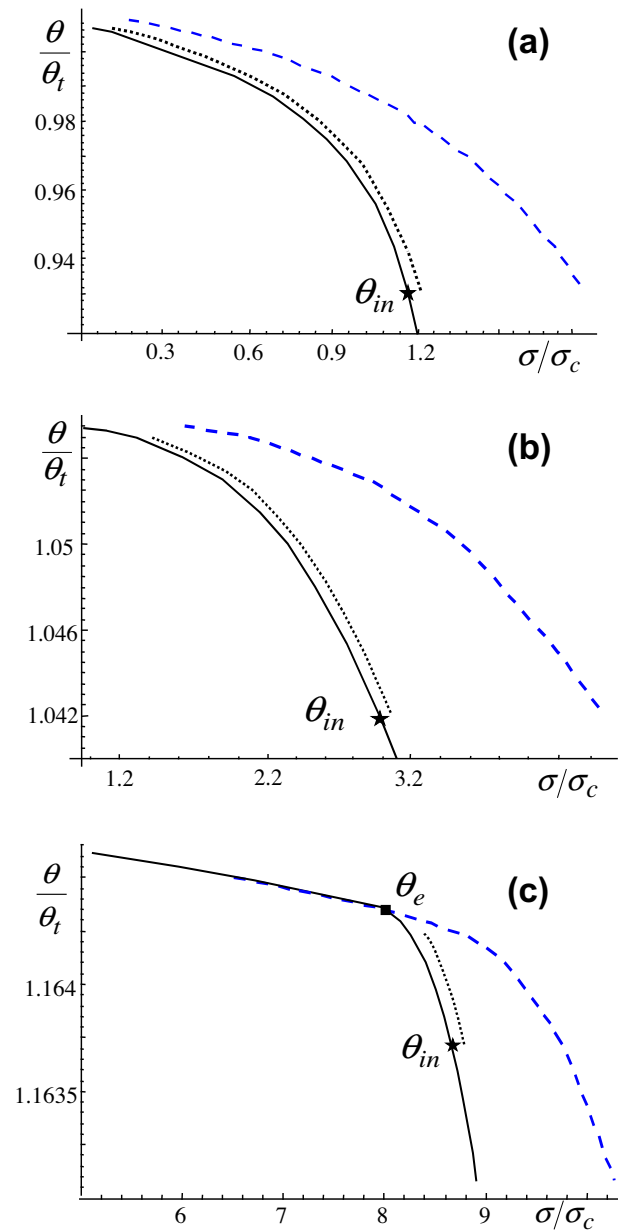


Fig. 8. Relationships between sublimation temperature and tensile pressure for nucleation via homogenous transformation for various surface energies (shown near curves). Dashed lines correspond to  $\sigma_y = 0$ , i.e. to cavitation in liquid.

The relationship between equilibrium sublimation pressure and temperature determined from Eq. (130) is presented in Fig. 5; it perfectly coincides with experimental curve presented in Lyman et al. (2002).



**Fig. 9.** Relationships between sublimation temperature and tensile pressure for nucleation via interface propagation (dashed blue line) and for nucleation via homogeneous transformation (solid black line) for  $\Gamma = 0.01$  (a),  $\Gamma = 0.05$  (b) and  $\Gamma = 0.12$  (c). For nucleation via homogeneous transformation and above temperature  $\theta_{in}$ , nucleus cannot grow after appearance. Parameters have to be increased to value corresponding to dotted line for spontaneous nucleus growth. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

## 10.2. Nucleation of a gas bubble via homogeneous transformation

### 10.2.1. Kinetic condition for sublimation

The kinetic relationships between sublimation temperature  $\theta$  and tensile pressure  $\sigma$  for nucleation via homogeneous transformation are shown in Figs. 6–9 for various surface energies.

Sublimation temperature is normalized by the thermodynamic equilibrium sublimation temperature  $\theta_t = 784.12$  K (see Eq. (76)) and sublimation pressure is normalized by the cavitation pressure  $\sigma_c = 15.77$  MPa (see Eq. (15)), calculated based on the minimal yield strength  $\sigma_y^m$ . We focus on the surface energy  $\Gamma$  smaller than typical equilibrium values for a solid–gas interface of  $1 \text{ J/m}^2$ . Under tensile stress, a solid is always thermodynamically unstable with respect to gas. It is known from the phase-field theory of phase transformation that surface energy decreases with the growing driving force for transformation and approaches zero when the parent phase completely loses its thermodynamic stability (see Chu et al. (2000) and Levitas et al. (2003)).

Based on the shape, there are three main regions on the curves in Fig. 6. At high temperature ( $\theta > \theta_e$ , region I) and low pressure, sublimation temperature is practically independent of  $\sigma$  because the change in volume is very small and stress

$\sigma$  does not contribute to the driving force. This region is described by an analytical Eq. (117) for elastic straining, which is the same for the nucleation via interface propagation. The temperature above which this equation is applicable is designated in Fig. 6 as  $\theta_e$ .

