

Atomistic modeling of brittleness in covalent materials

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Despite a large number of model potentials having been developed in the last decades for silicon and group-IV elements, only a few of them correctly reproduce the brittle propagation of fracture and provide a proper estimate of the failure strength for such materials. We prove that the inability to model the brittle crack opening shown by most model potentials is related to their short-range character, a feature which overestimates the atomic force necessary to snap a bond. By using the universal energy relation we prove that any model potential aimed at studying fracture in covalent crystals should include interactions longer than the second-neighbor distance. We adopt the Tersoff force model to illustrate such a concept in the case of Si-Ge-C systems. Finally, we demonstrate that by means of a suitable modification of the Tersoff force model it is possible to recover the brittle fracture in Si, C, Ge, and SiC and to provide a quantitative prediction of many mechanical properties.

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I. INTRODUCTION

The atomistic simulation of fracture has received much interest in recent years since it is a central issue of multiscale modeling of real materials.^{1,2} For metallic systems it was possible to atomistically investigate several aspects of fracture mechanics, like, e.g., the brittle-ductile transition³ or the Griffith criterion for crack stability.⁴ At variance, the brittle behavior of covalent materials (Si, Ge, C, SiC) turned out to be a more challenging problem.⁵ Interestingly enough, most of the classical potentials available for elemental as well as compound group-IV materials are not able to reproduce brittle fracture.⁵ In the case of silicon this holds for the Tersoff potential,⁶ the Stillinger-Weber (SW) potential,⁷ and the environment-dependent interatomic potential (EDIP):⁸ all of them predict unphysical behavior during fracture. Similar problems are found when simulating fracture in other group-IV materials, as detailed in the following. To our knowledge only a few force models are able to correctly predict the brittle behavior in these systems: namely, the potential developed by Kicuchi *et al.*⁹ used for SiC, the embedded-atom method,¹⁰ and a modified version⁷ of the SW potential used for Si. However, these improved potentials only work for a specific material, no transferability being searched for, or heuristically found.

By comparing the atomic force provided by the SW potential and EDIP with the universal energy relation (UER) obtained by *ab initio* calculations,¹¹ Holland and Marder⁷ concluded that none of the available models for silicon accurately describe the force-separation curve. Such conclusions have been recently supported by the use of the pseudo-potential method to study quasistatistically the creation of new surfaces.^{8,12} Therefore, several alternative approaches have been explored in order to atomistically investigate fracture in silicon and in other covalent materials by combining classical force fields with other theoretical methods.¹ In the spirit of the multiscale approach, the classical force field is used in the remote regions of the simulated system, while the chemical bonding nearby the crack tip is described by semi-

empirical tight-binding⁸ or by *ab initio* density functional calculations.¹³ Alternatively, the model potential is locally (i.e., at the very crack tip) improved through a learn-on-the-fly procedure.¹⁴ Very recently, a multiparadigm approach¹⁵ has been also proposed where a reactive force field is used.

The continued search for combined approaches is motivated by a real need: fracture is a truly multiscale phenomenon, where both the long-range elastic fields and the atomic separation forces must be accurately described at the same time. Despite the success of the above hybrid approaches, the search for classical model potentials still remains of great relevance. This is mainly due to the lower computational cost of model potentials with respect to methods involving *ab initio* or tight-binding calculations.

The aim of the present work is to investigate whether classical potentials can be developed to properly simulate fracture in covalent materials. By comparing classical potentials with the universal energy relation, we focus on the interatomic separation force. Our investigation shows that any model potential aimed at studying fracture should include interactions longer than the second-nearest-neighbor (2NN) distance. This is proved by developing a universal minimum-range model (MRM) for fracture. By using the Tersoff potential as the prototype of 1NN interaction force field, we substantiate the above conclusion by showing that the separation force during fracture is in fact largely overestimated, as a result of the potential short rangeness. Although the bypass of this artifact can be obtained by extending the range of interactions, this solution is unfortunately demanding in terms of the development of the new model potential. In particular, this approach would imply refitting the force field, possibly generating inconsistency with previous results. This is an unpleasant feature, since a huge body of valuable knowledge has been produced so far by the original short-range potentials. Therefore, by following a different path (i.e., by still keeping the 1NN range of the interactions) we propose an improvement of the Tersoff force model which will eventually be able to reproduce brittle fracture in elemental and compound group-IV materials. This result is obtained by affecting the cutoff function of the force field in

such a way so as to bypass the strict requirements of the universal MRM. This choice, however, introduces some limitation to the transferability of the model, as discussed below. Nevertheless, the present modified Tersoff model provides good estimates of important fracture-related properties, such as the failure strength and the crack resistance of a perfect and a cracked group-IV material.

