

Quasi-perfect elasticity

II. Experimental evidence

A. PAGLIETTI (CAGLIARI)

THE AIM of the present article is to show that the theory of quasi-perfect materials developed in [6] has experimental support. First of all, we shall prove that this theory is nearer than the classic theory to the experimental results about adiabatic temperature variations of elastic materials. We shall demonstrate next that the temperature of a quasi-perfect material has to increase as a result of adiabatic cycles of deformation and that, moreover, a quasi-perfect material can behave in an elastic way only if its deformation does not exceed certain limits. However realistic such a behaviour is, it is not implied by the classic theory. The analysis we present is not merely qualitative; qualitative results are accompanied by formulae for quantitative computation. A discussion on isothermal and adiabatic elastic moduli is also introduced. This may, we hope, be useful for a clearer understanding of the rather confusing experimental data on the subject. The problem of the experimental determination of free energy and entropy is briefly discussed.

Celem niniejszej pracy jest wykazanie, że teoria quasi-idealnych materiałów opracowana w [6] posiada fizyczne uzasadnienie. Przede wszystkim wykazemy, że teoria ta jest bliższa wynikom doświadczalnym otrzymanym przy adiabatycznych zmianach temperatury materiałów sprężystych niż teoria klasyczna. Wykażemy następnie, że temperatura w materiale quasi-idealnym wskutek adiabatycznych cykli odkształcenia musi wzrastać i że ponadto quasi-idealny materiał może zachowywać się w sposób sprężysty wtedy, gdy jego odkształcenie nie przekracza pewnej granicy. Chociaż takie zachowanie się materiału jest realistyczne, to jednak nie jest implikowane przez teorię klasyczną. Analiza, którą przedstawiamy, nie jest jedynie jakościowa; wynikiem jakościowym towarzyszą formuły dla obliczeń ilościowych. Załączona jest również dyskusja na temat izotermicznych i adiabatycznych modułów sprężystych. Wszystko to, mamy nadzieję, posłuży dla lepszego zrozumienia raczej sprzecznych danych doświadczalnych na ten temat. Przedyskutowany został w skrócie również problem doświadczalnego określenia energii swobodnej i entropii.

Целью настоящей работы является доказательство того, что теория квазилинейных материалов, развиваемая в [6], имеет физическое обоснование. Прежде всего покажем, что эта теория более близка экспериментальным результатам, полученным при адиабатических изменениях температуры упругих материалов, чем классическая теория. Затем покажем, что температура в квазиидеальном материале, вследствие адиабатических циклов деформаций, должна возрастать и что кроме этого квазиидеальный материал может вести себя упругим образом тогда, когда его деформация не превысит некоторого предела. Хотя такое поведение материала реалистично, однако не вытекает из классической теории. Анализ, который представим, не является только качественным, качественные результаты сопровождаются формулами для количественных расчетов. Приложено тоже обсуждение изотермических и адиабатических модулей упругости. Все это, надеемся, послужит для лучшего понимания довольно запутанных экспериментальных данных на эту тему. Обсуждена тоже в сокращении проблема экспериментального определения свободной энергии и энтропии.

1. Introduction

IN THE PREVIOUS article [6] the theory of quasi-perfect materials was developed as a generalization of the classical theory of perfect materials and the motivations for such a generalization were discussed. We didn't show, however, why the theory we proposed is exempt

from the objections which can be raised to the classical theory, nor did we point out the experimental support to our approach. This task is worked out in the present article which, therefore, has to be considered as a complement to the previous one. The same definitions and notations adopted in [6] will be maintained throughout this paper.

It has been known for a long time that a material undergoing a deformation process suffers, in general, changes in its temperature. For a perfect material in the range of infinitesimal deformations the theoretical determination of the variation of temperature consequent to an adiabatic deformation is due to KELVIN [7] and [8], and leads to a formula [see Sect. 3, Formula (3.1)] which has been accepted up till now. For a number of materials the experimental check of this formula dates back to a famous paper by JOULE [3], in which the rise or the fall in temperature was found to exceed, almost systematically, that foreseen by Kelvin. Although Joule concluded that Kelvin's theory was completely verified, nonetheless it is the above systematic—though slight—discrepancy between theory and experimental results which opens the way to proving the validity of our hypotheses. Indeed, as will be shown in this paper, the theory of quasi-perfect materials enables to foresee temperature variations greater than those calculated through Kelvin's formula. Our theory, therefore, will appear nearer to the results obtained by Joule.

We have been unable to find recent repetitions of the experiments reported in [3]. Those performed at the end of the last century are not well fitted to our ends. They were done with the aim of pointing out the existence of thermo-mechanical effects, rather than of comparing the latter with the inferences of Kelvin. For this reason precise information about some physical characteristics (like density, thermal expansion coefficient, specific heat) of the tested materials often lacks. On the other hand, a considerable amount of experimental work in this century has dealt with the determination of adiabatic moduli of elastic materials. Clearly, these experiments are equivalent to those of Joule because they give a description of the same phenomenon in terms of different quantities. It would be arduous, however, to deduce the variation of temperature due to an adiabatic process from data regarding adiabatic moduli. As pointed out recently by BELL [1, pp. 377–380], only experiments with the best precision available today may give a meaningful correlation between adiabatic and quasi-static (isothermal) moduli. Such a correlation is essential to calculate the temperature variations in an elastic material during an adiabatic process from the values of its isothermal and adiabatic moduli. As yet, no sufficiently precise experiments have been performed for the materials we are looking at.

Agreement with the experimental results of Joule is not the sole reason why we rely on the theory of quasi-perfect materials. As will be shown in Sect. 5, this theory leads us to predict that an elastic material undergoes an increase in temperature when it performs an adiabatic closed cycle of deformation. The heating of an elastic material following a rapid loading-unloading process is a well-known phenomenon. For perfect materials, however, this phenomenon has up till now been explained by introducing the somewhat artificial hypothesis that both the loading and the unloading adiabatic phase of the cycle are followed by an isothermal process at constant deformation. Clearly, such a hypothesis cannot be easily accepted when very fast cycles are considered. We remain, therefore, rather disappointed as we learn that if a cycle of deformation occurs so fast as to approximate an adiabatic situation, no heating of the material can occur. On the contrary, when

our approach is followed, not only are we able to find a reason for the increase in temperature but also we have a means of calculating it.