At higher stresses  $\sigma$  and lower temperature ( $\theta_m \leq \theta \leq \theta_e$ , region II), sublimation temperature strongly decreases with the increase of  $\sigma$ , until the magnitude of  $\frac{d\theta}{d\sigma}$  reaches maximum. The main reason for the strong effect of  $\sigma$  is that for  $\Gamma = 0$  the external pressure  $\sigma$  cannot exceed the cavitation pressure  $\sigma_c$ , which characterizes the maximum possible plastic resistance of the solid sphere. That is why the smaller the surface energy  $\Gamma$  is, the stronger the effect of the tensile pressure on the sublimation temperatures. Points  $\theta_m$  in the plots designate temperatures below which the radius of the critical nucleus in the reference configuration  $r_{0n} = r_{min}$ . It follows from Fig. 6 that this point corresponds to  $\frac{d^2\theta}{d\sigma^2} = 0$  – i.e., the magnitude of the rate of change of sublimation temperature  $\frac{d\theta}{d\sigma}$  reaches maximum. This maximum is related to the dependence of the volumetric expansion  $a_n$  on stress  $\sigma$  (Fig. 10), which shows three branches.

The expansion  $a_n$  is very close to 1 in the elastic region for  $\sigma < \sigma_e$ , then it grows very fast with increasing  $\sigma$  and reaches its maximum for the stress  $\sigma$  corresponding to  $r_{min}$ . Then  $a_n$  sharply decreases but less sharply than it increases for  $r_{0n} > r_{min}$ . These three branches in the  $a_n(\sigma)$  curve are reflected in the  $\theta$ – $\sigma$  sublimation curve: the effect of pressure is negligible for  $\theta > \theta_e$ , then it drastically increases,  $|\frac{d\theta}{d\sigma}|$ , and reaches maximum for  $r_{0n} = r_{min}$ ; then it decreases ( $\theta < \theta_m$  region III). Such a similarity in dependencies is understandable, because the larger  $a_n$  is, the larger is the contribution of the stress  $\sigma$  to the thermodynamic driving force. Also, a large value for  $a_n$  results in a large  $r_{nc}$  even for the smallest  $r_{0n} = r_{min}$  and for the relatively large  $\Gamma$  increase in tensile pressure necessary for nucleation. The maximum change in volume  $a_n$  has the order of magnitude 100 (for  $\Gamma = 0.05$ ) to 1000 (for  $\Gamma = 0.18$ ). Note that for all three branches of the variation of  $a_n(\sigma)$ , the radius of the critical nucleus in the actual configuration  $r_{nc}$  decreases with increasing external stress (Fig. 11).

However, while a nucleus can appear from the kinetic point of view at parameters corresponding to the  $\theta$ – $\sigma$  curve, the driving force for the interface propagation  $X_\Sigma < 0$  along this curve. This means that growth is impossible – i.e., it is a subcritical nucleus in the traditional sense. After nucleation, it is necessary to slightly increase  $\theta$  or  $\sigma$  to initiate growth of this nucleus (see dotted line in Fig. 9), which may happen due to thermal fluctuations. Thus, this nucleus is “almost critical”.

### 10.2.2. Mechanical instability of a nucleus

To better understand the mechanical instability of the nucleus, we will consider variation of gas pressure  $p_g$  and resistance to the hole expansion (i.e.,  $\frac{2\Gamma}{r} - \sigma_n$ ) versus  $a$  for two cases. The first one, which we used to determine the relationship

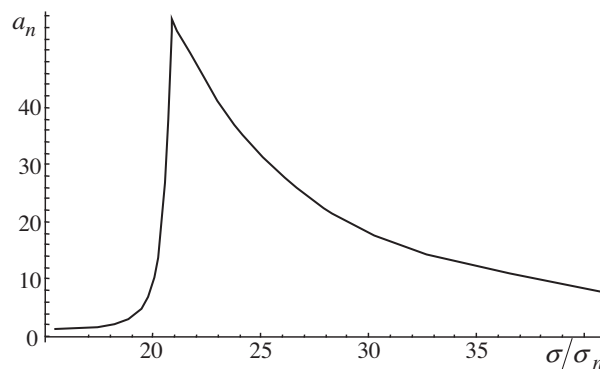


Fig. 10. Dependence of volumetric expansion  $a_n$  on  $\sigma_n$  for nucleation via homogeneous transformation and  $\Gamma = 0.18 \text{ J/m}^2$ .

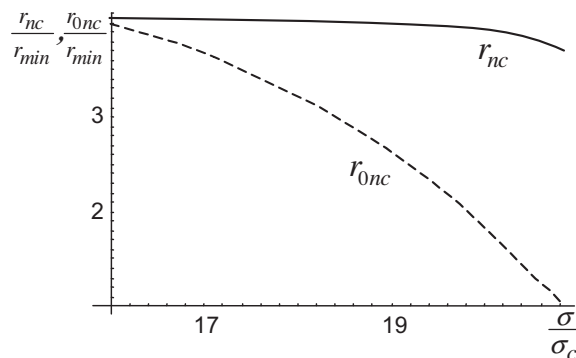


Fig. 11. Radiuses of the critical nucleus in the reference and deformed configuration versus tensile pressure for nucleation via homogeneous transformation and  $\Gamma = 0.18 \text{ J/m}^2$ .