The paper is organized as follows. In Sec. II we describe the universal energy relation, focusing on the case of covalent materials. In Sec. III we describe the MRM and we work out a comparison with the Tersoff one. Atomistic results are finally presented in Sec. IV, where a modification of the Tersoff model is introduced.

II. UNIVERSAL ENERGY RELATION

The UER is a two-parameter equation of state originally proposed by Rose *et al.*¹¹ to describe the dependence of the internal energy $u(s)$ of a metal upon the scaled interatomic separation s :

$$u(s) = -E_0(1+s)e^{-s}. \quad (1)$$

The UER equation also describes the binding energy of many nonmetallic systems and, in particular, of covalent solids such as silicon, germanium,¹¹ carbon, and silicon carbide.¹⁶ In the above equation, E_0 is the absolute value of the cohesive energy per atom and s is

$$s = \left(\frac{r}{r_0} - 1 \right) \frac{1}{\mu}, \quad (2)$$

where r and r_0 are the interatomic distances in the strained and in the equilibrium structure, respectively. μ is an adimensional parameter that depends on the system, providing a measure of the material anharmonicity. Such a quantity may be fitted on experiments or *ab initio* calculations, and it can be cast in the form¹¹

$$\mu = \frac{1}{3} \left(\frac{E_0}{BV_{at}} \right)^{1/2}, \quad (3)$$

where V_{at} is the atomic volume and B is the bulk modulus. To the aim of providing a physical interpretation of μ , let us assume an ideal linear elastic regime and let us define a critical state of strain corresponding to an atomic volume increment (ΔV) at which the elastic energy $E_e = \frac{1}{2}B(\Delta V/V)^2$ is equal to the cohesive energy E_0 . Such an equivalent volume, normalized by the equilibrium atomic volume, defines the parameter $\mu = \frac{1}{3} \left(\frac{\Delta V}{V_{at}} \right)^{1/2}$. In this work we will focus on the case of zinc-blende or diamond crystals. Accordingly, the atomic volume V_{at} is related to the interatomic distance through the relation $V_{at} = (2/\sqrt{3})^3 r_0^3$. The shell of 1NN contains 4 atoms and it is located at a distance $r_{1NN} = r_0$; for the second and third shells, both containing 12 atoms, $r_{2NN} = 2/3\sqrt{6}r_{1NN}$ and $r_{3NN} = 1/3\sqrt{3}r_{1NN}$ are found, respectively. It is interesting to calculate μ in the actual case of group-IV elements. In the case of silicon carbide, $\mu = 0.221$ is found by using $r_0 = 0.187$ nm, $E_0 = 6.19$ eV, and $B = 223$ GPa.¹⁷ In the case of carbon we obtain $\mu = 0.230$ (we used for B the value

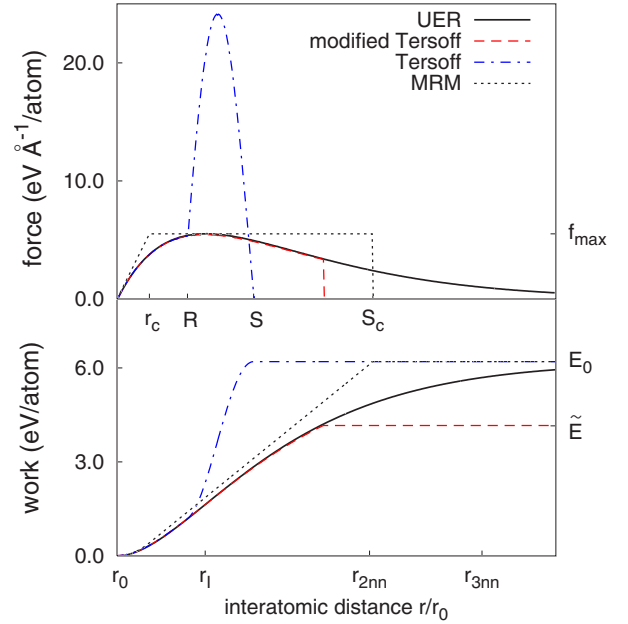


FIG. 1. (Color online) Work (bottom) and force (top) for hydrostatic separation of silicon carbide as a function of the interatomic distance (r/r_0).

