Second Law of thermodynamics and the failure of rock materials

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ABSTRACT:

The relation of nonequilibrium thermodynamics to some failure and fracture theories of rock mechanics is investigated. The basic concepts are given to connect failure to the properties of material equations describing the elastic properties. The resulted in thermodynamic conditions are proved to be compatible with classical localization and failure theories of solid materials. Compatibility with experiments and some empirical, adhoc failure criteria of rocks is also demonstrated.

1 INTRODUCTION

In continuum physical theories the complex mechanical properties of material are described by constitutive functions. One of the basic construction methods to get reasonable constitutive functions is based on the Second Law of thermodynamics. The material equations have to be compatible with the Second Law in every system where dissipation occurs, including fracture and failure of rock materials, too. Here (of course) thermodynamics is understood not only as a theory to deal with thermal phenomena and temperature changes, but as the theory dealing with the stability of materials. In this respect Second Law is understood as a requirement of stability, restricting the possible material equations of all media.

In rock mechanics the pure mechanical properties are modeled by continuum mechanical methods, and even the violations of material stability are understood in most cases as pure mechanical phenomena using fracture mechanics as modeling tool. Fracture mechanics deals with holes (cracks) and discontinuities embedded in an ideal mechanical continuum. Several works use statistical methods to understand the interaction and interlocking of cracks in the mechanical continuum. In rocks damage processes include not only microcracking and interlacking of cracks but several other different mechanisms, therefore the applicability of this kind of statistical considerations is questionable. To understand the appearing broad range of different phenomena different requires to apply

phenomenological methods and to understand, in what sense could be the different approaches unified. Some new developments in modern nonequilibrium thermodynamics give a hope to deepen our understanding of the role of the Second Law in mechanical modeling and to extend the existing models to give simple descriptions of several related phenomena.

Failure and change of elastic properties are treated as independent phenomena in mechanics. The situation is similar in the theories of plasticity, where the yield criteria is considered to be independent on elastic properties of the material (but not independent on the Second Law). Continuum damage mechanics (see e.g. Krajcinovic 1996) is a theory motivated by the need of unification of failure and nonlinear elasticity. The original idea is that growing damage can lead to failure. However, after some initial attempt the researchers in damage mechanics gave up to find a theoretical connection and nowadays the damage surfaces (critical damage) are given independently on the change of mechanic properties.

In this short paper we will show that a connection can be found, if the foundations of the underlying nonequilibrium thermodynamic theories are investigated. Failure and fracture can be considered as a kind of material instability. Moreover, we can use similar concepts and methods to the case of phase transitions in fluid and gaseous bodies. As particular applications we will show how the classical Griffith concept (and all the so called *energy methods*) includes thermodynamic instability

and show, how other specific rock mechanical failure criteria can be understood as violation of thermodynamic stability. At the end a thermodynamic improvement of the empirical criteria of Lade is given using the ideas above and a simple particular model.

2 DYNAMIC AND THERMODYNAMIC STABILITY

In nonequilibrium thermodynamics the Second Law introduces the entropy function as the manifestation and theoretical tool to deal with the stability of equilibrium. There are two different aspects to be considered here:

Thermodynamic stability; the convexity of entropy function. This is a static stability requirement that ensures the stability of equilibrium states of matter in case of small external perturbations of the thermodynamic state, independently of the particular dynamic equations. Phase boundaries appear where thermodynamic stability is violated.

Dynamic stability of thermodynamic equilibrium; positive entropy production, where particular dynamic equations of matter are considered. The connection between the two stability concepts is clear in case of the so called 'equilibrium' systems, where the state variables and the relations between them are those that can be measured in equilibrium. Thermodynamic and dynamic stability together restrict the possible functional form of the constitutive functions to give the asymptotic stability of specific equilibrium states (Glansdorff and Prigogine 1971, Gurtin 1975). For homogeneous (discrete) systems this idea was developed in detail giving a remarkable conceptual background of the Second Law (Matolcsi 1992, 1996a, b).

