

## Sublimation inside an Elastoplastic Material

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Thermodynamic and kinetic approaches for sublimation inside elastoplastic material under tensile stress are developed for large strains. Various conceptual problems related to irreversible plastic deformation are addressed for a spherical bubble. They include definitions of the thermodynamic driving forces and activation energies, nontraditional concepts of a critical nucleus, path dependence of its appearance, modes of its growth (sublimation or expansion due to loss of mechanical stability), and the possibility of reverse transformation. The kinetic relationships between sublimation pressure and temperature are obtained.

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During thermomechanical loading, high temperatures can be induced in local spots inside the material, e.g., due to void collapse. Also, large tensile stresses may appear in rarefaction waves during laser ablation [1] or in nanoparticles after dynamic shell fracture [2]. High temperature and tensile stresses can cause sublimation—i.e., phase transformation solid-gas. Sublimation can also be a mechanism of void nucleation. However, thermodynamic and kinetic conditions for homogeneous sublimation inside the body (that we determine in this Letter) are significantly different from the conditions at the body surface, where sublimation occurs at constant pressure. Inside the body, pressure grows drastically due to large volume increase, causing large plastic deformations of solid around the bubble. Resistance to plastic flow determines actual pressure variation during the sublimation. While nucleation of the gas bubble within liquid (when strength effects are absent) is a textbook problem, to the best of our knowledge, the problem of sublimation inside elastoplastic material has never been considered in the literature. At the same time, it is related to several conceptual problems and scenarios that are absent in bubble appearance within liquid or elastic solid. Large plastic deformations require application of geometrically nonlinear continuum mechanics. Because of plastic dissipation, traditional thermodynamic methods that determine the driving force for sublimation as the change in Gibbs potential of the system cannot be applied. For sublimation in elastic material, a classical critical nucleus can be considered that corresponds to the maximum of activation energy  $Q$  vs the nucleus radius. Also,  $Q$  is path-independent—i.e., it is independent of whether it is nucleation via homogeneous transformation (NHT) within a critical nucleus, nucleation by interface propagation (NIP) from zero size to a critical nucleus, or nucleation by any combination of these processes. In contrast,  $Q$  for sublimation in plastic material is found to be path-dependent. That is why we introduce and analyze several possible concepts of critical nucleus. It

looks like appearance of a nucleus by interface propagation up to the radius above which it grows by spontaneous sublimation is the most natural definition of the critical nucleus. However, at large tensile pressures, when critical nucleus consists of only a few molecules, NHT from solid to gas is more appropriate. Also, due to path dependence, we cannot consider interface propagation from zero size. Thus, the homogeneous appearance of a subcritical nucleus has been considered, followed by NIP. Thermodynamic force and  $Q$  are defined for both processes, and they essentially differ. The kinetic nucleation relationship between sublimation temperature  $\theta_s$  and tensile pressure  $\sigma_1$  is obtained from the condition  $Q = 80k\theta$  [3], where  $k$  is the Boltzmann constant for various interface energies. This criterion [more generally,  $Q = (40-80)k\theta$ ] is determined from the condition that, for larger  $Q$ , nucleation time exceeds any realistic time of observation, and it is widely used for nucleation [3-5].

The following results are obtained, which do not have counterparts in nucleation in elastic materials. For surface energy  $\Gamma \geq 0.1$  J/m<sup>2</sup> and in narrow range above some temperature  $\theta_g$ , NIP is slightly more favorable, and the classical definition of a critical nucleus is valid. In all other cases, NHT is significantly more probable, although such a homogeneously transformed nucleus (HTN) cannot grow. It is necessary to slightly increase  $\theta$  or  $\sigma_1$  (to a value well below that for NIP) to cause growth. However, below some critical temperature  $\theta_{in}$ , while the nucleus cannot grow because of solid-gas transformation, it expands 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. One more unusual result for small  $\Gamma$  is that HTN, while it starts to shrink, does not completely disappear. Instead, it represents a metastable void. Thus, subcritical sublimation represents a mechanism of void nucleation, and this void serves as an embryo for further sublimation.

While we consider homogeneous nucleation in defect-free nanovolumes of material, the effect of defects can be taken into account as the next approximation. We understand that operating with thermodynamic functions far from equilibrium and using a continuum concept at nanoscale can be questioned. However, these assumptions are routinely used in the classical nucleation theory, and our goal is to conceptually advance this theory for the case with plastic deformation, dissipation, and irreversibility in the simplest way. Because the results of the application of classical nucleation theory are in good correspondence with experiments involving the defect-free case (e.g., for martensitic phase transformations [4] and cavitation [6]), and because they are widely used for analysis of nucleation at the nanoscale (e.g., for melting [7]), we expect that our generalization of this theory will be a good approximation of reality as well. There are many other examples in which the continuum thermodynamic approach works surprisingly well even beyond its expected limit of small-scale applicability.