given in Ref. 18); furthermore, for silicon and germanium $\mu = 0.205$ and $\mu = 0.198$ are found,¹¹ respectively. These values are relatively large, and they are not compatible with the assumption that the covalent bonding is effectively modeled by using short-range interactions only, as shown below. The work $w(s)$ necessary to hydrostatically stretch a perfect crystal up to a scaled interatomic distance s can be obtained from Eq. (1) as follows:

$$w(s) = E_0 + u(s). \quad (4)$$

In the limit $s \rightarrow \infty$, $w \rightarrow E_0$ is obtained (work necessary to separate the solid into a set of isolated atoms). The curve $w(s)$ is completely controlled by the three constants E_0 , μ , and r_0 , which, in turn, depend on the actual material. For instance, the inflection point r_I of $w(s)$ corresponds to $r_I = r_0(1 + \mu)$, occurring at $s = 1$. Such an interatomic separation is obtained by spending a work $w(r_I) = (1 - 2/e)E_0$ as large as 26% of E_0 . In Fig. 1 (bottom) the work function $w(s)$ (solid line) is represented for the choice $\mu = 0.22$, corresponding to the SiC case.

The force $f(s)$ necessary to separate atoms at the interatomic distance s is straightforwardly obtained from $w(s)$:

$$f(s) = \frac{dw}{dr}[r(s)] = E_0 \frac{s}{\mu r_0} e^{-s}. \quad (5)$$

This force is positive in the case of tensile strain ($r > r_0$ —i.e., $s > 0$). $f(s)$ is represented in Fig. 1 (top panel) by a solid line. The maximum separation force $f_{max} = E_0(e\mu r_0)^{-1}$ is found at $r_I = r_0(1 + \mu) = 1.44r_0$, falling within the 1NN distance $r_0 = r_{1NN}$ and 2NN distance r_{2NN} ($r_{2NN} = 1.633r_0$). At distances $r > r_I$ ($s > 1$) the force $f(s)$ decreases as the separation increases. A 90% force reduction (i.e., $f = f_{max}/10$) is observed when $r \sim 2r_0 > r_{3NN} = 1.91r_0$ (see Fig. 1).

III. MINIMUM-RANGE MODEL

In this section we discuss how to correctly reproduce the fracture properties of a material by using a suitable short-range force model f_{sr} . The use of a short-range force model is, of course, preferable as for the corresponding computational workload. It is important to clarify that the hydrostatic separation energy described by the UER model does not correspond to any realistic fracture event. Nevertheless, we guess that any force model aimed at studying fracture must be able to correctly reproduce the UER curve.

The development of a short-range force model is worked out from the corresponding UER by imposing a small number of very fundamental requirements: (i) the force must be a continuous function of strain, (ii) the maximum separation force must be correctly reproduced (i.e., $f_{sr}^{max}=f_{max}$), (iii) the bulk modulus at equilibrium must fit the experimental (or *ab initio*) value, (iv) at tensile strains (up to r_l) the bulk modulus must not increase, and (v) the work of separation must correctly reproduce E_0 . The condition (ii) is related to the fracture toughness of the perfect material. For instance, if the maximum force is overestimated, the fracture toughness of the material is overestimated as well. Similarly, condition (iii) is needed in order to reproduce the elastic properties of the material. Furthermore, condition (iv) stands for a simple physical requirement: the atomic bonds cannot stiffen during tensile deformation up to the maximum force. Condition (v) is verified when the force model is the derivative of the energy (conservative force).