The situation is more involved in nonequilibrium systems where the hypotheses of local equilibrium is violated, the 'equilibrium' state variables are inadequate to characterize the processes (Ván 1995). For systems with internal variables (an important class of nonequilibrium systems) the requirement, the thermodynamic stability results in the desired theoretical tool to describe material instability of mechanical origin. Let us consider a simple mechanical system, where the traditional extensive state variables the specific entropy s and deformation ε are supplemented by a set of internal variables $\alpha = (\alpha_i, i=1,...,n)$. Each internal variable can be a tensor of any order. Different variable sets and thermodynamic potential functions are used in kind of investigations. In mechanics these traditionally we can meet the Helmholtz free energy $\phi(T, \varepsilon, \alpha)$ and the Gibbs free energy $\psi(T, \sigma, \alpha)$, too. The corresponding variables are the temperature T, deformation and stress ε and σ respectively. The

two free energies and the internal energy $e(s, \varepsilon, \alpha)$ are related by partial Legendre transformations:

$$e = \phi + Ts = \psi + Ts + \sigma : \varepsilon$$
,

where s is the entropy.

The thermodynamic stability appears as the requirement of concavity of the entropy function. A concave entropy results in conditions for the other thermodynamic potentials, too. In case of pure mechanical processes, when temperature is constant, concave entropy gives a convex Helmholtz free energy. The requirement of a convexity in the relevant variables for a two times differentiable Helmholtz free energy can be written as

$$(d\mathbf{\varepsilon}, d\mathbf{\alpha}) \cdot D^2 \phi \cdot (d\mathbf{\varepsilon}, d\mathbf{\alpha}) =$$

$$= (d\mathbf{\epsilon}, d\mathbf{\alpha}) \cdot \begin{pmatrix} \frac{\partial^2 \phi}{\partial \mathbf{\epsilon}^2} & \frac{\partial^2 \phi}{\partial \mathbf{\alpha} \partial \mathbf{\epsilon}} \\ \frac{\partial^2 \phi}{\partial \mathbf{\epsilon} \partial \mathbf{\alpha}} & \frac{\partial^2 \phi}{\partial \mathbf{\alpha}^2} \end{pmatrix} \cdot (d\mathbf{\epsilon}, d\mathbf{\alpha}) > 0$$
 (1)

for every $(d\varepsilon, d\alpha)$. Here a notation from the mechanical literature is applied where $d\varepsilon$ and $d\alpha$ are arbitrary vectors from the linear spaces where the deformation and internal variables are defined respectively. $D^2 \phi$ denotes the second derivative ϕ . To investigate the inequality (1) Sylvester condition for symmetric matrices can be applied. It is supposed that the functional form of the entropy (and the free energies consequently) does not contain differential or integral operators. However, the process dependence of the corresponding equations is considered through the introduced internal variables. Therefore the resulted stressstrain relations will be rate dependent, but a rate form notation is not necessary and could even be misleading.

A (partially) convex Helmholtz free energy gives requirements for the Gibbs free energy, but these requirements cannot be expressed as a simple concavity or convexity for all variables (one can say that Gibbs free energy is convex in the internal variables and concave in the other ones), therefore sometimes a conversion to Helmholtz free energy can be useful for thermodynamic stability calculations.

The subset of the state space where the conditions of thermodynamic stability are satisfied determines the static stability domain of the material. Outside this domain the material is unstable, without further constraint fails. From a physical point of view the situation is analogous to phase boundaries in case of fluid bodies but in solid bodies the observed phenomena can be qualitatively different. Here failure changes the properties of the material and the internal interactions (for example the cohesion vanishes and dry friction will be the dominating dissipation mechanism). Moreover, in this case all of

our previous implicit assumptions on the homogeneous representative volume elements can become meaningless. In solid materials we cannot speak unambiguously of an other homogeneous phase after the loss of thermodynamic stability, in a continuum description the phases are immediately localized. This is best seen if we give a closer look at the condition of stability loss and recognize that (1) can be interpreted as a generalization of the classical Hadamard-Hill localization condition of shear banding. Using purely mechanical arguments and investigating jump surfaces in the velocity field shear banding appears in the direction **n** if

$$\det(\mathbf{n} \cdot \mathbf{C} \cdot \mathbf{n}) = 0, \tag{2}$$

where C is the fourth order stiffness tensor, that can be given as the second partial derivative of the Helmholtz free energy

$$\mathbf{C} := \frac{\partial^2 \phi}{\partial \mathbf{\epsilon}^2}.$$

(Hadamard 1903, Hill 1962, Asaro & Rice 1977)

We can see that C is the (1,1) submatrix in our general thermodynamic stability condition (1). A necessary condition of this submatrix to be positive definite is closely related to the mentioned classical localization condition of Hadamard and Hill, the later gives the boundary of the stability domain when equality holds. A more general requirement of positive definite elastic moduli can be derived from energetic-stability considerations resulting in a localization condition. This general energetic localization condition considers shear-banding and cleavage type localization instabilities, too (see e.g. Krajcinovic 1996 and Broberg 1999). Our condition (1) can be considered as a generalization of these classical requirements (all energetic considerations can be interpreted as disguised thermodynamic train of thoughts).