A general thermodynamic and kinetic theory of solid-solid phase transformations in inelastic materials was developed in [5,8,9] and was applied to solve a number of problems (see review [5]). In this Letter, a new thermodynamic and kinetic approach for sublimation inside elasto-plastic material is developed as a modification of the theory [5,8,9]. The key point of the theory in [5,8,9] is that the driving force for the phase transition in plastic materials is equal to the dissipation due to only the phase transformation during the entire transformation in the nucleus for NHT or at the moving interface for NIP; they will be used here as well [Eqs. (1) and (7)]. Detailed treatment of NIP, taking into account the constitutive equations of gas (instead of solid), analytical treatment of large plastic deformations, and the combination of our approach for phase transformations in plastic materials and classical nucleation theory are contributions of the current Letter.

The total dissipation during the NHT,  $X_h$ , can be determined based on the second law of thermodynamics:  $X_h = X_v V_s - \Gamma S$ , where  $V_s$  is the volume of transformed solid;  $S = 4\pi r^2$  is the surface of the gas bubble;  $\Gamma$  is the solid-gas interface energy;

$$X_v = -W - \rho_s \Delta\psi \quad (1)$$

with  $W$  representing mechanical work and  $\rho$  being the mass density;  $\Delta\psi = \psi_g - \psi_s$ , where  $\psi$  is the Helmholtz free energy and  $g$  and  $s$  represent the gas and solid. An activation energy is defined as  $Q = -\min X_h$  with respect to  $V_s$ . For elastic material,  $X_v$  and  $Q$  coincide with the energy change in a system and maximum energy of the nucleus, respectively—i.e., with classical definitions.

Then for HTN, the volume of transformed solid and the activation energy corresponding to  $\min X_h$ , and the equilibrium condition at the interface are

$$V_c = (32\pi a^2 \Gamma^3)/(3X_v^3); \quad Q = 16\pi a^2 \Gamma^3/(3X_v^2) = 80k\theta; \quad (2)$$

$$p_g = \sigma_r + 2\Gamma/r, \quad (3)$$

where  $a = V/V_s$ ,  $p_g$  is the gas pressure and  $\sigma_r$  is the radial stress in solid at the interface. Solution to the large-strain problem is [10]

$$\sigma_r = -\sigma_1 + \frac{2}{3}\sigma_y \left[ 1 + \ln \left[ \frac{K}{\beta\sigma_y} \left( 1 - \frac{1}{a} \right) \right] \right], \quad (4)$$

where  $\beta = \frac{1-\nu}{1-2\nu}$ ,  $\nu$  is the Poisson's ratio,  $K$  is the bulk modulus, and  $\sigma_y$  is the yield strength. The von Mises plasticity condition,  $\sigma_\phi - \sigma_r = \sigma_y$ , was used, where  $\sigma_\phi$  is the circumferential stress. In comparison with [10], we added internal pressure and neglected elastic strains (to obtain an analytical solution). Then, we evaluate mechanical work

$$\begin{aligned} W &= \int_{a_1}^a \sigma_r da \\ &= -(a - a_1)\sigma_1 + \frac{2}{3}\sigma_y \left[ (a - a_1) + \ln \left( \frac{\varepsilon_1}{\varepsilon} \right) \right. \\ &\quad \left. + a \ln \left( \frac{\varepsilon K}{a\beta\sigma_y} \right) - a_1 \ln \left( \frac{\varepsilon_1 K}{a_1\beta\sigma_y} \right) \right], \end{aligned} \quad (5)$$

where  $a_1 = 1/[1 - \beta\sigma_y/(eK)]$  is introduced to avoid singularity in  $\sigma_r$  due to neglected elastic strains and is determined from the condition that before sublimation  $\sigma_r = -\sigma_1$ ,  $\varepsilon = a - 1$ , and  $\varepsilon_1 = a_1 - 1$ . We consider an ideal gas and use

$$\begin{aligned} p_g &= \rho R\theta/Ma, \quad \psi_g = \psi_g^\theta - \frac{R\theta}{M} \ln \left( \frac{p_0}{p_g} \right) - \frac{R\theta}{M} \ln \left( \frac{\theta}{\theta_0} \right), \\ \psi_s &= \psi_s^\theta + \frac{\sigma_1^2}{2K\rho_s}, \end{aligned} \quad (6)$$

where  $\theta_0$  and  $p_0$  are the reference temperature and pressure,  $M$  is the molecular mass,  $R$  is the gas constant, and  $\psi^\theta$  is the thermal part of free energy per unit mass. We assume that  $\Delta\psi^\theta = \Delta\psi_0^\theta - \Delta s(\theta - \theta_0)$ , where  $\Delta s$  is the jump in entropy.

