Mechanical stability of solids at negative pressures

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Abstract. The paper examines the reaction of an isotropic solid to infinitesimal and finite density perturbations. The boundary of stability against relatively small homogeneous and inhomogeneous deformations, and also the kinetic boundary of strength of a Lennard-Jones solid are determined in molecular dynamics experiments at negative pressures. It is shown that on the spinodal a solid retains its reducing reaction to small long-wave inhomogeneous perturbations. The work of formation of a critical pore also has a nonzero value on the spinodal.

1. Introduction

A solid under a negative pressure is metastable, i.e. not quite stable [1–3]. The loss of stability is connected with the formation of liquid-phase or cavitation voids (pores). The process of nucleation determines the limiting tensile strength of a solid. Serving as the kinetic boundary, the tensile strength depends on the sample volume and the time (rate) of the action.

Showing instability against nucleation, a metastable system retains its reducing reaction to infinitesimal perturbations. The boundary of stability against such actions, i.e. the boundary of essential instability, determines the theoretical or the ideal strength of a solid.

The present paper shows that at negative pressures there is a qualitative difference in the behavior of stability of a solid and a liquid phase. This difference is connected with the presence of shear stresses in solids and their absence in simple liquids.

2. Ideal strength of a solid

An isotropic ideally elastic solid under a hydrostatic pressure p at a temperature T is consider. Density fluctuations will be expressed as fluctuations of volume deformation $\upsilon \equiv u_{ll} = -\Delta\rho/\rho$, where u_{ij} is the tensor of infinitesimal deformations, summation is carried out over the repeating indexes.

A deformed state of an isotropic solid is characterized by the bulk modulus $K = -V(\partial p/\partial V)_T$ and the shear modulus μ. A necessary and sufficient condition of the body stability against homogeneous deformations, at which the deformation tensor is constant, is the possibility of the moduli K and μ. The vanishing of one of these moduli means the loss of stability. The stability may be lost against both volume and shear deformations.

If the deformation is accompanied by changes in the volume of the body but does not change its shape, then expanding the Gibbs thermodynamic potential G into a power series u_{ij} close to the equilibrium state ($u_{ij} = 0$) accurate to the term of the second order, we have

$$\Delta G(p, T, \upsilon)/V = \frac{1}{2} K \upsilon^2. \tag{1}$$

Root-mean-square fluctuations of v in some isolated volume V' of the body are calculated according to the well-known formula [4]

$$\langle(\Delta v)^2\rangle = \frac{k_B T}{V' K}. \tag{2}$$

Here k_B is the Boltzmann constant.

For prescribed p and T the equilibrium state will be stable if $K > 0$. At the boundary of essential instability $K = 0$, and at the approach to it fluctuations of volume deformation increase catastrophically. The line on which $K = 0$ is known as the spinodal [5].

In actual situations stresses and deformations are, as a rule, inhomogeneous. Inhomogeneous fluctuations of ρ, as distinct from homogeneous ones, are accompanied by shear deformations and depend on the wave vector $\vec{q}$. A change in the Gibbs potential of a deformed solid (1) with allowance for shear stresses will look like [6]

$$\Delta G(p, T, u)/V = \frac{1}{2} K u_{ll}^2 + \mu(u_{ij} - \frac{1}{3}\delta_{ij} u_{ll})^2. \tag{3}$$

In (3), the gradient term $v \equiv u_{ll}$ should also have been included, but since further we are interested only in long-wave fluctuations, we omit such a term. The value of inhomogeneous fluctuations is determined by only one component of the deformation tensor. If the vector $\vec{q}$ is directed along the x-axis, then it will be the component $u_{xx} = \partial u_x/\partial x \equiv u$. Assuming that in this case $u_{yy} = u_{zz} = 0$, from (3) we obtain

$$\Delta G(p, T, u)/V = \frac{1}{2}\tilde{K} u^2, \tag{4}$$

where $\tilde{K} = K + (4/3)\mu$ is the coefficient of unilateral compression, which describes the system reaction to an inhomogeneous (in the form of a plane wave) change in the density. For the Fourier component $u(\vec{q})$ we have

$$q^2\langle|u(\vec{q})|^2\rangle = \frac{k_B T}{V\tilde{K}}. \tag{5}$$

Equation (5) at $q \to 0$ does not coincide with expression (2).