Therefore the loss of thermodynamic stability, at least in some cases, does not result in a homogeneous change in the material but indicates the appearance of some localized patterns, for example shear bands. Hence the analogy with phase transitions can be misleading, instead of phase transitions we can call the related process as *phase breaking*. Of course more developed localization models considering the thickness of shear bands and other gradient dependent nonlocal effects can also be introduced.

Internal variables give the basic theoretical concept to thermodynamic motivated approaches of plasticity, damage mechanics or rheology. In this case the fundamental Helmholtz relation expressed by the Gibbs free energy $\psi(T, \sigma, \alpha)$ for a homogeneous representative volume element can be written as

$$d\psi = -sdT - \mathbf{\varepsilon} : d\mathbf{\sigma} - \mathbf{A} \cdot d\mathbf{\alpha} \,, \tag{3}$$

where T is the temperature, ε and σ are the stress and the deformation respectively, the double dot denotes the trace of the product of the two tensors and A is the affinity conjugated to the internal variables α This relation is a short and physically interpretable version of the potential property of the free energy. That property can be expressed also with partial derivatives

$$s = -\frac{\partial \psi}{\partial T}, \qquad \varepsilon = -\frac{\partial \psi}{\partial \sigma}, \qquad \mathbf{A} = -\frac{\partial \psi}{\partial \sigma}.$$
 (4)

Before continuing to discuss the consequences of thermodynamic stability and other static phenomena, we give some hint on the dynamics emerging from thermodynamic considerations. The other part of the Second Law beyond the thermodynamic stability is the requirement of positive entropy production. That postulate results in prescriptions and some very particular forms of the possible dynamic equations.

For solid bodies with small deformations the production of entropy multiplied by the temperature and written in terms of Gibbs free energy reads as

$$TP_{s} = \left(\frac{\partial^{2} \psi}{\partial \sigma^{2}}\right)^{-1} \left(\varepsilon + \frac{\partial \psi}{\partial \sigma}\right) : \dot{\varepsilon} + \frac{\partial \psi}{\partial \alpha} \cdot \dot{\alpha} \ge 0.$$
 (5)

Here the dot above the quantities denotes substantial time derivatives. It is easy to identify thermodynamic currents and forces in the above expression and give explicit relations for the dynamics of the different introduced quantities. On the other hand additional physical restrictions seem to be reasonable in most of the practical situations in mechanics. One of them that the mechanical equilibration is faster than the evolution of the internal variables (the terminal velocity of crack propagation in ideal elastic materials is not more than the half of the sound velocity). In this case we can suppose a mechanical equilibrium

$$\mathbf{\varepsilon} = -\frac{\partial \psi}{\partial \mathbf{\sigma}} \,. \tag{6}$$

The dynamics of the internal variables is determined as follows (as a first approximation)

$$\dot{\boldsymbol{\alpha}} = L \frac{\partial \psi}{\partial \boldsymbol{\alpha}} (\boldsymbol{\sigma}, \boldsymbol{\alpha}) \,,$$

where L is a material parameter, characterizing the speed of the damage propagation.

To investigate the theoretical and experimental relevance of this kind of dynamics is not the subject of this short paper. We remark here that typical damaging and failure mechanisms observed for brittle rocks (Bieniawski 1967 or Martin and Chandler 1994) can be modeled by a single vectorial internal variable (supposing that microcracking is

the dominating internal mechanism) and few material parameters.

A SIMPLE MODEL FOR BRITTLE FAILURE

In this section a simple model of brittle material is suggested and the static stability properties are investigated. For brittle materials the microstructure is formed by microcracks, that are growing and interlocking with increasing pressure. In case of brittle rocks with grains the structure of microcracks is not so simple as for homogeneous materials. According to the compressive stresses they can be intergranular and also can be formed inside the grains. The mode of failure depends on the direction of the loading for slow and also for fast processes. Therefore, it seems to be reasonable to introduce a single vectorial internal variable that incorporates the average properties of microstructure. In this case we can interpret it as the average of the microcrack vectors and we will call it as damage.