Finally, we shall show in Sect. 7 how the elastic range of the materials under consideration can be deduced in the grounds of thermodynamical arguments. We shall point out, moreover, that the values of the limit deformations at the boundary of the elastic range are related to the isothermal and adiabatic moduli at zero strain. It will become apparent, therefore, that the constitutive equations of a quasi-perfect material imply, in agreement with the experimental evidence, a limit to the deformations which an elastic material can undergo without yielding or breaking. In this way a great step can be made towards predicting the yield limit through non-destructive experiments.

2. Isentropic and adiabatic temperature variations

We shall henceforth refer to the formulae established in [6] by introducing between the parentheses containing their reference numbers the symbol **I**. Consider an element of material in a state of deformation **F** at temperature θ . Let $\dot{\mathbf{F}}^*dt$ be an *isentropic* loading deformation increment. By introducing Eq. ((4.10), **I**) and ((5.14), **I**) in Eq. ((7.5), **I**) we obtain

$$(2.1) \quad 0 = s'_{it} + c_v \dot{\theta}.$$

If we denote θ'_{ie} the time derivative of θ during this process, we can express Eq. (2.1) in the form

$$(2.2) \quad \dot{\theta}'_{ie} = -\frac{1}{c_v} \bar{s}'_{it}.$$

Similarly, by considering the isentropic unloading deformation increment $-\dot{\mathbf{F}}^*dt$ we can deduce from Eqs. ((4.11), **I**), ((5.15), **I**) and ((7.7), **I**).

$$(2.3) \quad \dot{\theta}''_{ie} = -\frac{1}{c_v} \bar{s}''_{it};$$

the meaning of the symbol θ'_{ie} is obvious. The relations (2.2) and (2.3) solve the problem of finding the temperature changes produced by an isentropic process in a quasi-perfect material.

We shall now pursue the analogous analysis for adiabatic processes. Observe, first of all, that Eq. ((7.3), **I**) is valid for every loading process (not necessarily an adiabatic one) and that by means of Eq. ((5.14), **I**) it can be written as

$$(2.4) \quad \dot{\epsilon} = \text{tr}[(\partial_{\mathbf{F}} \hat{\psi}')^T \dot{\mathbf{F}}] + \theta \text{tr}[(\partial_{\mathbf{R}} \hat{\eta}')^T \dot{\mathbf{F}}] + c_v \dot{\theta}.$$

On the other hand, the analogous relation valid for every unloading deformation increment can be obtained from Eqs. ((7.6), **I**), ((7.7), **I**) and ((5.15), **I**) and reads

$$(2.5) \quad \dot{\epsilon} = \text{tr}[(\partial_{\mathbf{F}} \hat{\psi}'')^T \dot{\mathbf{F}}] + \text{tr}[(\partial_{\mathbf{R}} \hat{\eta}'')^T \dot{\mathbf{F}}] + c_v \dot{\theta}.$$

Consider then a generic *adiabatic* loading deformation increment $\dot{\mathbf{F}}^*dt$. The relation (2.4) can be written as

$$(2.6) \quad \dot{\epsilon}_{ad} = \text{tr}[(\partial_{\mathbf{F}} \hat{\psi}')^T \dot{\mathbf{F}}^*] + \theta \text{tr}[(\partial_{\mathbf{R}} \hat{\eta}')^T \dot{\mathbf{F}}^*] + c_v \dot{\theta},$$

where $\dot{\mathbf{F}}^*$ and $\dot{\theta}$ are to be understood as constrained in such a way as to be relevant to an adiabatic process. If we introduce Eqs. ((4.10), I) and ((7.11), I) in Eq. (2.6) and if we denote explicitly $\dot{\theta}'_{ad}$ the quantity $\dot{\theta}$ which appears in Eq. (2.6), we get

$$(2.7) \quad \dot{\theta}'_{ad} = \frac{1}{c_v} \left\{ -\bar{s}'_{it} + \frac{1}{\varrho} \operatorname{tr}(\mathbf{T}\mathbf{F}^{-1}\dot{\mathbf{F}}^*) - \operatorname{tr}[(\partial_{\mathbf{F}}\hat{\psi})^T \dot{\mathbf{F}}^*] \right\}.$$

A similar reasoning for the adiabatic unloading deformation increment $-\dot{\mathbf{F}}^*dt$ leads from Eqs. (2.5), ((4.11), I) and ((7.11), I) to the relation

$$(2.8) \quad \dot{\theta}''_{ad} = \frac{1}{c_v} \left\{ -\bar{s}''_{it} - \frac{1}{\varrho} \operatorname{tr}(\mathbf{T}\mathbf{F}^{-1}\dot{\mathbf{F}}^*) + \operatorname{tr}[(\partial_{\mathbf{F}}\hat{\psi}')^T \dot{\mathbf{F}}^*] \right\}.$$

The relations (2.7) and (2.8) give the temperature variations caused by an adiabatic deformation process in a quasi-perfect material.

From Eqs. (2.7), (2.2) and ((2.9), I) we can deduce that

$$(2.9) \quad \dot{\theta}'_{ad} \geq \dot{\theta}'_{io}.$$

Similarly from Eqs. (2.8), (2.3) and ((2.15), I) we obtain

$$(2.10) \quad \dot{\theta}''_{ad} \geq \dot{\theta}''_{io}.$$

3. Comparison with Kelvin's formula and Joule's experiments

For perfect materials in the range of small deformations KELVIN [7] and [8] derived a formula relating temperature changes to adiabatic increments of deformation. This formula can be expressed as (cfr. [2] for a modern derivation)

$$(3.1) \quad \dot{\theta}_{ad} = -\frac{\theta}{\varrho_0 c_v} \operatorname{tr}(\boldsymbol{\beta}\mathbf{L}),$$

where ϱ_0 is the mass density in the initial stress-free configuration, $\mathbf{L} = \mathbf{F}\dot{\mathbf{F}}^{-1}$ and $\boldsymbol{\beta}$ is the second-rank tensor defined by

$$(3.2) \quad \boldsymbol{\beta} = -\varrho_0 \partial_{\theta} \partial_{\tilde{\mathbf{E}}} \hat{\Psi}(\tilde{\mathbf{E}}, \theta).$$

In Eq. (3.2) $\tilde{\mathbf{E}}$ is the infinitesimal strain tensor

$$(3.3) \quad \tilde{\mathbf{E}} = \frac{1}{2} (\mathbf{F} + \mathbf{F}^T) - \mathbf{1}$$

and $\Psi = \hat{\Psi}(\tilde{\mathbf{E}}, \theta)$ is the free energy of the perfect material, a quadratic homogeneous function of $\tilde{\mathbf{E}}$ (remember that for small deformations every perfect material can be considered as a linear elastic material). If the material is isotropic and if we denote α the *thermal expansion coefficient* (positive if an increment of θ produces an increment of volume), then $\boldsymbol{\beta}$ is given by

$$(3.4) \quad \boldsymbol{\beta} = \beta \mathbf{1} = \frac{M}{1-2\nu} \alpha \mathbf{1},$$

where β is a scalar, M is the isothermal Young's modulus and ν is the isothermal Poisson's ratio.