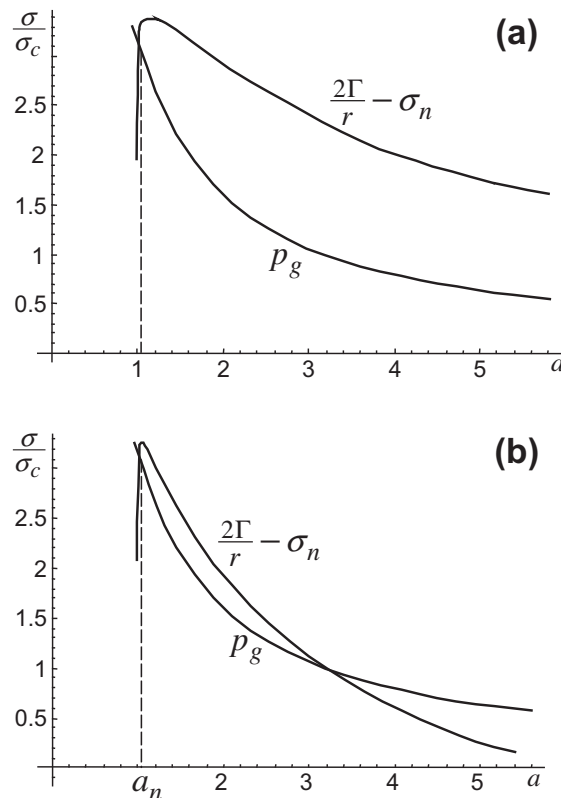
$a_n(\sigma, \theta)$  based on the equilibrium Eq. (28) with the expression for the driving force in Eq. (29), is determined for the variable size of the critical nucleus  $r_{0n}$  and presented in Fig. 12a and Fig. 13a. For the second case, gas pressure  $p_g$  and resistance to the hole expansion  $\frac{2\Gamma}{r} - \sigma_n$  are determined versus  $a_n$  for the found critical radius in the reference configuration  $r_{0n}$ , which is suitable for the analysis of the mechanical instability without further sublimation (Fig. 12b and Fig. 13b).

Numerical analysis shows that for prescribed stress  $\sigma$  and temperature  $\theta$  that satisfy the nucleation criterion (i.e., belong to  $\theta - \sigma$  plots in Figs. 6 and 7), and corresponding  $r_{0nc}$ , Eq. (79) (or Eq. (78)) that determines the critical instability condition has two roots (Fig. 12b and Fig. 13b).

For small  $\sigma$ , the smaller root coincides with the single root of the equilibrium Eqs. (28) and (29) when  $\sigma$  and  $\theta$  are fixed and  $r_{0nc}$  varies (Fig. 12a and Fig. 13a) – i.e., for the case when we try to find  $a_n$  for a critical nucleus. One has to focus on the coinciding root only. For small  $\sigma$  and  $a$ , the curve  $\sigma_n(a) + \frac{2\Gamma}{r_{0nc}(a)^{1/3}}$  is above the curve  $p_g(a)$  for  $a$  greater than the root  $a_n$  of Eqs. (28) and (29) (at least in some range of  $a > a_n$ , (see Fig. 12b) – i.e., mechanical equilibrium is stable.

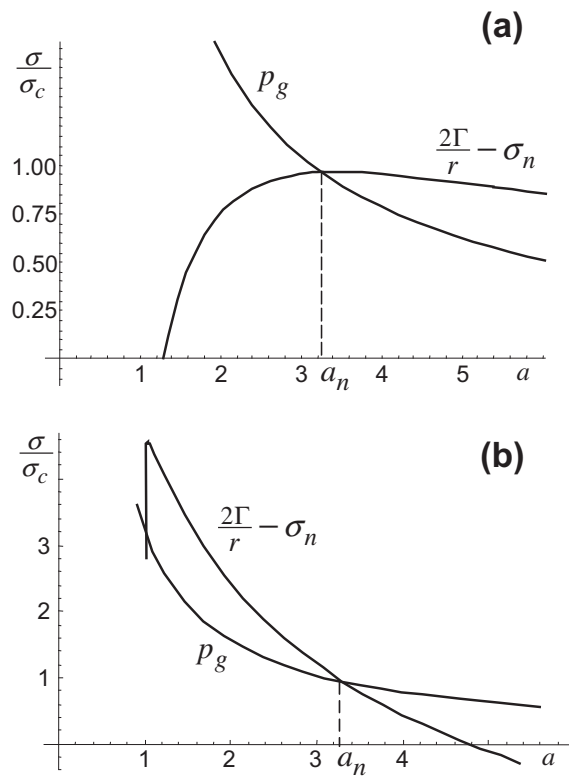
With increasing  $\sigma$ , the two roots of Eq. (79) move toward each other, then coincide, after which they exchange places. That means that the larger root coincides with the single root of the equilibrium Eqs. (28) and (29) when  $r_{0nc}$  varies (Fig. 12a and Fig. 13a), and that the larger root has to be considered only. For this root, the curve  $\sigma_n(a) + \frac{2\Gamma}{r_{0nc}(a)^{1/3}}$  is below the curve  $p_g(a)$  for  $a$  greater than the root  $a_n$  of Eqs. (28) and (29) (Fig. 13b), and mechanical equilibrium is unstable – i.e., a small fluctuational increase in  $a$  will lead to unlimited hole expansion. Thus, the equality of the two roots is an alternative condition to determine the critical value of  $\sigma$  corresponding to the stability limit. Geometrically, the equality of the two roots in Fig. 12b and Fig. 13b also means the touching of both curves  $\sigma_n(a) + \frac{2\Gamma}{r_{0nc}(a)^{1/3}}$  and  $p_g(a)$ , which in fact corresponds to the equality in Eq. (80). For larger  $\sigma$ , the smaller root becomes smaller than 1 and then disappears. For  $a \gg 1$ , Eq. (81) shows one root only (while this is not a proof that the second root disappears, because it just may not satisfy condition  $a \gg 1$ , it indeed disappears).