To deal with the static properties of particular materials a reasonable form of one of the potential functions is necessary. According to the experience and traditions a second order polynomial is suggested for the Gibbs free energy. Using the symmetry requirements for isotropic materials we can get the following functional form

$$\psi(\mathbf{\sigma}, \mathbf{\alpha}) =$$

$$\frac{\varsigma}{2}\boldsymbol{\alpha}^{2} + (\delta + k_{\delta}\boldsymbol{\alpha}^{2})Tr\boldsymbol{\sigma} + (\mu + \frac{k_{\mu}}{2}\boldsymbol{\alpha}^{2})\boldsymbol{\sigma} : \boldsymbol{\sigma} +
+ \frac{1}{2}(\lambda + k_{\lambda}\boldsymbol{\alpha}^{2})(Tr\boldsymbol{\sigma})^{2} + \frac{1}{2}(\beta + k_{\beta}Tr\boldsymbol{\sigma})\boldsymbol{\alpha} \cdot \boldsymbol{\sigma} \cdot \boldsymbol{\alpha} +
+ \frac{\gamma}{2}\boldsymbol{\alpha} \cdot \boldsymbol{\sigma} \cdot \boldsymbol{\sigma} \cdot \boldsymbol{\alpha}.$$
(7)

Due to the isotropy only ten material constants appear and only five of them can be considered as new. All the terms can be interpreted physically and measurement methods can be suggested for the material constants. There are some clues for the interpretation (a more detailed treatment is given in Ván 2000).

- The first term represents the energy attributed directly to the cracks.
- The second term is related to the hydrostatic energy conservation of the material. δ characterizes the damage independent and k_{δ} the damage dependent part. Pore fluid pressure can be a physical mechanism in the background. (All of the parameters can depend on temperature and density of the material.)
- The next two terms are the usual elastic free energy contributions where μ and λ are well known elastic coefficients related to the

- Young modulus E and Poisson ratio ν by μ =(1+ ν)/E and λ = μ /E. k_{μ} and k_{λ} characterize their damage dependence.
- $\alpha \cdot \sigma \cdot \alpha$ is the deformation in the direction of the crack surface, therefore the sixth term considers the opening of the cracks.
- The last term contains the square of the substantial crack vector, therefore it means an energy contribution necessary for turning the cracks with the deforming media.

Another clue to the interpretation of the material parameters can be given by the equation of the mechanical equilibrium (6) calculating the damage strain (the residual strain due to the growing damage).

$$\boldsymbol{\varepsilon}_0(\boldsymbol{\alpha}) \coloneqq \boldsymbol{\varepsilon}(\boldsymbol{0}, \boldsymbol{\alpha}) = (\boldsymbol{\delta} + k_{\boldsymbol{\delta}} \boldsymbol{\alpha}^2) \mathbf{I} + \boldsymbol{\beta} \boldsymbol{\alpha} \circ \boldsymbol{\alpha}.$$

Here I is the second order unit tensor and the circle \circ is the usual notation of the tensorial product in continuum mechanics.

With this particular free energy we can investigate the stability thresholds suggested in the condition (1). Calculating the (1,1) submatrix, related to the localization we can get that in case of zero damage $\mu>0$ and $\mu+\nu>0$.. Calculation of the damage related (2,2) submatrix we can get the requirement of thermodynamic stability in case of zero deformation is $\zeta>0$. On the other hand several different explicit upper limits can also be calculated for the damage parameter in case of specific loading conditions.

This particular Gibbs free energy function can be considered as a direct generalization of the ideas of Griffith in two different ways, applying the two conditions given in his original paper Griffith 1924. One of them is if we accept the interpretation of Rice 1978 and Lawn 1993 and assume that the energy condition is connected directly to the free energy. Therefore the free energy governing the evolution of crack extension is the reversible work *W* minus the surface energy (related to the energy release rate *G*) necessary for the crack separation. More properly, in two dimensions for uniaxial tensile loading and a crack perpendicular to the loading axis we can write

$$\psi(\sigma_1, \alpha_1) = W(\sigma_1, \alpha_1) - 2G\alpha_1 \tag{8}$$

where α_l is the length of the crack, σ_l is the tensile stress, W is the reversible work component and the last term is the specific surface energy. For perfectly elastic materials we can give the work in a more specific form

$$W(\sigma_1,\alpha_1) = -\frac{\sigma_1^2}{2E} + \frac{\pi\sigma_1^2\alpha_1^2}{E}.$$

Here the first term is the pure elastic work, while the second is the work necessary for the reversible crack extension (see e.g. the original work Griffith 1924). The expression (8) above is a special form of the free energy function (7) for this particular situation, where for example $\mu = 1/2E$, $k_{\mu} = \pi$ and the other material parameters are zero.