The shortest force model fulfilling the above conditions (i)–(v) is represented in Fig. 1 (top panel) as a dotted line (the proof is given in Appendix A). We will refer to such a model as minimum-range model. It consists in a linear elastic force over the range $r_0 \leq r \leq r_c$ (where the bulk modulus is given by the constant value B), while for $r_c \leq r \leq S_c$ the force is constant and it is equal to the f_{max} value provided by the UER. Finally, for any interatomic distance larger than S_c , the force is zero. The actual value of r_c is fixed by the intersection between the linear force with slope B , occurring in the region $[r_0, r_c]$, and the constant f_{max} . S_c is, in turn, fixed by the cohesive energy E_0 . It can be calculated (see Appendix A) that

$$S_c = r_0 [1 + (e + 0.5e^{-1})\mu]. \quad (6)$$

This value sets the minimum range below which it is not possible to find a force model satisfying the conditions (i)–(v); in other words, a model with force extension below S_c is unlikely to describe brittle fracture.

The value S_c/r_0 depends only on the parameter μ characterizing the material. We have found that in the case of covalent group-IV materials such a minimum value S_c is close to the equilibrium 2NN distance. In particular, in the case of carbon and silicon carbide, we get $S_c \approx 1.64r_0$ and $S_c \approx 1.66$, respectively: they are slightly larger than the 2NN distance $r_{2NN} \approx 1.63r_0$. In the case of silicon and germanium, $S_c \sim 0.9r_{2NN}$. These values suggest that only by taking into account interactions beyond the second neighbors ($\sim r_{2NN}$) is it possible to correctly describe the maximum separation force and, in turn, the fracture toughness of the investigated sys-

tem. At variance, the INN approximation is still valid when studying properties where an overestimation of the maximum separation force is not critical.

The minimum-range model is a very rough model, its only value being explicatory. In particular, this force model can hardly be used for practical purposes like, e.g., an atomistic simulation. A better device (still short ranged) is obtained by multiplying the ideally long-range energy function $u(s)$ by a cutoff function $h(s)$, so as to obtain a new force model $T(s)$:

$$T(s) = u(s)h(s). \quad (7)$$

Although other cutoff schemes¹⁹ (e.g., $T=u+h$) have been proposed in the literature, we point out that the following analysis does not depend on the details of the actual cutoff. The corresponding work separation $w_{sr}(s)$ is modified accordingly,

$$w_{sr}(s) = E_0 + T(s), \quad (8)$$

and it is short ranged as well. An example of such a model is represented in the bottom panel of Fig. 1 as a dot-dashed line; it corresponds to the Tersoff model.²⁰ Let $[R, S]$ be the range where the cutoff $h(s)$ operates; it vanishes for $r > S$ and it equals 1 for $r < R$. The cutoff function does not modify the total work of separation, $w_{sr}(\infty) = w_{sr}(S) = E_0$, so that condition (v) is satisfied. Furthermore, the cutoff (which is a continuous function, together with its derivative) does not modify the force field close to its equilibrium distance (always falling at $r < R$). Accordingly, conditions (i), (iii), and (iv) are always satisfied by construction. Condition (ii) is instead satisfied only if the range S of the force model is larger than S_c , as previously discussed. At variance, if $S < S_c$, then an overestimation of the force is expected. The above discussion is valid, in general, for any short-range potential and for any cutoff scheme. In particular, it applies to the Tersoff potential that corresponds to the case $S = 1.33r_0$,²⁰ i.e., to a range much shorter than S_c . In Fig. 1 the Tersoff model is represented by the dot-dashed line. As expected, the force is overestimated in the range $[R, S]$ and an unphysical peak is observed, resulting in being 4 times larger than the correct maximum value f_{max} (Fig. 1, top panel).

The unphysical artifacts due to the imposed short range-ness of the interatomic forces are easily explained by considering the derivative of the $T(s)$ energy function (see Appendix B). These artifacts prevent the correct description of brittle crack propagation in group-IV materials, as shown in Fig. 2 (right panels) where the original Tersoff model was used. In the case of SiC [panel (A')] crack does not propagate in the plane of maximum stress (the plane containing the initial crack seed); rather, it moves along a crystallographic equivalent plane. Similar features are observed in the case of silicon [panel (B')], germanium, and carbon (not shown here). Unphysical deviations from the ideal brittle behavior are observed as well in silicon, when described by the EDIP or by the SW force models.^{8,21} Once again, these problems arise from the existence of unphysical forces that contrast crack propagation.