Thus, the complete system includes Eqs. (1)–(6). To find the  $\theta_s - \sigma_1$  relation for HTN, the following steps are taken. For prescribed  $\theta_s$  and a number of values of  $\sigma_1$ , substituting the radius of the solid HTN  $r_{sc} = (3V_c/4\pi)^{1/3}$  in the equilibrium Eq. (3), we can find the relationships  $a(\sigma_1)$  and  $X_v[a(\sigma_1)]$ . Substituting them into Eq. (2) for  $Q$ , the stress  $\sigma_1$  can be found. Then, the radius of the HTN  $r_{sc}$  is found. We check whether  $r_{sc} > r_m$ , where  $r_m$  is the minimal radius for which  $V$  contains enough molecules to talk about gas. Otherwise, we use  $r_{sc} = r_m$  and repeat the same procedure. We also check  $a > a_1 + \delta$ , where  $\delta$  is a small number (we used  $\delta = 10^{-5}$ ). In the opposite case, we neglect deformation of  $V_h$  and use  $W = 0$  and  $a = 1$ .

After HTN is found, we check its mechanical stability  $p_g(a) < \sigma_r + \frac{2\Gamma}{r_{sc}a^{1/3}}$  for the prescribed  $r_{sc}$ . We also check whether it can grow or will shrink via interface propagation (see below).

For NIP, the total system includes Eqs. (3), (4), and (6), (excluding  $\psi_s$ ), and

$$X_{\Sigma} = -p_g(1/\rho_g - 1/\rho_s) - \Delta\psi - 2\Gamma/(\rho_s r); \quad (7)$$

$$\psi_s = \psi_s^{\theta} + \frac{1}{\rho_s} \left( \frac{1}{18K} (3\sigma_r + 2\sigma_y)^2 + \frac{1}{6\mu} \sigma_y^2 \right); \quad (8)$$

$$Q = Q_0 - \int_{m_m}^{m_c} X_{\Sigma} dm = 80k\theta. \quad (9)$$

Here,  $X_{\Sigma}$  is the driving force for interface propagation [5], which has the same form as for elastic materials;  $\psi_s$  takes into account the elastic energy at the point near the interface, where  $\sigma_{\phi} = \sigma_r + \sigma_y$ ,  $\mu$  is the shear modulus,  $Q_0$  is the activation energy for NHT of the bubble with  $r_s = r_m$  and mass  $m_m$  (calculated as described above), and  $dm = \rho_s v 4\pi r^2 dt$  is the mass covered during time  $dt$  by the interface moving with the velocity  $v$ . The condition  $X_{\Sigma} = 0$  determines the radius of the critical gaseous nucleus  $r_c$  with the mass  $m_c$ : for  $r > r_c$ , we have  $X_{\Sigma} > 0$ , and the nucleus will grow. For prescribed  $\theta_s$  and a number of values of  $\sigma_1$ , we express  $r_c(a)$  from Eq. (3) and substitute in Eq. (7). Then, the stress  $\sigma_1$  can be found from Eq. (9), which determines  $r_{sc}$  and  $r_c$ .

Calculations were produced for the following data (which are close to the data for energetic crystal HMX, if known):  $\theta_0 = 298.15$  K,  $p_0 = 1$  bar,  $\Delta s = 1.031$  J/K kg,  $\Delta\psi_0^{\theta} = 379.515$  J/g, reference mass density of gas  $\rho_{0g} = 10.1 \times 10^{-3}$  g/cm<sup>3</sup> and solid  $\rho_s = 1.71$  g/cm<sup>3</sup>,  $M = 250.151$  kg/mol,  $K = 15$  GPa,  $\sigma_y = 2.6$  MPa, and  $r_m =$