The thermodynamic stability condition (1) with the previous simple Gibbs free energy gives a three dimensional failure criteria. To check the validity it is reasonable to consider experiments with similar general loading conditions, or the related empirical failure criteria.

The damage (failure) surface of brittle materials (rocks, ceramics, etc..) has a particular three dimensional shape in the stress space as one can see qualitatively on Figure 1. Let us observe the rounded triangle shape on the octahedral plane (cross section perpendicular to the hydrostatic pressure line).

The rate dependence of the failure strength observed in experiments makes doubt that this form expresses real material properties (Martin and Chandler 1994), but here we accept it as an experimental evidence of the time independent strength surface of brittle materials.

Most of the strength criteria for rocks were suggested for special loading conditions and only some of them applies to explain the particular form of the failure surface. The first and oldest one is the original two dimensional Griffith criterion based on theoretical calculations for single cracks embedded in an elastic domain. Later it was generalized to three dimension by Murell extending some expected properties of the failure surface from two into three dimensions (Murell 1963, Jaeger and Cook 1971). This criteria suggests a parabolic failure envelope in case of pressure loading and a constant limit stress in case of tensile loading (see Griffith 1924).

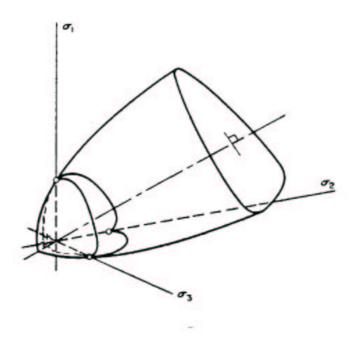


Figure 1. Failure surface in the stress space according to experimental evidence (Lade 1993).

Another three dimensional generalization of the criterion of Griffith was used by Theocaris 1987 in his Elliptic Paraboloid Failure Criterion. This criterion suggests an elliptic paraboloid open from the hydrostatic axis as initial failure surface in the stress field. It has been proved to be useful to describe the failure of anisotropic materials and results in a better fitting than the criterion of Griffith-Murell (Theocaris 1999). Here the failure loci are given by the next equation at the stress space

 $\sigma : \mathbf{B} : \sigma + \mathbf{b} : \sigma = 1$.

where **B** and **b** are fourth and second order tensors respectively. They are to be determined experimentally. The parameters should be given in a way that the failure loci form a paraboloid whose axis is the hydrostatic pressure line. Theocaris gives experimental procedures and calculation methods to determine the failure loci from the experiments. Let us remark that the anisotropic property introduced in criterion is not necessarily a material characteristics, because it can arise from an initially anisotropic damage distribution in case of originally and materially isotropic base continuum, too. On the other hand, the smooth paraboloid seems to be a strong simplification for tensile loadings. It is easy to see that the criteria of Theocaris can be considered as a special case of our thermodynamic condition in case of constant damage considering only the (1,1) submatrix of (1).

As a third possibility, the best fitting to the measured failure surfaces can be achieved by the criteria of Lade. It is simple and easy to apply, because contains only three material parameters m, η_1 , a and given by the next function in the stress space

$$\left(\frac{I_1^3}{I_3} - 27\right) \left(\frac{I_1}{p_a}\right)^m = \eta_1$$
(9).

where $I_1 = Tr\sigma$ and $I_3 = det\sigma$ are the first and third invariants of the stress tensor and p_a is the atmospheric pressure. Moreover, because the normal stresses contain a translation in the stress space along the hydrostatic axis, the mean stresses σ_i in the formula (9) should be replaced with $\tilde{\sigma}_i = \sigma_i + a$ p_a , where i=1,2,3. The corresponding material parameters has been calculated for several rocks from the available (three dimensional) experimental data (Lade 1993).

All the three criteria are empirical, they were suggested without any serious theoretical justification. In the following we will see that the thermodynamic stability condition of our simple model with one vectorial internal variable can give a comparable fitting, moreover, it has a strong

theoretical background as a direct thermodynamic generalization of Griffith criteria in three dimensions.