Thus, inhomogeneous and heterogeneous density fluctuations are determined by different elastic moduli, homogeneous by the bulk modulus and inhomogeneous by the coefficient of unilateral compression without any changes in the lateral dimensions of the body. If we regard the root-mean-square fluctuation $\langle|u(\vec{q})|^2\rangle$ as the result of thermal motion whose average energy is $k_B T$, equation (5) may be presented as

$$\omega^2 = \frac{k_B T}{\rho V\langle|u(\vec{q})|^2\rangle} = \frac{\tilde{K}}{\rho} q^2 = \mathrm{v}_a^2 q^2. \tag{6}$$

This equation expresses the dispersion law for acoustic phonons in the case of long waves. Thus, inhomogeneous density fluctuations in a solid are longitudinal acoustic waves whose square of rate v_a is proportional to the coefficient of unilateral compression.

Random density fluctuations in a solid lead to the appearance of stresses that cause the propagation of deformations in the medium. If the damping coefficient of such perturbations is small enough, then fluctuations are oscillations. A necessary condition for the stability of an oscillation process realized in a solid is the reality of all its characteristic rates [6]. The vanishing of the modulus $\tilde{K}$ signifies that $\omega = 0$ and points to the solid instability. Thus, the boundaries of stability of a solid against homogeneous and inhomogeneous density fluctuations do not coincide. If the deformation of a solid are a homogeneous nature, and a state is achieved in which the

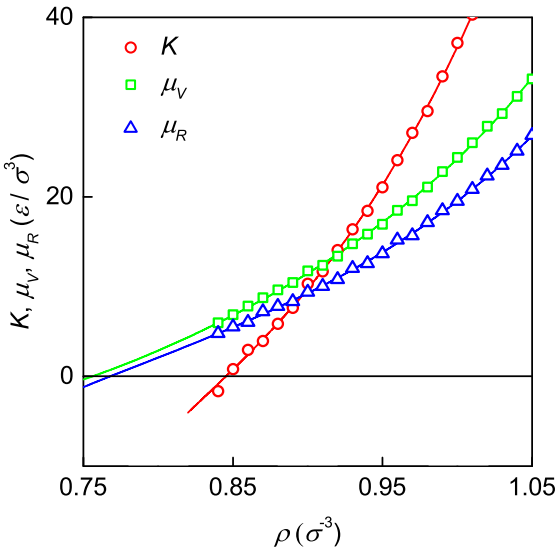

Figure 1. Density dependence of the elastic moduli of an isotropic Lennard-Jones solid at a temperature $T = 0.4$ (in units of ε/k_B).

bulk modulus becomes zero, with the shear modulus retaining a finite value, then the solid loses its stability against volume deformations. In this case, such a body retains its reducing reaction to inhomogeneous perturbations. By "squeezing" a solid it is possible to achieve a state $\tilde{K} = 0$, in which inhomogeneous long-wave fluctuations will diverge.

The molecular dynamics method has been used investigate the elastic properties of a Lennard-Jones FCC crystal at negative pressures. Models containing from 32000 to 500000 particles were used. The cutoff radius of the potential was taken to be equal to 6.58σ, where σ is a parameter of the Lennard-Jones potential. Further all the quantities calculated are given in dimensionless form. The parameters of reducing are the potential parameters σ and ε, the Boltzmann constant k_B, and the particle mass m. Calculations of properties were carried out in an NVT ensemble along isotherms $T = 0.3$, 0.4, 0.55 and 0.7 (in units of ε/k_B), and the phase decay kinetics was registered in NVE conditions.