Our previous formulae (2.7) and (2.8) are valid for a class of materials which is wider than that considered by Kelvin. For perfect materials both formulae (2.7) and (2.8) reduce to

$$(3.5) \quad \dot{\theta}_{ad} = \frac{1}{c_v} \left\{ -s_{it} + \frac{1}{\rho} w_{ad} - \text{tr}[(\partial_{\mathbf{F}}\hat{\psi})^T \dot{\mathbf{F}}] \right\},$$

where $\hat{\psi}$ is the free energy of the perfect material. We shall now demonstrate that in the range of small deformations — the only one in which Eq. (3.1) holds — the relation (3.5) is completely equivalent to Eq. (3.1). For a perfect material Eqs. (2.4) and (2.5) reduce to

$$(3.6) \quad \dot{\epsilon} = \text{tr}[(\partial_{\mathbf{F}}\hat{\psi})^T \dot{\mathbf{F}}] + \theta \text{tr}[(\partial_{\mathbf{F}}\hat{\eta})^T \dot{\mathbf{F}}] + c_v \dot{\theta},$$

where

$$(3.7) \quad \hat{\eta} = -\partial_{\theta} \hat{\psi}$$

is the entropy of the perfect material. Writing Eq. (3.6) for an adiabatic deformation increment and remembering Eq. ((7.11), I), we can express Eq. (3.5) in the form

$$(3.8) \quad \dot{\theta}_{ad} = \frac{1}{c_v} \{ -s_{it} + \theta \text{tr}[(\partial_{\mathbf{F}}\hat{\eta})^T \dot{\mathbf{F}}] + c_v \dot{\theta}_{ad} \}.$$

Since for perfect materials Eqs. (2.2) and (2.3) yield

$$(3.9) \quad s_{it} = -c_v \dot{\theta}_{ie} \equiv -c_v \dot{\theta}_{ad},$$

Eq. (3.8) becomes

$$(3.10) \quad -\dot{\theta}_{ad} = \frac{\theta}{c_v} \text{tr}[(\partial_{\mathbf{F}}\hat{\eta})^T \dot{\mathbf{F}}].$$

From this and from Eq. (3.7) we get

$$(3.11) \quad \dot{\theta}_{ad} = \frac{\theta}{c_v} \text{tr}[(\partial_{\theta} \partial_{\mathbf{F}} \hat{\psi})^T \dot{\mathbf{F}}] = \frac{\theta}{c_v} \text{tr}[\mathbf{F}(\partial_{\theta} \partial_{\mathbf{F}} \hat{\psi})^T \dot{\mathbf{F}} \mathbf{F}^{-1}] = \frac{\theta}{c_v} \text{tr}[\mathbf{F}(\partial_{\theta} \partial_{\mathbf{F}} \hat{\psi})^T \mathbf{L}].$$

As a consequence of the frame-indifferent character of $\hat{\psi}$, it can be shown (see [10, p. 309]) that

$$(3.12) \quad \partial_{\mathbf{F}} \hat{\psi}(\mathbf{F}, \theta)^T = \partial_{\mathbf{E}} \bar{\psi}(\mathbf{E}, \theta) \mathbf{F}^T,$$

where $\bar{\psi}$ is an appropriate function of \mathbf{E} and θ , while \mathbf{E} is the strain tensor defined by

$$(3.13) \quad \mathbf{E} = \frac{1}{2} (\mathbf{F}^T \mathbf{F} - \mathbf{1}).$$

For infinitesimal deformations \mathbf{E} and $\tilde{\mathbf{E}}$ coincide. Since the reference configuration is supposed to be stress-free, if we multiply from the left both sides of Eq. (3.12) by \mathbf{F} , if we remember that for infinitesimal deformations $\mathbf{F} = \mathbf{1} + \tilde{\mathbf{R}} + \tilde{\mathbf{E}}$ (where $\tilde{\mathbf{R}} = -\tilde{\mathbf{R}}^T$ is the infinitesimal rotation tensor), and if we expand $\bar{\psi}$ in power series of \mathbf{E} , then, we can easily obtain from Eq. (3.12) the relation

$$(3.14) \quad \text{tr}[\mathbf{F}(\partial_{\theta} \partial_{\mathbf{F}} \hat{\psi})^T \mathbf{L}] = \text{tr}[\partial_{\theta} \partial_{\tilde{\mathbf{E}}} \hat{\psi}(\tilde{\mathbf{E}}, \theta) \mathbf{L}].$$

Here of course the equality sign holds to within small quantities of the same order of magnitude as $\sup(|\tilde{\mathbf{E}}|^2, |\tilde{\mathbf{R}}|^2)$. From Eqs. (3.11)₃ and (3.2) we get, finally,

$$(3.15) \quad \dot{\theta}_{ad} = -\frac{\theta}{\rho_0 c_v} \text{tr}(\beta \mathbf{L}).$$

That is, in the range of infinitesimal deformations the relation (3.5) coincides with Kelvin's formula (3.1).

