# Moduli of an isotropic medium in the nonlinear theory of deformation and possibilities of their experimental investigation

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The value (six-dimensional) of the natural strain tensor is proposed as a measure of the strain at a point in a body. Since the expression for the strain energy in terms of this variable is very simple and since the isotropic compression and shear are independent of one another at any value of the strain, a description in its terms is very convenient in thermodynamic investigations, the treatment of phase diagrams, etc., even under high hydrostatic compressions, while the generally used nonlinear strain tensor is more suitable for calculations of a stressed equilibrium state. The possibility of studying the equation of state of an isotropic body on the basis of an experiment involving uniaxial extension of a sample under a hydrostatic pressure is considered. The deformation of rubber is considered in these terms as an illustrative example. © *1996 American Institute of Physics.* [S1063-7761(96)02205-6]

## 1. INTRODUCTION

Several corollaries of the formulation of the theory of finite strains of an isotropic body using the natural strain tensor in the general form proposed in Ref. 1 are considered in this paper. This tensor was considered for the first time in the principal axes by Hencky[2] (for a further discussion of this question, see Ref. 3), but, as it appears, proper attention was not focused on this question in the theory. This is apparently because two aspects of deformation, viz., a large isotropic compression, which can be studied in high-pressure physics and can be theoretically modeled in the thermodynamics of hydrostatic compression, and a small (for a solid) arbitrary strain-induced distortion under the action of small loads, which can be studied in the theory of elasticity, were developed independently of one another to a considerable extent. In addition, in the theory of elasticity, emphasis has been placed mainly on calculations of the stressed state (with the use of a nonlinear theory to possibly take into account the corresponding corrections). Also, it is simplest to calculate these corrections in terms of ordinary strains (see Sec. 8 below), because passage to the natural strain tensor and calculations of its representations require additional computational efforts.

However, as it turns out (and this is partially demonstrated by the present work), it is simplest to study questions of thermodynamics, such as the overall equation of state or phase diagrams of a solid under pressure, specifically in the variables of the natural strain tensor, although in concrete cases involving specific materials the choice of representation might be dictated by considerations of simplicity in recording the experimental facts.

For example, we write the equation of state in four equivalent forms: in two in terms of a natural strain tensor [see (10) and (42)] (which differ with respect to the choice of the independent invariants, i.e., the strain variables in the free energy) and in terms of an ordinary strain [(36) and (49a)]. Equation (10) is more suitable for considering a solid body when the shearing strains are known to be small, and Eqs. (42) and (49a) are more appropriate for describing the specific case of unfilled vulcanized rubber. As for the representation (36), it is proposed as the most convenient form for writing the equation of state in calculations of elastic equilibrium. All this, of course, presumes some skill in going from representation to representation, i.e., a problem which is solved in the form necessary for this work in Appendix B.

Since the moduli of elasticity of a solid can be studied only in a small (with respect to the shear) vicinity of an arbitrary hydrostatic compression, to illustrate their possible behavior in a broader range of shear the deformation of rubber is also considered from the proposed standpoint in Secs. 8 and 9 and in Appendix D.

## 2. BASIC ASSUMPTIONS UNDERLYING THE THEORY OF THE NATURAL STRAIN TENSOR

The main results in Ref. 1, in which the machinery for employing the natural strain tensor in the theory of finite strains in an isotropic body is proposed, are concisely presented in this section and Appendix A.

We assume that a point with the coordinates $\xi_i$ acquires the coordinates $x_i$ following displacement by the vector $u_i$ as a result of deformation:

$$x_i=\xi_i+u_i. \tag{1}$$

Small variations $\delta x_i$ of the coordinates of a point require the performance of work:

$$R(\delta)=\oint dS_i\sigma_{ij}\delta x_j+\int dVf_i\delta x_i$$
$$=\int dV\left(\frac{\partial\sigma_{ij}}{\partial x_j}+f_i\right)\delta x_i+\int dV\sigma_{ij}\frac{\partial\delta x_i}{\partial x_j}. \tag{2}$$

Here $\sigma_{ij}$ is the strain tensor, and the vector $u_i$ is assumed to depend on the current coordinates $x_k$ (Euler variables) of the point. Accordingly, the integration in (2) is carried out over the real volume of the strained body.