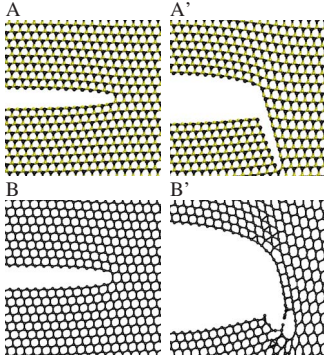


FIG. 2. (Color online) Crack tip morphology during fracture propagation in Si (bottom panels) and SiC (top panels). According to the original Tersoff model, artifacts are observed at the crack tip when simulating fracture both in SiC [panel (A')] and Si [panel (B')]; at variance, the modified force model correctly reproduces the brittle crack opening in SiC [panel (A)] and Si [panel (B)].

The deficiencies of the above force models are also quantitative. In the case of the Tersoff potential, we have verified that the failure strength $\sigma_f(c)$ of a uniaxially [111]-strained monocrystal containing a slit crack of semilength c [oriented along the (111) plane] is larger than the prediction by the linear elastic fracture mechanics (LEFM)

$$\sigma_{LEFM}(c) = \sqrt{\frac{2\gamma E}{\pi c}} \quad (9)$$

for the same system. In this equation γ is the ideal surface energy and E is the Young's modulus. In particular, we found an extremely high fracture toughness $\sigma_f(c)/\sigma_{LEFM}(c) > 2$ for any crack length in the range between c_0 and $\sim 50c_0$, where c_0 is the interbond separation along the slit crack. The same deviation is found when calculating the ideal strength σ_{th} of perfect crystal under similar loading conditions.

IV. RESULTS

In the previous section we have proved that any conservative force field shorter than the MRM cannot satisfy all the requirements (i)–(v). As for the Tersoff force field it would be necessary to use a larger cutoff ($S > r_{2NN}$), so as to take into account at least the second shell of neighboring atoms.

In this work we do not follow this path since it would require a new fitting of the whole set of the Tersoff parameters. Rather, we introduce an improvement of the Tersoff model, (hereafter labeled as \tilde{T}) that is obtained by removing the unphysical force due to the cutoff function (see Appendix B). The modified force model fulfills conditions (i)–(iv), but not condition (v). Under the only conditions (i)–(iv) the MRM is no longer valid. Therefore, it is possible to find a new model, shorter than the MRM, that does not overestimate the separation force. This new force model correctly reproduces the results of the original Tersoff potential when describing systems in the condition of small deformation (i.e., when the action of the cutoff function is not involved). For example, all the elastic bulk properties are unchanged.

TABLE I. Comparison of physical properties related to fracture under [111] uniaxial load in C, SiC, Si, and Ge.

	C	SiC	Si	Ge
E (GPa)	1276	565	189	167
γ (eV \AA^{-2})	0.256	0.157	0.080	0.067
$\tilde{\gamma}$ (eV \AA^{-2})	0.193	0.125	0.060	0.043
σ_{th} (GPa)	163	103	55	51
$\tilde{\sigma}_{th}$ (GPa)	114	58	23	17

The work of separation corresponding to the new force model is represented in Fig. 1 (dashed line): it is in very close agreement with the UER curve, up to the point where it is set to $h=0$.

The present scheme is suitable for the calculation of any mechanical or fracture-related properties at $T=0$ K. On the other hand, its major drawback is that the force is nonconservative and the energy is ill defined. As a result, the present solution is not good for simulating thermodynamical ensembles at finite temperatures or for performing free energy calculations. Moreover, some care is required for the calculation of quantities relevant to fracture mechanics (such as the work of separation or the work to create a surface in a perfect crystal): they are obtained by integrating the infinitesimal work performed by the modified forces \tilde{f} during the corresponding separation process. Another consequence of the violation of the condition (v) is that the work of separation \tilde{E}_0 is different from the original value E_0 . This difference corresponds to the removal of the work done by the cutoff forces, and it is,