We shall henceforth denote $\dot{\theta}_{ad}^{(K)}$ the value of $\dot{\theta}_{ad}$ calculated by means of Eq. (3.1). Since we have seen that Eq. (3.1)—when valid—is equivalent to Eq. (3.5) we may substitute (3.5) for (3.1) in the forthcoming reasoning. Consider an element of material in a certain state of deformation \mathbf{F} at temperature θ . Suppose we make it follow an adiabatic loading deformation increment $\dot{\mathbf{F}}dt$. If we consider the material as perfect, we can apply Eq. (3.5) to calculate the variation of θ during this process. Since for perfect materials $\mathbf{T} = \rho \mathbf{F}(\partial_{\mathbf{F}}\hat{\psi})^T$ and since for an infinitesimal deformation increment starting from a given value of \mathbf{F} and θ we have that $w_{ad} = w_{it} = \rho \text{tr}[(\partial_{\mathbf{F}}\hat{\psi})^T \mathbf{F}]$, we obtain

$$(3.16) \quad \dot{\theta}_{ad}^{(K)} = -\frac{1}{c_v} s_{it}.$$

On the other hand, if the hypothesis of perfect material is not introduced, the quantity $\dot{\theta}_{ad}$ has to be calculated by means of Eq. (2.7). By subtracting Eq. (3.16) from Eq. (2.7) and remembering Eq. ((4.8), I) we obtain

$$(3.17) \quad \dot{\theta}'_{ad} - \dot{\theta}_{ad}^{(K)} = \frac{1}{c_v} (-\bar{s}'_{it} + s'_{it}) = \frac{1}{c_v} \left\{ -\frac{1}{\rho} w_{it} + \text{tr}[(\partial_{\mathbf{F}}\hat{\psi}')^T \dot{\mathbf{F}}] \right\}.$$

From Eq. (3.17)₁ and from Eq. ((4.12), I) we get

$$(3.18) \quad \dot{\theta}'_{ad} \leq \dot{\theta}_{ad}^{(K)}.$$

A similar reasoning for the adiabatic unloading deformation increment $-\dot{\mathbf{F}}dt$ leads to

$$(3.19) \quad \dot{\theta}''_{ad} - \dot{\theta}_{ad}^{(K)} = \frac{1}{c_v} (-\bar{s}''_{it} + s_{it}) = \frac{1}{c_v} \left\{ -\frac{1}{\rho} w_{it} + \text{tr}[(\partial_{\mathbf{F}}\hat{\psi}'')^T \dot{\mathbf{F}}] \right\}.$$

From Eqs. (3.19) and ((4.13), I) we get

$$(3.20) \quad \dot{\theta}''_{ad} \geq \dot{\theta}_{ad}^{(K)}.$$

In view of the hypotheses on a and b made in [6, Sect. 3] the equality sign in the relations (3.18) and (3.20) can hold only at the reference state or for values of strain which are at the boundary of the elastic range. Therefore, for states of deformation within the elastic range the relations (3.18) and (3.20) are, in general, strong inequalities.

The above results can be checked experimentally if we compare them with the experiments of JOULE [3] and [4]. It has to be said, however, that Joule's papers are concerned only with loading processes. For unloading processes we have been unable to find adequate experimental works. As observed in the Introduction, the experiments of Joule give values of $\dot{\theta}_{ad}$ which are systematically in slight disagreement with those foreseen by Kelvin. Let $\dot{\theta}_{ad}^{(J)}$ denote the value of $\dot{\theta}_{ad}$ measured by Joule. For uniaxial increment of traction in axially-

loaded rods Joule found that $\dot{\theta}_{ad}^{(J)} < \dot{\theta}_{ad}^{(K)} < 0$ for steel and for a number of other materials with $\alpha > 0$. Similar experiments for vulcanized rubber in situations in which $\alpha < 0$ (remember the anomalous behaviour of rubber as far as the thermal expansion coefficient is concerned) showed that $0 < \dot{\theta}_{ad}^{(J)} < \dot{\theta}_{ad}^{(K)}$. These results are collected in [3, Sect. 93]. Joule also performed experiments in simple compression. The latter, however, do not seem sufficiently accurate. Joule himself pointed out a possible source of error in his compression experiments on specimens of vulcanized rubber (cfr. [3, Sects. 115–116]). Since specimens of the same shape were used in all his compression tests, it seems likely that an analogous error also affects (at least under large compressive forces) the results on the other materials he tested. For small compressive forces, however, Joule's experiments on wrought iron(*) are still in agreement with the relation (3.18); see [3, Sects. 94–95]. The same can be said for the compression experiments on vulcanized rubber (cfr. [3, Sect. 114]) provided that we confine our attention to the results relevant to small loads and remember that the anomaly of the thermal expansion coefficient of rubber disappears in compression (that is $\alpha > 0$ for every value of the compressive force). In a subsequent work Joule performed experiments on compression of water. The results are reported in [4, Table 1]. The latter show that at temperatures for which water has a positive thermal expansion coefficient the relation $0 < \dot{\theta}_{ad}^{(J)} < \dot{\theta}_{ad}^{(K)}$ is almost always verified for loading deformation increments. At temperatures for which water has a negative expansion coefficient, the same experiments show that $\dot{\theta}_{ad}^{(J)} < \dot{\theta}_{ad}^{(K)} < 0$. These results on water are again in complete agreement with the relation (3.18) and, therefore, afford further support to the hypothesis of quasi-perfect elasticity.

4. Adiabatic and isothermal Young's moduli

Confining our attention to the case of infinitesimal deformations, consider an isotropic thermoelastic material for which the stress-strain relation is given by the familiar linear equation

$$(4.1) \quad \mathbf{T} = \frac{M\nu}{(1+\nu)(1-2\nu)} (\text{tr}\tilde{\mathbf{E}})\mathbf{1} + \frac{M}{1+\nu} \tilde{\mathbf{E}} - \frac{M}{1-2\nu} \alpha \Delta\theta \mathbf{1}$$

or, equivalently, by

$$(4.2) \quad \tilde{\mathbf{E}} = -\frac{\nu}{M} (\text{tr}\mathbf{T})\mathbf{1} + \frac{1+\nu}{M} \mathbf{T} + \alpha \Delta\theta \mathbf{1}.$$

In these relations M and ν are respectively the isothermal Young's modulus and the isothermal Poisson's ratio already introduced in the previous Section; $\tilde{\mathbf{E}}$ is the infinitesimal stress tensor (3.3) and $\Delta\theta$ is defined by

$$(4.3) \quad \Delta\theta = \theta - \theta_0.$$

θ_0 is the absolute temperature relevant to the stress-free reference configuration.

(*) Joule did not perform compression experiments on steel.