For all examples, we obtained that, with increasing  $\sigma$ , first the mechanical instability condition is met and then the condition  $r_{on} = r_{min}$  is fulfilled (Fig. 6). When condition  $r_{on} = r_{min}$  is met, equilibrium condition Eq. (28), which we use to find the critical nucleus, coincides with Eq. (79), which we use to study stability. They have one root and the system is mechanically unstable (Fig. 13). Note that because during the nucleation via homogeneous transformation the nucleus radius  $r_{on}$  in the reference configuration is fixed, Fig. 12b and Fig. 13b (rather than Fig. 12a and Fig. 13a) seem to be appropriate figures to analyze pressure variation during the homogeneous sublimation process. Then, for the case in Fig. 13b, a question may arise: how can the expansion  $a_n$  be reached if for all  $a < a_n$  pressure in the gas is smaller than resistance to expansion due to  $\sigma_n$  and



**Fig. 12.** Variation of gas pressure  $p_g$  and resistance to the hole expansion  $\frac{2\Gamma}{r} - \sigma_n$  versus  $a$ : (a) for the case, which was considered to determine the relationship  $a_n(\sigma, \theta)$  based on the equilibrium Eq. (28) with the expression for the driving force in Eq. (29), i.e. for the variable size of the critical nucleus  $r_{0n}$ ; (b) for the fixed critical radius in the reference configuration  $r_{0n}$ , in order to analyze the mechanical instability. Since the curve  $\sigma_n(a) + \frac{2\Gamma}{r_{0nc}(a)^{1/3}}$  is above the curve  $p_g(a)$  for  $a > a_n$  (at least in some range of  $a > a_n$ ), mechanical equilibrium is stable.





**Fig. 13.** Variation of gas pressure  $p_g$  and resistance to the hole expansion  $\frac{2\Gamma}{r} - \sigma_n$  versus  $a$ : (a) for the case, which was considered to determine the relationship  $a_n(\sigma, \theta)$  based on the equilibrium Eq. (28) with the expression for the driving force in Eq. (29), i.e. for the variable size of the critical nucleus  $r_{0n}$ ; (b) for the fixed critical radius in the reference configuration  $r_{0n}$ , in order to analyze the mechanical instability. Since the curve  $p_g(a)$  is above the curve  $\sigma_n(a) + \frac{2\Gamma}{r_{0n}(a)^2}$  for  $a > a_n$ , mechanical equilibrium is unstable.

surface tension? The answer is that for the transformation process, Eq. (12) should be used, in which pressure in the transforming region is not determined by the equation of state of a gas but varies from the initial tensile pressure in solid to the pressure in gas, and the surface energy varies from zero to its final value. That means that Fig. 12b and Fig. 13b cannot be used for analysis of the pressure variation during the sublimation process. The final point  $a_n$  only, in which the equation of state in the transforming region is a gas equation of state, and surface energy reaches its final value, corresponds to the theory.

### 10.3. Nucleation of a gas bubble via interface propagation and the final choice of the critical nucleus

The relationships  $\theta - \sigma$  between tensile sublimation pressure and temperature for nucleation via interface propagation are shown in Figs. 6 and 9, for various surface energies. The following scenarios are considered.

1. For temperature above  $\theta_e$  (for those  $\Gamma$  for which  $\theta_e$  exists), kinetic curves for nucleation via interface propagation via homogeneous transformation coincide, i.e. this nucleus is indeed the critical one. Without change in external stresses, the nucleus can appear and immediately grow.
2. In the temperature range  $\theta_e > \theta > \theta_{in}$ , the nucleus can appear via homogeneous transformation, but because for this nucleus  $X_\Sigma < 0$ , it cannot grow. If this nucleus does not disappear due to the reverse transformation (see below), then it represents a metastable rather than the critical gas bubble. If stress or temperature slightly increase fluctuationaly or deterministically up the values corresponding to the dashed lines in Fig. 9, then the nucleus becomes critical and can grow.
3. For temperatures  $\theta < \theta_{in}$ , the equilibrium of the gas nucleus that appeared via homogeneous transformation is mechanically unstable. That means that for any fluctuational expansion, the gas pressure is larger than the value that plastic sphere can withstand. Thus, while this nucleus cannot grow due to the sublimation (since  $X_\Sigma < 0$ ) – i.e., it is a subcritical nucleus in the traditional sense – it expands like a balloon. After the radius of the nucleus in the actual configuration exceeds the critical radius  $\bar{r}_c$  determined from the condition  $X_\Sigma = 0$ , sublimation can occur instead of or along with mechanical expansion. To our best knowledge, this is the only known example of the mechanism of transformation of the subcritical nucleus into the supercritical nucleus.