The elastic moduli K and μ of an isotropic medium under a pressure p were calculated through the effective elastic constants of an FCC crystal with the use of the procedure of their averaging by Voigt and Reuss [7]. The distinction between the two means of averaging of elastic moduli consists in the fact that in the Voigt method averaging is realized at a fixed external deformation, and in the Reuss method at a fixed applied stress. Since the formulas used in calculations are cumbersome, they are not given here. These formulas can be found in works [8–10].

Figure 1 shows the density dependence of the bulk modulus K (the value of this modulus does not depend on the procedure of averaging) and the shear moduli obtained by the Voigt averaging μ_V and by the Reuss averaging μ_R at a reduced temperature $T = 0.4$. The temperature of the triple point of a Lennard-Jones crystal is $T_t = 0.692$. At temperatures lower than T_t the bulk modulus is always the first to manifest the tendency toward vanishing. At the point where the value of K is equal to zero μ_V and $\mu_R > 0$. At $T \leq 0.5$ a solid also retained its stability for a finite time in states where $K < 0$.

The spinodal of a stretched Lennard-Jones solid in (p, T) and (T, ρ)-coordinates is presented in figure 2. Shown ibidem is the boundary of stability against inhomogeneous infinitesimal

perturbations, on which $\tilde{K} = 0$. Since μ_V and μ_R give the upper and the lower estimation of the ideal value of μ of an isotropic solid, in calculations of $\tilde{K}$ use was made of the arithmetic mean values of μ_V and μ_R. As is evident from figure 2, in the region of negative pressures the boundary of the solid stability against inhomogeneous deformations is behind the spinodal. In this case, as has already been mentioned, at high negative pressures it is possible not only to approach the spinodal, but also to get past it retaining the reducing reaction of a solid to infinitesimal inhomogeneous perturbations. To substantiate this result, it is necessary to turn to the problem of nucleation of a new phase.

3. Limiting strength of a solid

If in a metastable system there are no available or readily activated centers, new-phase nuclei form at the cost of fluctuations. The rate of fluctuation nucleation is mainly determined by the minimum work required for the creation of a nucleus of a prescribed size. In a solid this work is made up of the volume, surface, and elastic parts and depend not only on the size, but also on the shape of a nucleus.

At negative pressures a phase decay may proceed with the formation of liquid drops and pores. As shown in [10], pores form below the temperature of the endpoint of the melting line (for a Lennard-Jones system $T_K = 0.529$ [11]) and drops form above it.

We shall restrict ourselves to the case where the fracture of a solid is connected with the fluctuation nucleation of pores. In the case of a lens-shaped pore with a radius R and a thickness $h \ll R$, using the result of Sneddon [12], from the theory of cracks, for a critical pore we have [13]

$$R_* = \frac{\pi\gamma\mu}{(1-\nu)p^2}, \tag{7}$$

$$h_* = -\frac{2\gamma}{p}, \tag{8}$$

$$W_* = \frac{2\pi^3\gamma^3\mu^2}{3(1-\nu)^2p^4}, \tag{9}$$

where W_* is the work of formation of a critical pore, γ is the solid–gas interface free energy, and ν is the Poisson ratio

$$\nu = \frac{(3K-2\mu)}{2(3K+\mu)}. \tag{10}$$

According to (7), (8) $h_*/R_* \sim -p$, i.e. typical of small stretches are critical pores that are highly flattened in one dimension. At large stretches for a given volume of a critical pore its shape will be determined from the condition of minimum of the interfacial energy. This must lead to the spheroidization of a nucleus.