It was shown in Ref. 1 that if $\sigma$ satisfies the equilibrium equations

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$$\frac{\partial \sigma_{ij}}{\partial x_j}+f_i=0, \tag{2a}$$

so that only the last term remains in (2), it can be brought into the form

$$R(\delta)=\int dV\sigma_{ij}\delta s_{ij}=\int dV\langle \sigma\delta s\rangle, \tag{3}$$

where the natural strain tensor $s$ is specified by the relations

$$s=-(1/2)\ln\gamma, \quad \gamma=(E-\beta)(E-\beta^T)=(E-2u), \tag{4}$$

$B_{ij}=\partial u_j/\partial x_i$ is the distortion tensor, and $u=(\beta+\beta^T-\beta\beta^T)/2$ is the ordinary nonlinear (see Ref. 4) strain tensor (in Euler variables). We use $\langle ab\rangle$ to denote $\mathrm{Tr}(ab)$, which, in fact, has the meaning of a scalar product in the space $\mathrm{Sym}E(3)\otimes E(3)$ of symmetric second-rank tensors over the three-dimensional Euclidean space; expressions of the form $\langle a\rangle=\langle aE\rangle$, where $E=\{\delta_{ij}\}$ is a unit operator of three-dimensional space, are allowed.

This makes it possible to write an expression for the free-energy increment $f$ of a unit mass of the material (so that $F=\int\rho dVf$ is the total free energy of the body) in the form[5]

$$df=-\eta dT+(1/\rho)\langle \sigma ds\rangle, \tag{5}$$

whence it follows that

$$\sigma=\rho(\partial f/\partial s)_T. \tag{6}$$

The function $s$ can be expressed in terms of its deviator [see (A4)]:

$$s=\Delta+I_1E/3. \tag{7}$$

The superscript $s$ on the deviator and the invariants of the natural strain tensor $s$ will henceforth be omitted in view of its decisive role.

As the basis invariants of the tensor $s$ we choose the quantities

$$I_1=\langle s\rangle, \quad k_2=\langle \Delta^2\rangle/2, \quad k_3=\langle \Delta^3\rangle/3, \tag{8}$$

in terms of which its other invariants can be expressed (see Appendix A).

It was shown in Ref. 1 that

$$I_1=\ln(\rho_0/\rho), \tag{8a}$$

where $\rho$ is the density at the point under consideration in the body and $\rho_0$ is the initial (uniform) density before deformation.

The free energy $f$ of an isotropic body depends on $s$ only through its invariants. It is easily seen using (A5)–(A5c) and (A6) that

$$\partial I_1/\partial s=E, \quad \partial k_2/\partial s=\Delta, \quad \partial k_3/\partial s=\Delta_2=\Delta^2-(2k_2/3)E, \tag{9}$$

therefore, it follows from (6) that

$$\sigma=-pE+2\mu\Delta+\nu\Delta_2, \tag{10}$$

where

$$p=-\rho\left(\frac{\partial f}{\partial I_1}\right)_T, \quad 2\mu=\rho\left(\frac{\partial f}{\partial k_2}\right)_T, \quad \nu=\rho\left(\frac{\partial f}{\partial k_3}\right)_T \tag{10a}$$

are functions of the invariants $I_1$, $k_2$, and $k_3$. This is nothing but the tensor equation of state of an arbitrary strained isotropic body. The invariants were specially chosen so that under small strains, under which $s\approx u$ [see (4)], the expression for $\sigma$ would become the familiar expression from the linear theory with $\mu$ having the meaning of the ordinary shear modulus.[4] We call $\Delta_2$ the second shear, and we call $\nu$ the second shear modulus.

### 3. DEPENDENCE OF ELASTIC MODULI ON THE STRAIN

We assume that the free energy of a hydrostatically loaded body $f_0(I_1)=f(I_1,0,0)$ is known. If we introduce the function $p_0(I_1)=p(I_1,0,0)$, the equation of state of a body under the pressure $P$ is written in the form [see (10) and (10a)]

$$p_0(I_1)=P, \tag{11}$$

which, with consideration of (8), is equivalent to the usually used expression $q(P,\rho,T)=0$ (we write only the strain variables, but, as is clear from (5) and (6), the temperature is present everywhere).