$$\tilde{E}_0 = \int_{r_0}^{\infty} d\tilde{T} < E_0. \quad (10)$$

The difference $\tilde{E}_0 - E_0$ corresponds to the shift of the dashed horizontal line with respect to the value E_0 (Fig. 1, bottom panel). Similarly, the difference $\tilde{\gamma} - \gamma$ may be evaluated from Table I. In particular, $\tilde{\gamma}$ was computed as the work performed by the forces \tilde{f} during the rigid separation of two semibulks obtained by cutting a perfect crystal along a [111] shuffle plane. Notably, the modified force model \tilde{f} is able to reproduce the brittle behavior of silicon, carbon, germanium, and silicon carbide. First of all, the model predicts correctly the brittle crack opening for all these material, as shown in Fig. 2 for silicon and silicon carbide [panels (B) and (A)]. In addition, the calculated failure strength $\tilde{\sigma}_f$ of cracked systems is nicely close to the continuum Griffith predictions. This is shown in Fig. 3, where we report the failure strength of SiC, Si, Ge, and C samples containing a crack of semilength c . The systems were uniaxially loaded along the [111] crystallographic direction in all cases. The LEFM Griffith curve $\sigma_{LEFM}(c)$ for any material is reported in Fig. 3, as well. The deviations of the atomistic data from the Griffith theory are of the order of few tens of a percent and do not depend on the cutoff functions. We observe that at small crack lengths the calculated failure strength is lower than the the-

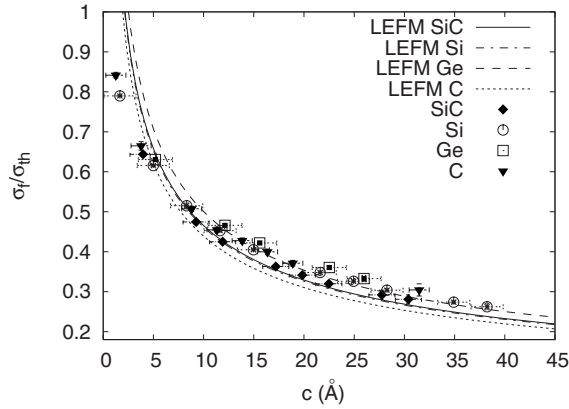


FIG. 3. Failure strength σ_f , normalized with respect to the ideal strength σ_{th} as a function of the crack semilength c . They are reported the results for cracked Si, C, Ge, and SiC samples uniaxially loaded along the $[111]$ direction. The corresponding Griffith curves, obtained with the calculated parameters E and $\tilde{\gamma}$, are reported as well.

oretical expectation (that predicts an unphysical divergence). Similarly to previous findings,^{22,23} this is a consequence of nanoscale effects since the crack size is close to the lattice spacing and a continuum Griffith-like approach is not adequate. These effects can be accounted for in modern continuum theories by introducing into the Griffith theory a nanosized process zone close to the crack tip.²⁴ Concerning the limit of large cracks, we observe that the ratio $\sigma_f(c)/\sigma_{LEFM}(c)$ is slightly larger than 1. Although the deviations are within the error bar, this may be attributed to lattice trapping effects as we already reported for the case of silicon carbide.²²

In order to better quantify the difference between the original T and the modified \tilde{T} Tersoff models, we have compared the failure strength in the two cases. The results for a cracked SiC sample are reported in Fig. 4. Circles and diamonds refer to T and \tilde{T} , respectively. We can observe that the original Tersoff model overestimates the failure strength of an amount of about 24–32 GPa with respect to the modified model. Both results have been compared with the Griffith curve calculated using for the surface energy the values γ (dashed line) and $\tilde{\gamma}$ (solid line) reported in Table I. As already observed above, the atomistic data obtained according to the modified Tersoff potential well reproduce the corresponding LEFM curve (solid line) except for small deviations at very short crack lengths. At variance, according to the original Tersoff model, the failure strength calculated atomistically is at least 24 GPa higher than the related LEFM curve (dashed line). This is a consequence of the unphysical “force barrier” predicted according to the original formulation of the Tersoff potential. Finally, we observe that the modified Tersoff model strongly improves also the ideal strength $\tilde{\sigma}_{th}$ of perfect C, Si, Ge, and SiC crystals under the condition of uniaxial loading. For the SiC case, in particular, we observe that the calculated strength $\tilde{\sigma}_{th}=58\pm 1$ GPa is close to the density functional theory result²⁵ $\sigma_{th}^{DFT}\simeq 50.4$ GPa, whereas we get $\sigma_{th}=103\pm 1$ GPa by using the original Tersoff potential. In Table I a comparison of some