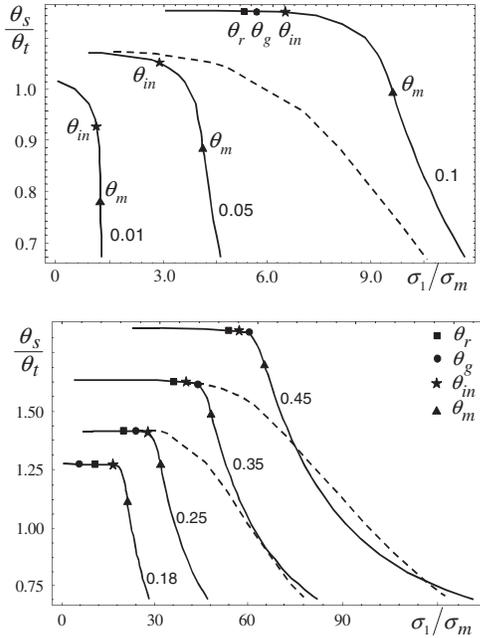


FIG. 1. Relationships between sublimation temperature  $\theta_s$  and tensile pressure  $\sigma_1$  for NHT (solid near curves) (in J/m<sup>2</sup>). Below temperature  $\theta_m$ , radius of nucleus  $r_{sc} = r_m$ . Below temperature  $\theta_{in}$ , the nucleus is mechanically unstable and expands spontaneously. Above temperature  $\theta_r$ , deformation of the nucleus is negligible. Above temperature  $\theta_g$  (for  $\Gamma \geq 0.1$ ), NIP is slightly kinetically favorable than NHT (see Fig. 2). Dashed lines are for NIP.

0.3 nm. Sublimation temperature and pressure are divided by  $\theta_t = 784.12$  K (defined from  $X_v = 0$  at  $\sigma_1 = 0$ ) and  $\sigma_m = 15.77$  MPa (pressure for unlimited plastic expansion of the cavity for  $\Gamma = 0$ , see below), respectively.

The relationships  $\theta_s - \sigma_1$  for NHT are shown in Fig. 1. We focus on the  $\Gamma$  smaller than typical equilibrium values for a solid-gas interface of 1 J/m<sup>2</sup>. 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.

There are two main regions on the curves in Fig. 1. At high temperature and low pressure, sublimation temperature is practically independent of  $\sigma_1$  because the change in volume is very small and  $\sigma_1$  does not contribute to the driving force. At lower temperature and higher  $\sigma_1$ , sublimation temperature is strongly reduced with the growth of  $\sigma_1$ , and for small  $\Gamma$ , this reduction is drastic. The main reason for a strong effect of  $\sigma_1$  is that an external pressure (for neglected  $\Gamma$ ) reaches the maximum possible plastic

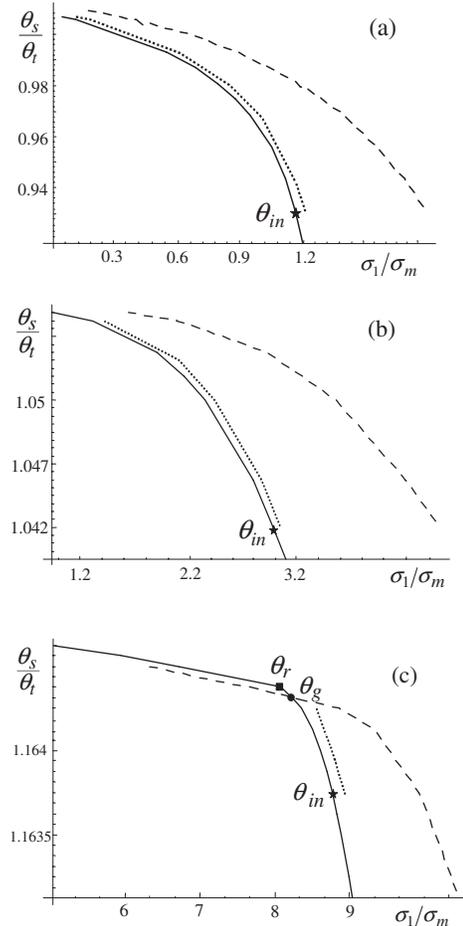


FIG. 2. Relationships between sublimation temperature  $\theta_s$  and tensile pressure  $\sigma_1$  for NIP (dashed line) and for NHT (solid line) for  $\Gamma = 0.01$  (a),  $\Gamma = 0.05$  (b), and  $\Gamma = 0.12$ . (c) For NHT and above temperature  $\theta_{in}$ , nucleus cannot grow after appearance. Parameters have to be increased to value corresponding to dotted line for spontaneous nucleus growth.