The formulas (7) and (9) differ from similar formulas for the liquid phase by the presence in them of elastic moduli and the character of the pressure dependence of R_* and W_*. In the liquid phase the governing parameter in the expressions for R_* and W_* is the surface tension, which on the spinodal is equal to zero, and the size of a nucleus and the work of its formation here take zero values. In a solid γ is evidently finite [14], and the behavior of R_* and W_* close to the spinodal will be determined by the behavior of the elastic moduli. As was shown earlier, at negative pressures μ is also positive when K becomes zero. The Poisson ratio varies in the range from -1 (at $K = 0$) to $1/2$ (at $\mu = 0$). From (7)–(9) in this case it follows that on the spinodal finite values have the size of a critical pore and the work of its formation. This makes it possible not only to achieve a spinodal state, but also to penetrate behind the spinodal.

Figure 3 gives the density dependence of R_*, h_* and W_* at a temperature $T = 0.4$. All the quantities in formulas (7)–(9) have been calculated in a model of an isotropic Lennard-Jones solid. As is evident from figure 3, an approach to the spinodal is accompanied by the

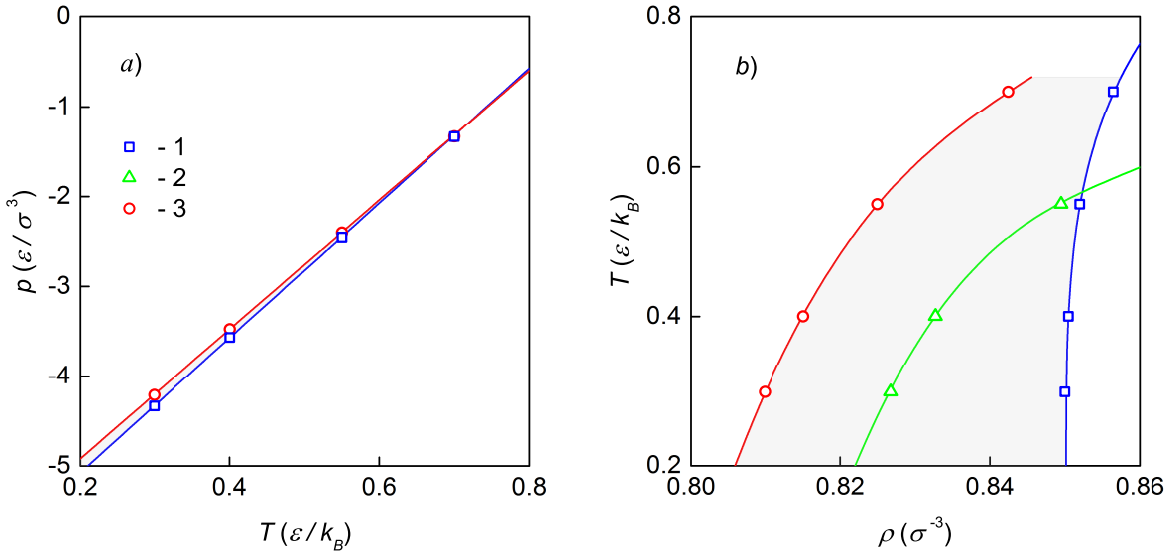

Figure 2. Spinodal (1), line of attainable stretching in calculating properties (2) and boundary of stability of a solid against inhomogeneous deformations (3) in (p, T) (a) and (T, ρ) (b) coordinates.

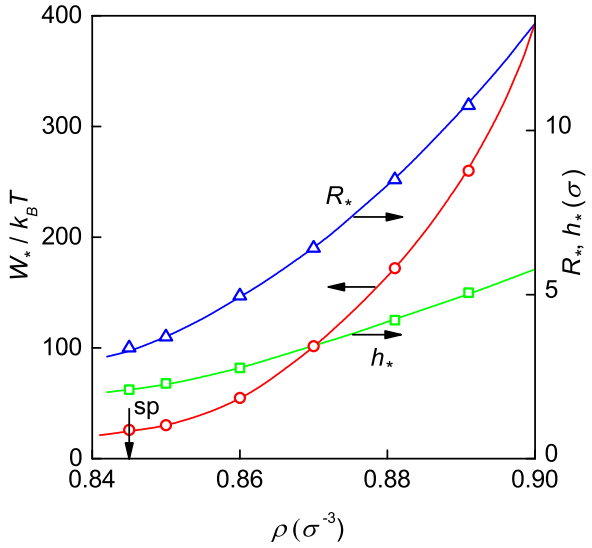

Figure 3. Reduced work of formation W_*/k_BT, radius of a critical void R_* and its thickness h_* at a temperature $T = 0.4$. The vertical arrow shows the value of density on the spinodal of a solid.