Consider a right cylinder of material with the axis parallel to the x_1 -axis of a reference system which for simplicity's sake will be assumed to be rectangular. Since we are considering infinitesimal deformations, the superposition principle holds. We can, therefore, suppose that the cylinder is in a stressed state represented by a certain stress tensor ${}^0\mathbf{T}$ and, notwithstanding this, we can refer to the initial configuration when we consider further increments of deformation. To avoid complicated formulae, we shall assume that ${}^0\mathbf{T}$ has the following form:

$$(4.4) \quad {}^0T_{11} = T \quad \text{and} \quad {}^0T_{ij} = 0 \quad \text{for} \quad [i, j] \neq [1, 1]$$

where, of course, $(i, j) \in \{1, 2, 3\}$. We shall denote ${}^0\mathbf{F}$ and ${}^0\mathbf{E}$ respectively the deformation gradient and the infinitesimal strain tensor relevant to the state of stress ${}^0\mathbf{T}$. Let the cylinder be in the stressed state ${}^0\mathbf{T}$ and suppose we increase the tension at the bases of the cylinder by applying an infinitesimal force dT (per unit area) directed along the axis and uniformly distributed over the bases. The components of the homogeneous stress field ${}^1\mathbf{T}$ induced in the body by dT are

$$(4.5) \quad {}^1T_{11} = dT \quad \text{and} \quad {}^1T_{ij} = 0 \quad \text{for} \quad [i, j] \neq [1, 1].$$

The strain tensor ${}^1\tilde{\mathbf{E}}$ produced by dT when the latter is applied in an isothermal way is given by

$$(4.6) \quad {}^1\tilde{E}_{11} = \frac{1}{M} dT,$$

$$(4.7) \quad {}^1\tilde{E}_{22} = {}^1\tilde{E}_{33} = -\frac{\nu}{M} dT, \quad {}^1\tilde{E}_{ij} = 0 \quad \text{for} \quad i \neq j,$$

as follows from Eqs. (4.5) and (4.2) because in this process $\Delta\theta = 0$. On the other hand, if dT is applied when the body is thermally insulated, we have

$$(4.8) \quad \Delta\theta = d\theta_{ad} = \dot{\theta}_{ad} dt,$$

where $d\theta_{ad}$ is the variation of temperature produced by dT whereas dt is the infinitesimal time interval in which the process takes place. If we assume that the body is made up of a perfect material, Kelvin's formula applies. From Eq. (3.1), from Eqs. (4.6) to (4.8) and from Eq. (3.4) we can, therefore, obtain

$$(4.9) \quad \Delta\theta = \dot{\theta}_{ad}^{(K)} dt = -\theta_0 \frac{\alpha}{\rho_0 c_v} dT.$$

Inserting Eqs. (4.9) and (4.5) in Eq. (4.2) we can calculate the components of the strain tensor ${}^2\tilde{\mathbf{E}}$ which are produced in the cylinder when dT is applied adiabatically:

$$(4.10) \quad {}^2\tilde{E}_{11} = \frac{1}{M} + \alpha \dot{\theta}_{ad}^{(K)} dt = \frac{1}{M} dT - \theta_0 \frac{\alpha^2}{\rho_0 c_v} dT,$$

$$(4.11) \quad {}^2\tilde{E}_{22} = {}^2\tilde{E}_{33} = -\frac{\nu}{M} dT - \theta_0 \frac{\alpha^2}{\rho_0 c_v} dT, \quad {}^2\tilde{E}_{ij} = 0 \quad \text{for} \quad i \neq j.$$

Since the adiabatic Young's modulus is defined by

$$(4.12) \quad M_{ad} = dT_{11} / {}^2\tilde{E}_{11},$$

we get from Eqs. (4.10) the following relationship:

$$(4.13) \quad \frac{1}{M_{ad}^{(K)}} = \frac{1}{M} - \theta_0 \frac{\alpha^2}{\rho_0 c_v},$$

which was deduced in 1878 by Kelvin in his article on Elasticity in the Encyclopedia Britannica [9]. The index (K) attached to M_{ad} reminds us that M_{ad} is calculated on the assumption that the material is a perfect elastic one, that is on the assumption that $\dot{\theta}_{ad} = \dot{\theta}_{ad}^{(K)}$.

Let us discuss now the case in which the material is quasi-perfect. Consider again the above cylinder under the deformation process produced by dT and assume, for the time being, that this process is a loading deformation process. If dT is applied adiabatically, we can repeat an analogous reasoning to that done to arrive at Eqs. (4.10) and we get

$$(4.14) \quad {}^3\tilde{E}_{11} = \frac{1}{M} dT + \alpha \dot{\theta}'_{ad} dt.$$

In this relation ${}^3\tilde{E}_{11}$ is the $(1, 1)$ -component of the strain tensor ${}^3\tilde{\mathbf{E}}$ which is produced by the adiabatic loading dT . By means of Eq. (3.17) we can express Eq. (4.14) in the form

$$(4.15) \quad {}^3\tilde{E}_{11} = \frac{1}{M} dT + \alpha \dot{\theta}'_{ad} dt - \frac{\alpha}{c_v} \left\{ \frac{1}{\rho_0} w_{it} - \text{tr}[(\partial_{\mathbf{F}}\hat{\psi}')_0^T \dot{\mathbf{F}}] \right\} dt.$$

Here the index 0 attached to $(\partial_{\mathbf{F}}\hat{\psi}')^T$ means that this derivative has to be calculated at the state of deformation relevant to the stress ${}^0\mathbf{T}$. Remembering Eq. (4.10)₁ we get from Eq. (4.15)

$$(4.16) \quad {}^3\tilde{E}_{11} = {}^2\tilde{E}_{11} - \frac{\alpha}{c_v} \left\{ \frac{1}{\rho_0} w_{it} + \text{tr}[(\partial_{\mathbf{F}}\hat{\psi}')_0^T \dot{\mathbf{F}}] \right\} dt.$$