To demonstrate the differences a simple example is given here, based on the experimental data of Brown performed on Wombeyan marble in biaxial experiments with brush plattens (Brown 1974). According to biaxial experiments, contrary to Mohr assumptions, not only the difference of the biggest and lowest principal stresses determine the strength of the rock: the influence of intermediate stresses is not negligible. Lade fitted his criteria with the experimental data of Brown (Lade 1993).

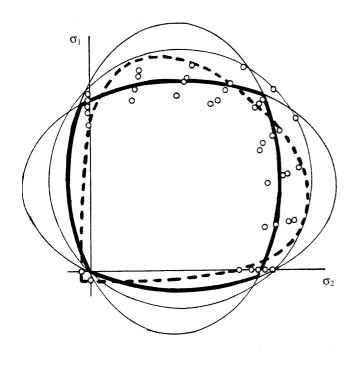


Figure 2. Biaxial experimental data, criterion of Lade and thermodynamic failure envelope.

Figure 2 shows the results of biaxial experiments, the corresponding fitted failure surface of Lade and the failure surface proposed by the thermodynamic stability condition. The empty dots denote the experimental results and the broken line is the threshold of the criterion of Lade with the parameter values m=1.162, $\eta_1=601500$ and a=38.0. The thermodynamic criterion results in the three elliptic curves. Their internal hull gives the boundaries of thermodynamic stability an denoted by the thickest line on the figure. The parameters are $\delta=0$, $k_{\delta}=10.9976$, $\mu=50000$, $k_{\mu}=0.03$, $\lambda=0.14$, $k_{\lambda}=0$, $\zeta = 100$, $\beta = 11.2156$, $k_{\beta} = 0$ and $\gamma = 0.0353352$. Only three parameters are used for the fitting, the other non-zero parameters are calculated from the known properties of the material or estimated suitably. The initial damage vector is chosen supposing $\alpha = (0.003, 0.003, 0.003),$ a uniform directional distribution. The chosen particular values

are not too important, because the failure surface is independent on the damage if it is sufficiently small. It can be seen on the figure that the thermodynamic condition gives a piecewise continuous failure threshold.

Let us observe some important qualitative empirical differences between the and the thermodynamic criteria. The thermodynamic failure surface is a cross section of several surfaces, therefore it has some vertices. One of the vertices is on the hydrostatic axis for tensile stresses. It is similar to the construction of the Griffith-Murell criteria, where also some cross sectional surface was proposed (a very special one). The published data on this experiment of Brown is not sufficient to determine all of the thermodynamic parameters (for the fitting we have chosen a suitable parameter set, considering some physical mechanisms). Measurements to determine the material parameters for a brittle rock and the compatibility with the predictions on the dynamics are under way.

CONCLUSIONS AND DISCUSSION

paper a theoretical concept this nonequilibrium phase breaking is proposed as a tool to extend the frames of the phenomenological thermodynamic modeling. As an application of this idea a particular phenomena, the microcrack induced damage is investigated in detail. A simple internal variable theory is suggested, using a single vectorial internal variable and based on the most general second order approximation of the Gibbs free energy. We have seen that the model can be considered as a generalizations of the classical energetic Griffith model of failure. The boundary of the domain of thermodynamic stability is proved to be a generalization of traditional mechanical localization criteria. A comparison with empirical failure criteria showed that this simple model with thermodynamic stability results in the best fitting to the available experimental data in a three dimensional stress space.

The concept of failure deserves some attention from an experimental point of view. The material can be kept together even when its internal structure is completely destroyed. First it was pointed out by Orowan 1960 analyzing the classical experiments of von Kármán with Carrara marble. The marble became powdered, chalk like with large lateral pressures, which indicates a change in the internal structure. In this case the phase breaking is closely related to a real phase transition, and supposedly another free energy can be introduced to characterize the powdered, frictional state.

The dynamical properties of the phenomena are not investigated in this paper, but it is clear that our simple model can be considered only as a first approximation. The orientation sensitivity of the Kaiser effect, the fact that the microcracking is initiated separately in different orientations is surely not included in our model with a single averaging type internal variable. However, the present study demonstrates, that a nonequilibrium thermodynamic approach to the description of the evolution of the whole microcrack distribution seems to be promising.

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