resistance of the solid sphere  $\sigma_m$ . For  $\Gamma = 0$ , it is determined from Eq. (3) for  $p_g = \sigma_r = 0$  and  $a \rightarrow \infty$ ; i.e.,  $\sigma_m = \frac{2}{3}\sigma_y[1 + \ln(\frac{K}{\beta\sigma_y})]$ . For  $\sigma_1 > \sigma_m$ , unlimited plastic expansion of the cavity, beginning with zero radius, starts even for  $p_g = 0$ . For finite  $\Gamma$ , the change in volume  $a$  has the order of magnitude 100 (for  $\Gamma = 0.05$ ) to 1000 (for  $\Gamma = 0.18$ ); i.e., for such a large  $a$ , the contribution of  $\sigma_1$  to the driving force is large. Also, a large  $a$  produces a large  $r_c$  even for the smallest  $r_{sc}$  and for the relatively large  $\Gamma$  increase in tensile pressure necessary for nucleation.

The relationships  $\theta_s - \sigma_1$  for NIP are shown in Fig. 2. For  $\Gamma \geq 0.1$  J/m<sup>2</sup> and  $\theta > \theta_g$ , NIP occurs at slightly lower temperatures than for NHT, and in this region, the classical definition of the critical nucleus is valid. For  $\Gamma < 0.1$  J/m<sup>2</sup> for small  $\sigma_1$  and for any  $\Gamma$  at large  $\sigma_1$ , NHT occurs at lower temperatures—i.e., it is kinetically more favorable. However, at the curve corresponding to NHT,  $X_\Sigma < 0$ ; i.e., growth is impossible. The following scenarios are considered. 1. For the part of the curves in Fig. 1 below  $\theta_{in}$ , the equilibrium of the gas bubble is mechanically unstable: for any gas expansion, the gas pressure is larger than what solid can support. Thus, despite the fact that this nucleus cannot grow due to the solid-gas transformation—i.e., it is a subcritical nucleus in the traditional sense—its radius grows due to gas expansion. After exceeding the critical radius determined from the condition  $X_\Sigma = 0$ , sublimation is activated as well. That is why there is no sense in continuing the curves  $\theta_s - \sigma_1$  for NIP below  $\theta_{in}$ . To our knowledge, this is the only known mechanism that can stabilize the subcritical nucleus and transform it to supercritical one. 2. Above  $\theta_{in}$ , it is necessary to slightly increase  $\theta$  or  $\sigma_1$  to initiate growth [dotted line in Figs. 2(b) and 2(c)]. This may happen fluctuationally. 3. Above  $\theta_{in}$ , it is also necessary to check whether reverse transformation via interface propagation is possible. During reverse transformation, gas pressure is reduced and solid material initially undergoes elastic unloading. For  $p_g < 2\Gamma/r$ , stresses at the internal surface of a solid become tensile and pull upon material, trying to reduce the bubble, and when the plasticity criterion is satisfied, plastic flow starts 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. This problem will be presented in detail elsewhere. Here, we will make a simple estimate related to possible scenario. Just after the appearance of HTN,  $X_\Sigma^r = -X_\Sigma > 0$ ; i.e., reverse transformation starts. 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  $r_h$ ;  $r_h > 0$  because of plastic expansion during nucleation. Next, we find cases in which the surface tension  $2\Gamma/r_h$  is not sufficient to start plastic flow toward closing the hole. Then, it is guaranteed that a residual void remains and that, consequently, some gas will sublime in it. This is possible at least for  $\Gamma < 0.05$  J/m<sup>2</sup>. Thus, above  $\theta_{in}$ , HTN does not become completely reversed, and it

represents a metastable embryo. Subcritical sublimation in this case represents a mechanism of void nucleation, and this void serves as an embryo for further sublimation. Activation energy for its transformation into a supercritical nucleus (for which  $X_\Sigma > 0$ ) is much lower than that for its appearance. For large  $\Gamma$ , surface tension closes the hole—i.e., HTN is in fact a subcritical nucleus between  $\theta_{in}$  and temperature  $\theta_g$ , above which NIP is kinetically more favorable for the NHT.

To check the predictions of our theory either experimentally or using molecular dynamic simulations, 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. Unloading wave will generate high tensile pressure in the central region of the particle; corresponding equations can be found in [2]. The obtained relationship between sublimation pressure and temperature can be compared with the prediction of our 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 Fig. 1) can be used to check theoretical predictions qualitatively, if quantitative comparison is a problem. 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. During rapid laser heating, internal compressive pressure is generated in the particle, which overloads and spallates the external shell, causing fast pressure release (see detail in [2]).

To summarize, thermodynamic and kinetic approaches for sublimation inside elastoplastic material under tensile stress were developed that exhibited various nontraditional conceptual problems and phenomena.

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