From this relation, from Eq. (4.12) and from Eq. (4.13) we obtain

$$(4.17) \quad \frac{1}{M'_{ad}} = \frac{1}{M_{ad}^{(K)}} - \frac{\alpha}{c_v} \frac{1}{dT} \left\{ \frac{1}{\rho_0} w_{it} - \text{tr}[(\partial_{\mathbf{F}}\hat{\psi}')_0^T \dot{\mathbf{F}}] \right\} dt,$$

where M'_{ad} denotes the adiabatic Young's modulus relevant to the loading process of the quasi-perfect material. Since the process we are considering starts from a state in which the stress tensor is ${}^0\mathbf{T}$, we can deduce from the relations (4.4) that for this process

$$(4.18) \quad w_{it} dt = {}^0T_{11} \frac{dT}{M}.$$

To calculate the quantity $\text{tr}[(\partial_{\mathbf{F}}\hat{\psi}')_0^T \dot{\mathbf{F}}] dt$ which appears in Eqs. (4.15) to (4.17), observe that $\dot{\mathbf{F}} dt$ is the deformation gradient consequent to the application of dT . Therefore, since dT does not produce any rotation of the cylinder and since we are considering infinitesimal deformations, we have

$$(4.19) \quad \dot{\mathbf{F}} dt = \overline{(\mathbf{1} + {}^3\tilde{\mathbf{E}})} dt = {}^3\dot{\mathbf{E}} dt = {}^3\tilde{\mathbf{E}}.$$

By exploiting the relations (4.19) we can write

$$(4.20) \quad \text{tr}[(\partial_{\mathbf{F}}\hat{\psi}')_0^T \dot{\mathbf{F}}] dt = \text{tr}[(\partial_{\mathbf{F}}\hat{\psi}')_0^T {}^3\tilde{\mathbf{E}}]$$

or, equivalently,

$$(4.21) \quad \text{tr}[(\partial_{\mathbf{F}}\hat{\psi}')_0^T \dot{\mathbf{F}}] dt = \text{tr}[{}^0\mathbf{F}^{-1} {}^0\mathbf{F} (\partial_{\mathbf{F}}\hat{\psi}')_0^T {}^3\tilde{\mathbf{E}}].$$

In this relation ${}^0\mathbf{F}$ is the deformation gradient relevant to the state of stress ${}^0\mathbf{T}$. Since ${}^0\mathbf{T}$ does not cause any rotation of the cylinder, we have

$$(4.22) \quad {}^0\mathbf{F} = \mathbf{1} + {}^0\tilde{\mathbf{E}}.$$

We can, therefore, infer from Eq. (4.21) the following relations:

$$(4.23) \quad \text{tr}[(\partial_{\mathbf{F}}\hat{\psi}')_0^T \dot{\mathbf{F}}] dt = \text{tr}[{}^0\mathbf{F}(\partial_{\mathbf{F}}\hat{\psi}')_0^T {}^0\mathbf{F}^{-1} {}^3\tilde{\mathbf{E}}] = \\ = \text{tr}[{}^0\mathbf{F}(\partial_{\mathbf{F}}\hat{\psi}')_0^T (\mathbf{1} + {}^0\tilde{\mathbf{E}})^{-1} {}^3\tilde{\mathbf{E}}] = \text{tr}[{}^0\mathbf{F}(\partial_{\mathbf{F}}\hat{\psi}')_0^T {}^3\tilde{\mathbf{E}}].$$

The relation (4.23)₃ follows from the relation (4.23)₂ since ${}^0\tilde{\mathbf{E}} {}^3\tilde{\mathbf{E}}$ is a negligible quantity for infinitesimal deformations. Since the only non-vanishing component of ${}^0\mathbf{T}$ is ${}^0T_{11}$, it follows from Eq. ((3.22), I) that the only non-vanishing component of ${}^0\mathbf{F}(\partial_{\mathbf{F}}\hat{\psi}')_0^T$ is $[{}^0\mathbf{F}(\partial_{\mathbf{F}}\hat{\psi}')_0^T]_{11}$. We can therefore deduce from Eqs. (4.23)₃ and (4.14) that

$$(4.24) \quad \text{tr}[(\partial_{\mathbf{F}}\hat{\psi}')_0^T \dot{\mathbf{F}}] dt = [{}^0\mathbf{F}(\partial_{\mathbf{F}}\hat{\psi}')_0^T]_{11} {}^3E_{11} = [{}^0\mathbf{F}(\partial_{\mathbf{F}}\hat{\psi}')_0^T]_{11} \left(\frac{dT}{M} + \alpha \dot{\theta}'_{ad} dt \right).$$

Introducing Eqs. (4.24) and (4.18) in Eq. (4.17) we finally get

$$(4.25) \quad \frac{\dot{1}}{M'_{ad}} = \frac{1}{M_{ad}^{(K)}} - \frac{\alpha}{\varrho_0 c_v M} \{ {}^0T_{11} - \varrho_0 [{}^0\mathbf{F}(\partial_{\mathbf{F}}\hat{\psi}')_0^T]_{11} \}$$

to within negligible quantities. A similar procedure for unloading processes would lead to the analogous relation

$$(4.26) \quad \frac{1}{M''_{ad}} = \frac{1}{M_{ad}^{(K)}} + \frac{\alpha}{\varrho_0 c_v M} \{ {}^0T_{11} - \varrho_0 [{}^0\mathbf{F}(\partial_{\mathbf{F}}\hat{\psi}'')_0^T]_{11} \},$$

where M''_{ad} is the adiabatic Young's modulus relevant to unloading processes.

From Eqs. (4.25), (4.26) and ((3.21), I) we can deduce that for $\alpha > 0$

$$(4.27) \quad M_{ad}^{\prime\prime} \geq M_{ad}^{(K)} \quad \text{and} \quad M_{ad}'' \geq M_{ad}^{(K)}.$$

When $\alpha < 0$ the inequality sign in the above relations has to be reverted. The relations (4.25) to (4.27) offer another clue for an experimental check of the proposed theory. As mentioned in the Introduction, however, no sufficiently accurate experiments have been as yet performed. We think it better, therefore, to refrain from discussing the available experimental results.

