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Surface thermodynamics of cracks

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ABSTRACT

Although a crack is a typical detail of a real solid, the theory of cracks in surface science was reduced to studying flat-parallel slits for a long time. The last decade has brought a number of new results related to the thermodynamic and surface science fundamentals of wedge-shaped cracks including the crack line tension. These results, essentially correcting and developing the theory of cracks, could not yet be included in the previous reviews of the author [A.I. Rusanov, Surf. Sci. Rep. 23 (1996) 173–247 and A.I. Rusanov, Surf. Sci. Rep. 58 (2005) 111–239] and make a subject for reviewing in this paper. Surface characteristics of a crack are described including the crack line tension as a new property that can be important for nanocracks. General thermodynamic relationships are derived, and the calculation of the thermodynamic surface and line tensions for solids with dispersion forces is given as an example. The dependence of the crack line tension on the crack size is analyzed for the conformal change (when a crack changes its size with maintaining its geometrical similarity) and the depth growth (when the distance between the crack lips is fixed). The latter has been found to be more favorable energetically. Since the presence of a crack is more probable for a loaded body, a general and rigorous approach to the thermodynamic description of loaded solids is presented including correcting earlier mistakes and terminology. The thermodynamic consideration presented outputs a useful contribution to the theory of solid strength. A generalized brittle fracture criterion is deduced and the ultimate strength is calculated for both the above mechanisms of the crack growth. The influence of the line tension on the ultimate strength is estimated both for the 2d and 3d cases.

Contents

1. Introduction ... 118
2. Thermodynamic surface tension of a crack ... 119
   2.1. A novel definition of the thermodynamic surface tension of a solid ... 119
   2.2. Calculation of the thermodynamic surface tension of a crack ... 120
      2.2.1. Flat-parallel crack ... 120
      2.2.2. Wedge-shaped crack ... 121
3. Thermodynamic line tension of a crack ... 122
   3.1. Rectilinear crack ... 123
      3.1.1. Case of a macrocrack ... 123
      3.1.2. Case of a nanocrack ... 124
   3.2. Circular crack ... 125
      3.2.1. Definition of the thermodynamic line tension of a circular crack ... 125
      3.2.2. Crack size effect ... 126
   3.3. Line tension of a crystal edge ... 127
4. General thermodynamic description of a loaded solid ... 127
   4.1. Choice of thermodynamic potential ... 128
   4.2. Work of crack formation ... 129
      4.2.1. General relationships ... 129
      4.2.2. Comparing two mechanisms of the crack growth ... 130

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5. Contribution to the theory of ultimate strength ... 131
 5.1. Historical background ... 131
 5.2. General theory ... 133
  5.2.1. The 2d case ... 133
  5.2.2. The 3d case ... 133
 5.3. Theory for solids with dispersion forces ... 135
  5.3.1. The 2d case ... 135
  5.3.2. The 3d case ... 136
6. Effects of adsorbed matter ... 137
 6.1. Surface and linear adsorption equations ... 137
 6.2. Influence of adsorption on the solid strength ... 138
7. Summary and horizons ... 139
References ... 139