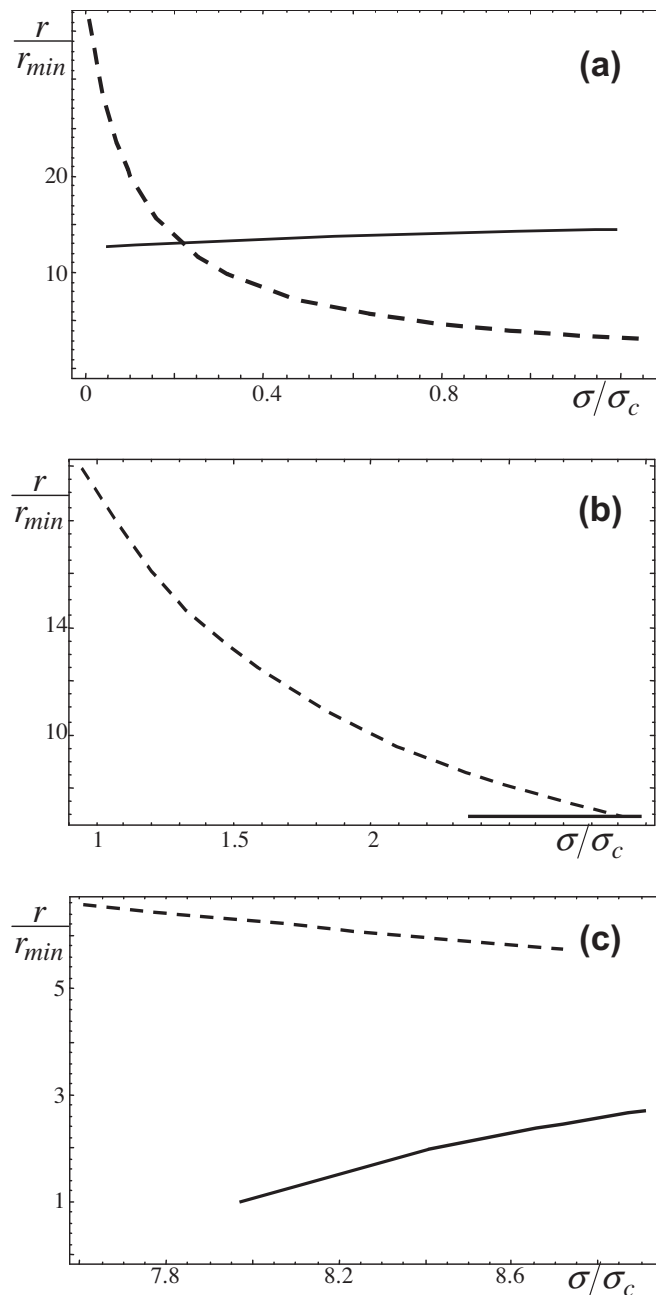
Note that  $\bar{r}_c$  is not equal to the critical radius at the  $\theta - \sigma$  curve for the interface propagation for the same temperature  $\theta$  because the stresses and radius of the nucleus in the reference configuration are different. Also, there is no sense in

continuing the curves  $\theta$ - $\sigma$  for nucleation via interface propagation much below the temperatures corresponding to mechanical instability  $\theta_{in}$  because it deviates significantly from the curve for homogeneous transformation at which nucleation and growth are possible.

We would like to mention that while the process that corresponds to the smaller sublimation pressure for the same temperature or smaller sublimation temperature for the same pressure are more probable, processes corresponding to the higher curve are not excluded. The higher pressure (or temperature) process can occur in experiments, (a) if the characteristic time of pressure (or temperature) growth is significantly shorter than the characteristic time of the lower-pressure (low-temperature) process, (b) if the corresponding kinetic criterion for the higher-pressure (or higher-temperature) process is satisfied, and (c) if the process corresponding to the upper curve is faster than that to the lower curve.

10.4. Reverse transformation and residual void

Detailed treatment of the problems of reverse transformation and retaining a residual void after external stress is completely released and temperature reduces to some steady temperature (for example room temperature) will be performed



**Fig. 14.** The radius of the hole that will not close under action of surface tension (dashed line) and the radius of the critical nucleus in the actual configuration versus  $\sigma$ : (a) for  $\Gamma = 0.01 \text{ J/m}^2$ , for stresses  $\sigma/\sigma_c > 0.254$  the void will not collapse; (b) for  $\Gamma = 0.05 \text{ J/m}^2$ , for stresses  $\sigma/\sigma_c > 2.9$  the void will not collapse, because  $r_h > r_c$ ; (c) for  $\Gamma = 0.12 \text{ J/m}^2$ , there is no guarantee that the void will not close.

elsewhere. This treatment requires solution of the problem of unloading and reverse plastic flow of a sphere with the hole reduced by both plastic flow and solidification of a gas, after expanding flow. Here, we just discuss possible options and make a rough estimate.

The main concern here is for a nucleus that appeared via homogeneous nucleation above the temperature corresponding to mechanical instability  $\theta_{in}$ , when external stress  $\sigma$  is kept constant. Just after the appearance of a nucleus via homogeneous transformation, the driving force for the interface motion for the reverse transformation  $X_{\Sigma}^r = -X_{\Sigma} > 0$  because it depends on the parameters across the interface at the given instant only. Thus, the solidification of gas starts. During solidification, gas pressure and void radius in the actual configuration reduce, and tensile stresses at the internal surface of a solid  $\sigma_n = -p_g + 2\Gamma/r$  increase. Initially,  $\sigma > \sigma_n$ , then solid material undergoes elastic unloading, and then, when  $\sigma_n$  is getting larger than  $\sigma$  and the difference reaches some critical value to satisfy the plasticity criterion, material starts plastic flow in the opposite direction, trying to close the hole. The driving force for the interface propagation for reverse transformation  $X_{\Sigma}^r$  has the same expression as  $X_{\Sigma}$  but with a different expression for elastic energy.