5. Adiabatic loading-unloading cycles

Let an element of material be in a state of deformation \mathbf{F} at temperature θ . Consider two opposite deformation increments, say $\dot{\mathbf{F}}^* dt$ and $-\dot{\mathbf{F}}^* dt$ and suppose that $\dot{\mathbf{F}}^* dt$ is a loading deformation increment. If both these increments are performed adiabatically, we can argue from Eqs. (2.9), (2.10), (2.2) and (2.3) that the temperature variations they produce are as follows:

$$(5.1) \quad \dot{\theta}'_{ad} \geq -\frac{1}{c_v} \bar{s}'_{it}$$

and

$$(5.2) \quad \dot{\theta}'_{\varepsilon d} \geq -\frac{1}{c_v} \bar{s}'_{it}$$

Since the behaviour of the materials we are considering is for many respects very near to that of a perfect material, we have to expect the differences between \hat{T} , $\rho \mathbf{F}(\partial_{\mathbf{F}} \hat{\psi}')$ and $\rho \mathbf{F}(\partial_{\mathbf{F}} \hat{\psi}'')$ to be small. Thus we can reasonably argue from Eqs. ((4.8), I) and ((4.9), I) that \bar{s}'_{it} and \bar{s}''_{it} have the same sign of the quantity s_{it} when the latter is respectively relevant to loading or to unloading deformations. Since the amount of heat absorbed by the body during an isothermal deformation increment is equal to the amount of heat lost by the body during the opposite deformation increment(*), it turns out that \bar{s}'_{it} and \bar{s}''_{it} are quantities of opposite sign when calculated for $\dot{\mathbf{F}}^*$ and $-\dot{\mathbf{F}}^*$, respectively. From this observation and from Eqs. (2.7) and (2.8) we can, moreover, argue that $\dot{\theta}'_{ad}$ and $\dot{\theta}''_{ad}$ too assume values of opposite sign when calculated for $\dot{\mathbf{F}}^*$ and $-\dot{\mathbf{F}}^*$, respectively.

We have seen in Sect. 2 that a quasi-perfect material undergoing an adiabatic deformation process suffers changes in its temperature. We want to demonstrate here that the positive variation of temperature relevant to a certain adiabatic deformation increment is always greater than the absolute value of the negative variation of temperature relevant to the opposite adiabatic deformation increment. This implies, clearly, that the temperature of a body at the end of an adiabatic deformation cycle between two different states of deformation must be greater than the temperature possessed by the body at the beginning of the cycle. As observed in the Introduction, this result is much more realistic than that foreseen by the theory of perfect materials. According to the latter, indeed, no temperature variation is brought about by an adiabatic closed cycle of deformation. The analysis which follows should, therefore, provide further support to the hypothesis of quasi-perfect elasticity.

Consider a quasi-perfect material (e.g. non cold-worked mild steel) with a positive thermal expansion coefficient. This material absorbs heat during the isothermal loading increment $\dot{\mathbf{F}}^* dt$ and loses heat during the isothermal unloading $-\dot{\mathbf{F}}^* dt$. From the above remarks on the sign of s_{it} , \bar{s}'_{it} and \bar{s}''_{it} we can argue that in this case

$$(5.3) \quad \bar{s}'_{it} > 0 \quad \text{and} \quad \bar{s}''_{it} < 0,$$

and that, consequently,

$$(5.4) \quad \dot{\theta}_{ad} < 0 \quad \text{and} \quad \dot{\theta}'_{ad} > 0.$$

Since s_{it} relevant to $\dot{\mathbf{F}}^* dt$ is equal and opposite to s_{it} relevant to $-\dot{\mathbf{F}}^* dt$, we can easily infer from Eqs. (5.3), ((4.12), I) and (4.13, I) that

$$(5.5) \quad (\bar{s}'_{it}/\bar{s}''_{it}) \geq -1.$$

On the other hand, keeping in mind the inequalities (5.3) and (5.4) we can deduce from the inequalities (5.1) and (5.2) that

$$(5.6) \quad (\dot{\theta}'_{ad}/\dot{\theta}''_{ad}) \geq (\bar{s}'_{it}/\bar{s}''_{it}).$$

(*) This is a direct consequence of the energy conservation principle and of our assumptions on $\hat{\varepsilon}$ and \hat{T} .

Finally, from the inequalities (5.5) and (5.6) we get

$$(5.7) \quad \dot{\theta}'_{ad} \geq -\dot{\theta}'_{ad}.$$

The relations (5.4) and (5.7) prove that for opposite adiabatic deformation increments the positive variation of temperature is greater than the negative one. Since an adiabatic cycle between any two states of deformation is composed of opposite deformation increments, it turns out that the temperature at the end of the cycle must be greater than that at the beginning. Observe that from the hypotheses on a and b introduced in [6, Sect. 3] the equality sign in the inequality (5.7) cannot hold during all the cycle.

The case of a material with $\alpha < 0$ (e.g. vulcanized rubber under appropriate tensile forces) can be studied in the light of the previous one. Instead of the inequalities (5.3) and (5.4) we have in this case

$$(5.8) \quad \bar{s}'_{it} < 0, \quad \bar{s}''_{it} > 0$$

and

$$(5.9) \quad \dot{\theta}'_{ad} > 0, \quad \dot{\theta}''_{ad} < 0.$$

From the relations (5.8), ((4.12), I) and ((4.13), I) we can arrive at

$$(5.10) \quad (\bar{s}'_{it}/\bar{s}''_{it}) \leq -1.$$

On the other hand, from the inequalities (5.1), (5.2), (5.8) and (5.9) we can derive

$$(5.11) \quad (\dot{\theta}'_{ad}/\dot{\theta}''_{ad}) \leq (\bar{s}'_{it}/\bar{s}''_{it}).$$

Finally, from the inequalities (5.10) and (5.11) we get

$$(5.12) \quad \dot{\theta}'_{ad} \geq -\dot{\theta}''_{ad},$$

which proves that also when $\alpha < 0$ the positive variation of temperature caused by an adiabatic increment of deformation is greater than the absolute value of the negative variation of temperature caused by the opposite deformation increment.

6. On the experimental determination of free energy and entropy

Information about $\hat{\psi}'$, $\hat{\psi}''$ and, hence, about $\hat{\eta}'$ and $\hat{\eta}''$ can be experimentally obtained in a number of ways. The formulae (3.17) and (3.19) relate $\partial_{\mathbf{F}}\hat{\psi}'$ and $\partial_{\mathbf{F}}\hat{\psi}''$ to the experimentally measurable quantities $\dot{\theta}'_{ad}$, $\dot{\theta}''_{ad}$ and w_{it} . Analogously, $\partial_{\mathbf{F}}\hat{\psi}'$ and $\partial_{\mathbf{F}}\hat{\psi}''$ can be determined by means of Eqs. (4.25) and (4.26) once the adiabatic elastic moduli are experimentally determined. We shall discuss in this section how $\hat{\psi}'$, $\hat{\psi}''$, $\hat{\eta}'$ and $\hat{\eta}''$ can be determined from experimental measurements of the amount of heat s_{it} absorbed in the unit time during an isothermal deformation process.