convergence of the sizes R_* and h_*, i.e. a critical pore assumes a spherical shape, and the value of the work of formation of a critical pore W_* on the spinodal is approximately $20k_BT$. For molecular dynamics models this is a sufficiently high activation barrier, which the system can overcome after spending a rather long time, which exceeds that required for calculating the physical properties. Therefore, while on the spinodal, a solid will possess a finite lifetime, and behind the spinodal, retain a finite value of the activation energy.

4. Conclusion

It is shown that the reactions of a solid and liquid to infinitesimal homogeneous and inhomogeneous, and finite actions are qualitatively different. This difference is caused by shear stresses in solids and their absence in liquids. First, at homogeneous deformations and negative pressures a solid loses its stability against volume and retains it against shear deformations. Second, in solids the boundaries of essential instability against homogeneous (spinodal) and inhomogeneous long-wave perturbations do not coincide, which is not characteristic of liquids. At negative pressures in a solid the boundary of stability against inhomogeneous perturbations is behind the spinodal. Third, owing to the finite nonzero value of the crystal–gas interfacial free energy, the work of formation of a critical pore and its size on the spinodal of a solid also differ from zero. Thus, if homogeneous deformations in a solid are suppressed, then not only spinodal, but also overspinodal states may be achieved in it. In this case a phase decay of a solid behind the spinodal will be of actuation rather than relaxation character [15].

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References

[1] Ashitkov S I, Komarov P S, Struleva I A, Agranat M B, Kanel G I and Khishchenko K V 2015 *J. Phys.: Conf. Ser.* **653** 012001
[2] Belikov R S, Krasyuk I K, Rienecker T, Semenov A Y, Rosmej O N, Stuchebryukhov I A, Tomut M, Khishchenko K V and Schoenlein A 2015 *Quantum Electron.* **45** 421–425
[3] Kanel G I, Savinykh A S, Garkushin G V and Razorenov S V 2015 *JETP Lett.* **102** 548–551
[4] Landau L D and Lifshitz E M 1980 *Course of Theoretical Physics. Vol. V. Statistical Physics, Part 1* (Oxford: Pergamon)
[5] Skripov V P 1974 *Metastable Liquids* (New York: Wiley)
[6] Landau L D and Lifshitz E M 1986 *Course of Theoretical Physics. Vol. VII. Theory of Elasticity* (Oxford: Pergamon)
[7] Katsnelson M I and Trefilov A V 2002 *Crystal Lattice Dynamics and Thermodynamics* (Moscow: Energoatomizdat)
[8] Baidakov V G, Galashev A E and Skripov V P 1980 *Fiz. Tverd. Tela* **22** 2681–2687
[9] Jin Z H, Gumbsch P, Lu K and Ma E 2001 *Phys. Rev. Lett.* **87** 055703
[10] Baidakov V G and Tipeev A O 2015 *J. Chem. Phys.* **143** 124501
[11] Baidakov V G and Protsenko S P 2005 *Phys. Rev. Lett.* **95** 015701
[12] Sneddon I N 1946 *Proc. Roy. Soc. London A* **221** 229–260
[13] Brener E A and Marchenko V I 1992 *JETP Lett.* **56** 381–385
[14] Baidakov V G and Tipeev A O 2012 *J. Chem. Phys.* **136** 074510
[15] Levanyuk A P 1974 *Sov. Phys. JETP* **39** 1111–1114