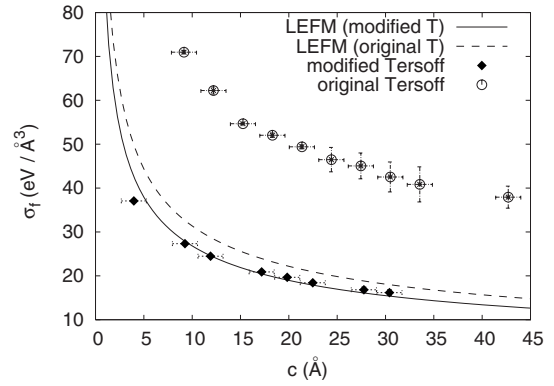


FIG. 4. Comparison of the failure strength σ_f for a cracked SiC sample, uniaxially loaded along $[111]$ crystallographic direction, calculated according to both original (circles) and modified (diamonds) Tersoff model. They are reported also the two Griffith curves, obtained by using the surface energy calculated according to the original (dashed line) and to the modified (solid line) Tersoff model.

physical properties of the original versus modified Tersoff model is presented.

V. CONCLUSIONS

By using the UER we have studied the separation force under hydrostatic tensile deformations in group-IV materials. We have found that it is not possible to reproduce the fracture related properties by using a short-range model. In particular, we have identified the minimum range required by an empirical force model to correctly describe fracture and we have expressed it in terms of the anharmonicity parameter of the UER theory. More importantly, we proved that interactions up to the second-nearest-neighbor distance are required. This proof is validated by a detailed analysis of the Tersoff atomic force model that overestimates the separation force because of its short-range cutoff function.

In order to bypass the limit imposed by the MRM, we proposed a modified Tersoff model in which, at the price of affecting the original cohesive energy, a correct separation force is obtained. The modified model properly describes the brittle fracture in any group-IV materials while incorporating only first-nearest-neighbor interactions. Although the present modification is not good for simulating thermodynamical ensembles at finite temperatures, it nevertheless gives reliable estimates of the failure strength and other crack-related quantities.

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APPENDIX A

Let us consider a force model as described in Sec. III (see also Fig. 1, dotted line). The bulk modulus B is defined by the relation

$$B = V \frac{d^2 w}{dV^2} \Big|_{eq} = \frac{1}{9} \frac{r_0^2}{V_{at}} \frac{df}{dr} \Big|_{r=r_0} = \frac{1}{9} \frac{r_0}{\mu V_{at}} \frac{df}{ds} \Big|_{s=0}. \quad (\text{A1})$$

By using scaled coordinates [see Eq. (2)] it is easy to prove that

$$\frac{d^n w}{ds^n} = (-1)^{n+1} E_0 (s+1-n) e^{-s}. \quad (\text{A2})$$

The minimum of $w(s)$ is reached when $s=0$ and the inflection point occurs at $s=1$. According to Sec. III, r_c is calculated as the point where the function in the linear regions intersects the horizontal line f_{max} . The equivalent of r_c in scaled coordinates is $s_c = \frac{1}{\mu} \left(\frac{r_c}{r_0} - 1 \right)$. Since

$$\frac{d^2 w}{ds^2} \Big|_{s=0} = \frac{dw}{ds} \Big|_{s=1}, \quad (\text{A3})$$

where $\frac{d^2 w}{ds^2} \Big|_{s=0} = E_0$ and $\frac{dw}{ds} \Big|_{s=1} = E_0 e^{-1}$, we get

$$s_c = e^{-1} \quad (\text{A4})$$

corresponding to $r_c = r_0(1 + \mu/e)$. Finally, the distance S_c (which scaled becomes s_2) is fixed by the condition (iii), i.e., $\int_{r_0}^{s_2} f_{sr} dr = E_0$. This condition can be expressed in terms of the work and scaled coordinates as follows:

$$\int_0^{s_2} \frac{dw}{ds}(s) ds = w(s_2) - w(0) = E_0, \quad (\text{A5})$$

which gives $w(s_2) = E_0$. By using the linearity of $w(s)$ in the range $[r_c, S_c]$,

$$w(s) = w(s_c) + (s - s_c) \frac{dw}{ds} \Big|_{s=1}, \quad (\text{A6})$$

and by using the square dependence in the range $[r_0, r_c]$, it is found that

$$\frac{1}{2} \frac{d^2 w}{ds^2} \Big|_{s=0} s_c^2 = w(s_c). \quad (\text{A7})$$

By combining Eqs. (A6) and (A7)