Consider an isothermal loading process. From the first principle of thermodynamics ((4.2), I) it can be easily seen that s_{it} can be always expressed as

$$(6.1) \quad s_{it} = \hat{s}_{it}(\mathbf{F}, \theta, \dot{\mathbf{F}}) = \text{tr}(\mathbf{H}\dot{\mathbf{F}}).$$

Here

$$(6.2) \quad \mathbf{H} = \hat{\mathbf{H}}(\mathbf{F}, \theta) = (\partial_{\mathbf{F}}\hat{\varepsilon})^T - \frac{1}{\rho} \mathbf{F}^{-1}\mathbf{T}$$

is a second-rank tensor which can be determined from Eq. (6.1) once $\hat{s}_{it}(\mathbf{F}, \theta, \dot{\mathbf{F}})$ is known from experiments. Introducing Eqs. ((3.8), I), ((6.3), I) and (6.1) in Eq. ((4.6), I) we can deduce the relation

$$(6.3) \quad -\theta \operatorname{tr}[(\partial_\theta \partial_{\mathbf{F}} \hat{\psi}')^T \dot{\mathbf{F}}] = \operatorname{tr}(\mathbf{H}\dot{\mathbf{F}}) + \frac{1}{\rho} \operatorname{tr}(\mathbf{T}\mathbf{F}^{-1}\dot{\mathbf{F}}) - \operatorname{tr}[(\partial_{\mathbf{F}} \hat{\psi}') \dot{\mathbf{F}}].$$

Since Eq. (6.3) is valid for arbitrary loading deformation increments, we get from it

$$(6.4) \quad \theta \partial_\theta (\partial_{\mathbf{F}} \hat{\psi}')^T - (\partial_{\mathbf{F}} \hat{\psi}')^T + \frac{1}{\rho} \mathbf{F}^{-1} \mathbf{T} + \mathbf{H} = 0.$$

This relation represents 9 linear differential equations in the unknown components $[\partial_{\mathbf{F}} \hat{\psi}']_{ij}$ of the tensor-valued function $\partial_{\mathbf{F}} \hat{\psi}'$. Observe that each of these differential equations involves only one component of $\partial_{\mathbf{F}} \hat{\psi}'$ at a time. These equations can, therefore, be integrated with respect to θ independently of each other and allow us to find $\partial_{\mathbf{F}} \hat{\psi}'$. A further integration with respect to \mathbf{F} gives $\hat{\psi}'(\mathbf{F}, \theta)$ provided that the compatibility conditions for the existence of a unique function $\hat{\psi}'(\mathbf{F}, \theta)$ are met. Finally, $\hat{\eta}'(\mathbf{F}, \theta)$ can be determined from (6.3). The analysis for the determination of $\hat{\psi}''$ and $\hat{\eta}''$ is completely analogous and will not be repeated.

7. Thermodynamical deduction of the elastic range

To conclude this paper we shall advance some ideas about the way in which the elastic range of a quasi-perfect material can be determined by means of non-destructive experiments. This section, however, does not attempt to be definitive. Its main importance is that it shows how a relation between quantities calculated in the elastic range on the one hand and yield limits on the other can be inferred. Hitherto, the existence of such a relation has been seldom suspected.

Consider for simplicity's sake an axially-loaded thin rod. In this case a standard procedure allows us to simplify the analysis so that a full one-dimensional situation can be considered. This will be emphasized by adopting light-face letters for the quantities which, being tensors, have been previously denoted by bold-face letters. Let θ be constant and consider in the (T, F) -plane the curves $T = \hat{T}(F, \theta)$ and $T^* = \rho F(\partial_{\mathbf{F}} \hat{\psi}')$. Suppose that these two curves intersect at a point $[{}_0T, {}_0F]$. By means of the thermodynamical arguments set forth in [5, Sect. 6] it can be easily shown that the body cannot suffer deformations greater than ${}_0F$ keeping the stress-strain relation $\hat{T} = T(F, \theta)$ unaltered.

A discussion on whether or not the material can really reach the state ${}_0F$ without suffering previous plastic strains, as well as a discussion on whether or not an intersection between \hat{T} and $\rho F(\partial_{\mathbf{F}} \hat{\psi}')$ exists, would lead far away from the scope of the present article. We shall be content here to assume that a point such as $[{}_0T, {}_0F]$ exists and that this point can be attained through the stress-strain relation $T = \hat{T}(F, \theta)$. We shall suppose, moreover, that for a given θ the function $T = \hat{T}(F, \theta)$ is represented in the (T, F) -plane by a straight line. This occurs, for instance, when non cold-worked mild steel is considered. In such circumstances, since the stress-strain response has to change when $F > {}_0F$, the behaviour of the material cannot be elastic for $F > {}_0F$. Therefore, ${}_0F$ must be the yield limit.

Since materials like non cold-worked mild steel can, for many purposes, be approximated to perfect materials, we have to expect that the curve $\rho F(\partial_F \hat{\psi}')$ is very near to $\hat{T}(F, \theta)$. It appears reasonable, therefore, to approximate $\rho F(\partial_F \hat{\psi}')$ to a parabola whose axis is perpendicular to the straight line represented by $\hat{T}(F, \theta)$. This parabola, moreover, has to pass through the point $[T = 0, F = 1]$ in order to meet ((3.22), I). It turns out that the curve $\rho F(\partial_F \hat{\psi}')$ is completely determined once its tangent at the point $[T = 0, F = 1]$ is known. This tangent may be obtained by means of Eq. (4.25) once the adiabatic modulus M'_{ad} relevant to a state ${}_1F$ very near to $F = 1$ is determined from experiments. When this adiabatic modulus is known, it is therefore, an elementary task to find the second intersection of the parabola $\rho F(\partial_F \hat{\psi}')$ with the line $\hat{T}(F, \theta)$ that is to determine the yield limit ${}_0F$. If the parabolic approximation for $\rho F(\partial_F \hat{\psi}')$ is not sufficient, the previous reasoning does not essentially change: we have simply to determine the values of M'_{ad} for a greater number of states of deformation in the elastic range.

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ISTITUTO DI SCIENZA DELLE COSTRUZIONI
UNIVERSITÀ DI CAGLIARI, ITALY.

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