1. Introduction

Three departments of knowledge meet at formulating the theory of solid strength: mechanics, thermodynamics, and surface science. Up to the present time, a major contribution was made by mechanics whose task is calculating the mechanical state (stresses and strains) of a solid in the presence of a crack, as well as describing the processes of the crack propagation and the solid fracture. The world literature in this field is immense and is no subject to reviewing in this paper. As for thermodynamics, several early attempts to improve it were reviewed by Rice [1] who analyzed the thermodynamics of quasi-static growth of cracks. However, it was round about to the main unsolved problem, the formulation of the thermodynamics of loaded bodies. Indeed, the formation of cracks leading to the solid fracture is typical for loaded bodies, but the thermodynamics of such bodies was not elaborated until recently. Classical thermodynamics of free bodies operated with the mechanical term $-pdV$ (p is pressure and V is volume), which implies the uniform external pressure (say, atmospheric pressure) to be the only possible kind of loading. With this precondition, the whole thermodynamic apparatus was developed and the main thermodynamic potentials (energy, enthalpy, free energy, Gibbs energy, and grand potential) were introduced as practical calculating tools. Although thermodynamic consequences of passing from uniform pressure to the pressure tensor were declared in theoretical mechanics and even some possible thermodynamic potentials were suggested [2], fundamental equations were not formulated. When touching thermodynamic problems for loaded bodies in mechanical papers, they typically addressed free energy, which should be qualified, strictly speaking, as a mistake. Indeed, free energy is known to be a thermodynamic potential provided the body boundaries are fixed. However, loading itself can change the volume and shape of a body, and this makes free energy unacceptable as a thermodynamic potential. The same can be said about energy and other classical characteristic functions. In his time, the author developed the formalism of so-called "directed thermodynamic potentials" for bodies under uniaxial stress [3,4] as a new class of thermodynamic functions. As for the general solution for an arbitrarily loaded solid, it was attained only recently [5].

Formulating the theory of solid fracture is impossible without the use of quantities of surface science since any fracture is the creation of a new surface. Griffith, the founder of the theory, operated with surface tension [6], and this was natural because this quantity is of mechanical origin (an excess surface stress). In this case, however, rather an energetic factor was needed, so that other authors used the terms "surface energy" or "surface free energy", which was also not quite correct. In fact, surface tension itself can be defined thermodynamically as the excess grand potential σ per unit surface area, which yields the work of formation of a new surface. The mechanical surface tension γ can be also interpreted as the work of formation of unit surface area by stretching the old surface of a body. Both the definitions lead to the same numerical values for σ and γ in the case of fluids, but exhibit a certain difference for solids. Gibbs [7] was first to notice such a discrepancy. The physical cause of it was explained by the author [8,9] as related to the non-uniformity (even at equilibrium) of the chemical potentials of immobile components forming the crystalline lattice. Since the grand thermodynamic potential was constructed only for fluids, a new hybrid thermodynamic potential (behaving as free energy with respect to the immobile components and as grand thermodynamic potential with respect to the mobile components of a solid) was introduced to define σ as its excess quantity (per unit surface area) for the equimolecular dividing surface [8,9]. Recently, a novel approach to the definition of σ was elaborated [10] by introducing a modified form for grand thermodynamic potential applicable to solids. This has yielded the universal definition of the thermodynamic surface tension commonly valid for fluids and solids.

In the mechanics of brittle fracture (see, e.g., [11]), it is important to consider surface tension as a constant. However, still Rice [1] noted that the surface tension of the crack wall should depend on the distance from the crack tip. Rice neglected this dependence by considering macroscopic cracks well exceeding the tip region in size, but the effect can be of significance for sufficiently small cracks and especially for nanocracks (when a crack as a whole consists only of the tip region). In any case, the energetics of the tip region of a crack is of a certain interest itself. Therefore, the general thermodynamic description of cracks should include the analysis of the dependence of surface tension on the location on the crack walls. Corresponding results have been published recently [5,12].

In contrast with surface tension, the line tension of a crack even has been never mentioned in former crack theories. In the mean time, a crack does possess line tension since two crack surfaces meet each other at the crack tip. The concept of the crack line tension was introduced and analyzed only recently [5,12]. The line tension of a crack is dependent on the angle at which the crack walls meet. If the crack propagation is accompanied by a change in the crack-tip angle (which is typical for practice), the line tension becomes an influential factor. Another cause of the action of line tension is a change in the length of the crack front line in the process of propagation. This can happen if the crack front line is not straight. Naturally, the influence of line tension cannot exceed the influence of surface tension and only plays the role of a correction. Nevertheless, the inclusion of line tension in the theory of cracks is important for two reasons: (a) the effect can be well noticeable for nanocracks; (b) this approaches the theory to a more rigorous and complete form.

The above problems concern simultaneously thermodynamics and surface science and will be described in this paper within the frames of surface thermodynamics whose extensive survey was presented earlier [4,9]. The thermodynamics of cracks was not included in it, but now new results in this field allow us to create a