Assuming that the entire gas solidifies (i.e.,  $p_g = 0$ ), we distribute solidified volume  $V_{sc}$  evenly over the hole surface and determine the radius of the new hole  $r_h$  in the actual configuration;  $r_h > 0$  because of plastic expansion during nucleation. It follows from the volume balance that  $r_h = r_{onc}(a_n - 1)^{1/3}$ . Taking the solution for elastic sphere without internal stresses (Hill, 1950) with the stress at the internal surface  $\sigma_n = 2\Gamma/r_h$ , we obtain that the von Mises (and Tresca) plasticity condition  $\sigma_n - \sigma_{\theta} = \sigma_y$  at the internal surface is satisfied if  $1.5(2\Gamma/r_h - \sigma) = \sigma_y$ . Thus, the radius of the hole that will definitely not close is  $r_h = 6\Gamma/(3\sigma + 2\sigma_y)$  or larger because the condition for the initiation of the reverse plastic flow is not satisfied. This radius is plotted in Fig. 14 as dashed lines.

Solid lines in these figures correspond to the radius of the critical nucleus in the actual configuration vs.  $\sigma$ . For example, for  $\Gamma = 0.05 \text{ J/m}^2$ ,  $r_h > r_c$  for stresses  $\sigma/\sigma_c > 2.9$ , corresponding to the intersection point. This means that for such stress the void will not collapse if nucleation occurred at these stresses or at higher stresses but then stress dropped to the determined value. For  $\Gamma = 0.12 \text{ J/m}^2$ , these two curves do not intersect up to the stresses corresponding to nucleation stress at  $\theta = \theta_{in}$ . In this case, we cannot guarantee that the void will not close. Our main result here is that for some surface energies there is a metastable void that cannot grow or collapse.

Note that if  $\theta_{in}$  is greater than the melting temperature, then even when the nucleus cannot grow due to sublimation its internal surface can melt. Also, instead of reverse transformation gas–solid, transformation gas–liquid may occur. On the other hand, let us consider temperature below  $\theta_{in}$  and melting temperature and assume that mechanical instability did not start before reverse transformation started. For large stresses and  $a_n$ ,  $r_h = r_{onc}(a_n - 1)^{1/3} \simeq r_{onc}a_n^{1/3} = r_c$  (i.e., surface tension practically does not increase due to gas solidification) when the pressure in the gas is low – i.e.,  $\sigma_n$  does not increase significantly due to solidification and reverse plastic flow will not start even for large  $\Gamma$  we have a situation leading to a metastable void.

## 11. Appearance of the critical nucleus during the evaporation of liquid under tension

We are not aware of a solution to this problem in the literature, but due to lack of plastic irreversibilities it does not represent basic problems, since classical nucleation theory is applicable. The nontrivial parts are related to the fact that we pay special attention to the case in which the radius of the critical nucleus is smaller than  $r_{min}$  and that mechanical instability takes place for this case as well. There is no difference between nucleation via homogeneous transformation and via the interface propagation. Formally, all equations can be obtained from equations for nucleation via homogeneous transformation in an elastoplastic material (Box 1) but substituting  $\sigma_n$  with  $\sigma$  and putting  $W = \sigma(a_n - 1)$ . The resulting equations are given in Box 3.

### Box 3. Equations for nucleation of a spherical gas bubble in liquid

#### I. Intermediate stresses $\sigma$

##### 1. The mechanical equilibrium condition at the interface

$$p_g = -\sigma + \frac{2\Gamma}{r_{nc}}; \quad p_g = \frac{L\theta}{a} \quad \frac{2\Gamma}{r_{nc}} = \frac{X_v}{a_n} \Rightarrow \sigma = \frac{1}{a_n}(X_v - L\theta). \quad (131)$$

##### 2. Volumetric driving force for evaporation

$$X_v = \sigma(a_n - 1) - \rho_s \Delta\psi \quad \text{with} \quad (132)$$

##### 2.1. Change in free energy

$$\rho_s \Delta\psi = \rho_s (\Delta\psi_0^\theta - \Delta s(\theta - \theta_0)) - L\theta \ln \left( \frac{a_n p_0}{L\theta_0} \right) - \frac{\sigma^2}{2K}. \quad (133)$$

**3. Nucleus volume in the reference configuration**

$$V_{n0c} = \frac{32\pi a^2 \Gamma^3}{3X_v^3}. \quad (134)$$

**4. Activation energy and kinetic nucleation criterion for evaporation**

$$Q = \frac{16\pi a^2 \Gamma^3}{9X_v^2} = 80k\theta. \quad (135)$$

**II. Large stresses  $\sigma$  and minimal radius of the critical nucleus  $r_{0n} = r_{min}$**

**1. The mechanical equilibrium condition at the interface**

$$\sigma = \frac{2\Gamma}{r_{min} a_n^{1/3}} - \frac{L\theta}{a_n}. \quad (136)$$

**2. Volumetric driving force for sublimation**

$$X_v = \sigma(a_n - 1) - \rho_s(\Delta\psi_0^\theta - \Delta s(\theta - \theta_0)) + L\theta \ln\left(\frac{a_n p_0}{L\theta_0}\right) + \frac{\sigma^2}{2K}. \quad (137)$$

**3. Activation energy and kinetic nucleation criterion**

$$Q = -X_{PT} = (4\pi)^{1/3} 3^{2/3} \Gamma V_{min}^{2/3} a_n^{2/3} - X_v V_{min} = 80k\theta. \quad (138)$$