$$w(s) = \frac{1}{2} \frac{d^2 w}{ds^2} \Big|_{s=0} s_c^2 + (s - s_c) \frac{dw}{ds} \Big|_{s=1}. \quad (\text{A8})$$

is finally obtained. From the condition $w(s_2) = E_0$ it follows that

$$s_2 = e + \frac{1}{2e} \quad (\text{A9})$$

and the absolute distance S_c is

$$S_c = r_0 [1 + (e + 0.5e^{-1})\mu]. \quad (\text{A10})$$

The work associated with the force model f_{sr} described above is parabolic in the interval $[r_0, r_c]$ and linear in the range $[r_c, S_c]$ with a slope equal to f_{max} . The relevant property is that the above interaction model f_{sr} is the shortest force model satisfying all the conditions (i), (ii), (iii), and (iv). By choosing a smaller r_c either the slope of the force is modified at r_0 [and condition (ii) fails] or, because of the mathematical continuity of the force, the concavity has to be positive at some point in the range $[r_0, r_c]$ [and therefore the condition (iii) fails]. As a result, we conclude that r_c is the smallest possible value. On the other side, it is not possible to choose a range S' smaller than S_c . In fact, because of the mathematical continuity, if $S' < S_c$, then the total work of separation $\int_{r_c}^{S'} f_{sr} ds$ would be equal to $f_{sr}(\xi)(S' - r_c)$, where ξ is a point within $[r_c, S_c]$. Since, according to (iv), the total work is E_0 and $E_0 = f_{max}(S_c - r_c)$, it follows that $f_{sr}(\xi)(S' - r_c) = f_{max}(S_c - r_c) > f_{max}(S' - r_c)$ or, equivalently, $f_{sr}(\xi) > f_{max}$. This is in contrast to condition (i). We conclude that S_c is the shortest possible choice.

APPENDIX B

The work dT associated with an infinitesimal separation is calculated as

$$dT = u dh + h du = dC + d\tilde{T}. \quad (\text{B1})$$

The term $d\tilde{T} = h du$ is the work associated with the short-range equivalent of the force f and it does not contain any force overestimation; the term dC is due to the force $f_C = w \frac{dh}{dr}$, which, on the contrary, may be very large (if the range is too short). f_C is of the order of $\sim E_0 w(R)/(S-R)$, and it becomes arbitrarily large if R is close to S .

The original Tersoff energy is calculated as a sum over two-body terms,

$$T = \sum h(u^r - bu^a), \quad (\text{B2})$$

where the indices i and j have been omitted for simplicity and, therefore, it must be understood that $\sum_{ij} \rightarrow \sum$; $u^a(r_{ij}) \rightarrow u^a$, $u^r(r_{ij}) \rightarrow u^r$, and $h(r_{ij}) \rightarrow h$. We remark that h is the cutoff function. The term b is a functional depending on the quantity ζ_{ij} , which counts the number of local bonds; more explicitly, we write $\zeta_{ij} = \sum_{k \neq i} h_{ik} g_{ijk}$ where each term is weighted by an angle-dependent term $g(\theta_{ijk})$ (θ_{ijk} is the angle formed by the bonds ik and ij).

The work done by the Tersoff forces as a result of the infinitesimal atomic displacements dr_{ij} is the sum of two contributions,

$$dT = d\tilde{T} + dC, \quad (\text{B3})$$

where dC contains all terms related to the derivative of the cutoff function,

$$dC = \sum dh(u^r - u^a b) - \sum hu^a d_h b, \quad (\text{B4})$$

and $d\tilde{T}$ is the remaining part

$$d\tilde{T} = \sum h(du^r - bdu^a) - \sum d_g b u^a. \quad (\text{B5})$$

We made use of the notation

$$d_g b = \frac{db}{d\zeta_{ij}} \sum_{k \neq i} h_{ik} d g_{ijk} \quad (\text{B6})$$

and

$$d_h b = \frac{db}{d\zeta_{ij}} \sum_{k \neq i} g_{ijk} d h_{ik}. \quad (\text{B7})$$

The modified short-range force field \tilde{f} associated with $d\tilde{T}$ is expected to remove the artifacts due to the cutoff forces (dC terms).

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