**III. Small stresses  $\sigma$  and  $a_n \simeq 1$**

**1. Volumetric driving force for evaporation**

$$X_v = -\rho_s(\Delta\psi_0^\theta - \Delta s(\theta - \theta_0)) + L\theta \ln\left(\frac{p_0}{L\theta_0}\right) + \frac{\sigma^2}{2K}. \quad (139)$$

**2. Radius of the critical nucleus**

$$r_c = -\frac{2\Gamma}{\rho_s \Delta\psi_E}. \quad (140)$$

**3. Kinetic nucleation criterion**

$$\frac{\sigma^2}{2K} = \left(\frac{\pi\Gamma^3}{15k\theta}\right)^{1/2} + \rho_s(\Delta\psi_0^\theta - \Delta s(\theta - \theta_0)) - L\theta \ln\left(\frac{p_0}{L\theta_0}\right). \quad (141)$$

**B. Growth conditions**

**1. By mechanical instability**

$$p_g(a_n + \delta) > \sigma + \frac{2\Gamma}{r_{0nc}(a_n + \delta)^{1/3}} \quad \text{for } \delta > 0. \quad (142)$$

**2. By further evaporation**

$$X_v^f > 0 \Rightarrow \text{growth} \quad (143)$$

Substituting the equation for the volumetric driving force for evaporation Eq. (132) into equilibrium equation at the interface Eq. (131) we obtain

$$\sigma + \rho_s(\Delta\psi_0^\theta - \Delta s(\theta - \theta_0)) - \frac{\sigma^2}{2K} = L\theta \left( \ln\left(\frac{a_n p_0}{L\theta_0}\right) - 1 \right) \quad (144)$$

with the solution

$$a_n = \frac{L\theta_0}{p_0} \exp\left[\left(\rho_s(\Delta\psi_0^\theta - \Delta s(\theta - \theta_0)) + \sigma - \frac{\sigma^2}{2K}\right) / (L\theta) + 1\right]. \quad (145)$$

Substitution of Eqs. (132) and (145) into the kinetic nucleation criterion Eq. (135) will lead to the desired kinetic  $\theta$ - $\sigma$  relationships. Eq. (134) determines the volume of the critical nucleus in the reference configuration.

Equations for the case with large stresses and the minimal radius of the critical nucleus  $r_{0n} = r_{min}$  are presented in Section II of Box 3. The only difference in comparison with sublimation is the substitution of  $\sigma$  instead of  $\sigma_n$ . Equations for the case with small volumetric expansion ( $a_n \simeq 1$ ) are given in Section III of Box 3. The only difference in comparison with sublimation is the substitution of the elastic energy of a solid with void  $\frac{3(1-\nu)}{4E}\sigma^2$  with the elastic energy of liquid  $\sigma^2/2K$ . Similar to our statement after Eq. (41), the neglected difference  $a_n - 1$  in the energy of gas should be negligible in comparison with elastic energy  $\sigma^2/2K$ . Otherwise, we have to use  $\ln\left(\frac{a_n p_0}{L\theta}\right) \simeq \ln\left(\frac{a_n p_0}{L\theta}\right) + a_n - 1$  and find  $a_n$  from the equilibrium condition. The final kinetic  $\theta$ - $\sigma$  relationship is getting complicated in this case.

Conditions for mechanical instability Eqs. (78) and (80) simplify to

$$\frac{L\theta}{a_n + \delta} > \sigma + \frac{2\Gamma}{r_{0nc}(a_n + \delta)^{1/3}} \quad \text{for } \delta > 0 \quad (146)$$

and

$$a_n > \left(\frac{3L\theta r_{0nc}}{2\Gamma}\right)^{3/2}. \quad (147)$$

Results for evaporation are shown in Fig. 8.

Note that instead of using the thermodynamic properties of liquid, we used the same properties of solid. Our goal here is not to study evaporation but to demonstrate the effect of the strength of solid on sublimation curves, i.e. to compare with cavitation in liquid. The effect of strength reduces with the growth of the surface tension. Since the condition for evaporation can be obtained by substituting  $\sigma_n$  with  $\sigma$  and for  $a_n \gg 1$  one has  $\sigma_n = \sigma - \sigma_c$  - i.e., for a large  $a_n$  the kinetic  $\theta - \sigma$  plot for evaporation is shifted to the left by 1 unit plot for sublimation.

The important result here is that for evaporation the same mechanical instability is observed as for sublimation and at approximately the same tensile stress. That means that mechanical instability is not related to the plasticity and irreversibility but rather is a universal property of a gas bubble that can appear at a given temperature from a kinetic point of view. For sublimation, it is the subcritical bubble in a traditional sense, while for evaporation it is the critical nucleus that can grow due to both evaporation and mechanical expansion.

## 12. Concluding remarks

In this paper, nucleation of a gas bubble as a result of sublimation inside an elastoplastic material is treated in detail. A number of conceptual problems that have been outlined in the general theory (Levitas (2012)) are treated here explicitly. They include determination of the driving forces and activation energies for two different nucleation scenarios, finding the explicit kinetic relationship between sublimation temperature and tensile pressure, and demonstration of the path-dependence of nucleation. Explicit treatment became possible because of the analytical solution for the stress in a solid at the solid-gas interface vs. the large bubble expansion and explicit expression for the mechanical work. Mechanical instability of the bubble was revealed, which plays a crucial role in the final determination of the critical nucleus. Thus, while the nucleus that appears via homogeneous transformation rather than interface propagation is kinetically more probable, it cannot grow by further sublimation. However, it may expand like a balloon due to mechanical instability above the critical size, and then sublimation will contribute to its growth as well. We are not aware of any other example of transformation of the subcritical nucleus into a supercritical one due to mechanical instability. This instability is found for evaporation as well - i.e., it is more related to the properties of gas than to plastic deformation of the solid. Also, it is demonstrated that due to path-dependence some nuclei can be metastable rather than sub- or supercritical. That means that they cannot grow and shrink.

To check the predictions of our theory using molecular dynamic simulations or experimentally, a nanoparticle covered by a few-nanometer shell with a coherent interface (to suppress surface nucleation) can be quickly heated up to the desired temperature and subjected to compressive pressure that sharply reduces to zero. The rarefaction wave generates high tensile pressure in the central region of the particle; corresponding analytical solution is presented in Levitas et al. (2007). The relationship between sublimation pressure and temperature obtained experimentally or by atomistic simulations can be compared with the prediction of our current theory. The large difference between sublimation pressures for a critical nucleus calculated based on the thermodynamic driving force for growth  $X_\Sigma$  and on mechanical instability (see Figs. 6 and 9) can be used to check the theoretical predictions qualitatively, if quantitative comparison is impossible. In experiments, high compressive pressure and fast pressure release can be provided by an additional external shell with a thermal expansion coefficient essentially smaller than that of the particle - e.g., by an alumina shell on an aluminum particle. During rapid laser heating, internal compressive pressure is generated in the particle, which overloads and spallates the external shell, causing fast pressure release (see details in Levitas et al. (2007)). Such a process has an important implication for the melt dispersion mechanism developed in Levitas et al. (2007), Levitas (2009) and Levitas et al. (2008).

Note that alternative processes leading to a gas bubble formation should be compared with the suggested scenarios. Thus, under some conditions sublimation can be two-stage: first, appearance of the melt drop, then its evaporation inside the elastoplastic material (Levitas and Altukhova, 2009). Alternatively, void nucleation may occur due to a fracture process rather than sublimation. Comparison of different scenarios will be a topic of future research.

## Acknowledgements

NSF (CBET-0755236 and CMMI-0969143), AFOSR (FA9300-11-M-2008), ARO (W911NF-09-1-0001), DTRA (HDTRA1-09-1-0034), ISU, and TTU support for this research is gratefully acknowledged.

## References

- Chu, Y.A., Moran, B., Reid, A.C.E., Olson, G.B., 2000. A model for nonclassical nucleation of solid-solid structural phase transformations. *Metal. Mater. Trans. A – Phys. Metal. Mater. Sci.* 31, 1321–1331.
- Fischer, F., Antretter, T., 2009. Deformation, stress state and thermodynamic force for a growing void in an elastic-plastic material. *Int. J. Plast.* 25, 1819–1832.
- Fischer, F., Waitz, T., Vollath, D., Simha, N., 2008. On the role of surface energy and surface stress in phase-transforming materials. *Prog. Mater. Sci.* 53, 481–527.
- Hill, R., 1950. *The Mathematical Theory of Plasticity*. Clarendon press, Oxford.
- Landau, L., Lifshitz, E., 1980. *Statistical Physics*, third ed. Pergamon Press, Oxford.
- Levitas, V., 2000. Structural changes without stable intermediate state in inelastic material. Part II. *Int. J. Plast.* 16, 851–892.
- Levitas, V., Asay, B., Son, S., Pantoya, M., 2007. Mechanochemical mechanism for fast reaction of metastable intermolecular composites based on dispersion of liquid metal. *J. Appl. Phys.* 101 (1–20), 083524.
- Levitas, V.I., 2009. Burn time of aluminum nanoparticles: Strong effect of the heating rate and melt dispersion mechanism. *Combust. Flame* 156, 543–546.
- Levitas, V.I., 2012. Sublimation, chemical decomposition, and melting inside elastoplastic material: general continuum thermodynamic and kinetic theory. *Int. J. Plasticity*. doi:10.1016/j.ijplas.2012.01.006.
- Levitas, V.I., Altukhova, N., 2008. Sublimation inside elastoplastic material. *Phys. Rev. Lett.* 101, 145703.
- Levitas, V.I., Altukhova, N., 2009. Sublimation via virtual melting inside an elastoplastic material. *Phys. Rev. B* 79, 212101.
- Levitas, V.I., Pantoya, M., Dikici, B., 2008. Melt-dispersion versus diffusive oxidation mechanism for aluminum nanoparticles: critical experiments and controlling parameters. *Appl. Phys. Lett.* 92, 011921.
- Levitas, V.I., Preston, D.L., Lee, D.W., 2003. Three-dimensional Landau theory for multivariant stress-induced martensitic phase transformations. Part III. alternative potentials, critical nuclei, kink solutions, and dislocation theory. *Phys. Rev. B* 68, 134201.
- Lyman, J.L., Liao, Y.C., V., B.H., 2002. Thermochemical functions for gas-phase, 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (hmx), its condensed phases, and its larger reaction products. *Combust. Flame* 130, 185–203.
- Porter, D., Easterling, K., 1992. *Phase Transformation in Metals and Alloys*. Van Nostrand Reinhold, New York.
- Wolfram Research, I., 2005. *Mathematica* ed.: Version 5.2. Wolfram Research, Inc., Champaign, Illinois.
- Zeldovitch, Y.B., 1943. To the theory of new phase formation. cavitation. *Acta Physicochim. USSR* 18, 1–22.