Since plastic flow or, alternatively, fracture begins in a solid when $\Delta\sim\tau_c/\mu\sim10^{-2}-10^{-4}$ ($\tau_c$ is the yield point or, in the case of brittle materials, the ultimate strength), $k_2$ cannot exceed values of the order of $(\tau_c/\mu)^2$, and $k_3$ cannot exceed values of the order of $(\tau_c/\mu)^3$. In addition, as is clear from (A36) and (A56), the condition $k_3^2\leqslant 4k_2^3/27$ always holds. Therefore, in the case of general loading the free energy $f$ can be expanded in powers of the shear invariants $k_2$ and $k_3$:

$$f=f_0+\frac{1}{\rho_0}\sum k_2^nk_3^mA_{nm}/n!m!. \tag{12}$$

The summation over $n$ and $m$ is carried out here from unity to infinity, and it is convenient to treat the $A_{nm}$ as functions of the variable [see (8)]

$$\zeta=\rho_0/\rho=V/V_0=\exp I_1. \tag{12a}$$

Now, using (10a) and taking into account the obvious identity

$$\partial/\partial I_1=V\partial/\partial V=\zeta\partial/\partial\zeta, \tag{12b}$$

we obtain

$$-p=-p_0+\sum k_2^nk_3^m\frac{A'_{nm}}{n!m!},$$

$$2\mu=\frac{1}{\zeta}\sum\frac{k_2^nk_3^mA_{n+1,m}}{n!m!}, \tag{13}$$

$$\nu=\frac{1}{\zeta}\sum\frac{k_2^nk_3^mA_{n,m+1}}{n!m!},$$

and for the ordinary isothermal bulk compressibility modulus

$$K=-V\frac{\partial p}{\partial V}=-\frac{\partial p}{\partial I_1}=-\zeta\frac{\partial p}{\partial\zeta}, \tag{14}$$

after defining the function $K_0=-\partial p_0/\partial I_1$, we have

$$K=K_0+\zeta\sum \frac{k_2^n k_3^m A''_{nm}}{n!m!}. \tag{13a}$$

Here the primes denote differentiation with respect to $\zeta$.

We shall not perform the expansion in the invariant $I_1$, which, however, is quite trivial (see Ref. 1). In the linear theory (i.e., under small, including volumetric, strains, under which $I_1 \ll 1$)

$$f_0 \approx K_\infty I_1^2/2+\ \dots \tag{12a}$$

($K_{00}$ is the bulk modulus of the unstrained body), whence

$$p_0 \approx -K_\infty I_1+\ \dots. \tag{15}$$

Under strains in a solid body of order unity, $\sigma$ reaches values of the order of the elastic moduli, and it should generally be assumed that they are all of the same order of magnitude (in the absence of a special factor, such as the character of the interatomic interaction, proximity to a phase transition or a critical point, etc.). Stability of a hydrostatically compressed body (see Refs. 4 and 5) requires satisfaction of the inequalities $K>0$ and $\mu>0$, while the value of the modulus $\nu$ can influence the stability only when $\mu$ is anomalously small [since $\Delta \leqslant \tau_c/\mu$, when $\mu$ and $\nu$ are of the same order of magnitude, the last term in (10) is smaller than the second term by a factor of at least $\tau_c/\mu$]. Moreover, since $k_3$ can take either sign, so can $\nu$: when $\Delta$ is replaced by $-\Delta$ in the linear theory, the shearing stress $\tau$ [the traceless part of $\sigma$ in (10)] is replaced by the reverse stress, although it is clear, especially if a strained cube is properly depicted, that this does not follow from anything; the sign of $\nu$ is fixed, for example, in the case of uniaxial deformation, in which the absolute value of $\tau$ is large in the case of extension or compression.

## 4. DEFORMATION OF A BODY UNDER PRESSURE

Let the point $\xi_i$ in a body obtain the coordinates $x_i=\xi_i/\alpha+u'_i$ as a result of uniform compression by a factor of $\alpha$ followed by displacement by the vector $u'_i$ [with the total displacement vector $u_i=(1-\alpha)x_i+\alpha u'_i$], so that

$$\xi_i=\alpha(x_i-u'_i). \tag{16}$$

Therefore,

$$(E-\beta^T)_{ij}=\partial\xi_i/\partial x_j=\alpha(\delta_{ij}-\partial u'_i/\partial x_j)=\alpha(E-\beta^{T'})_{ij},$$

and consequently $s$ and $s'$ differ only with respect to the spherical part, i.e., they lead to the same value of the shear (see Ref. 1):

$$s=-\ln\alpha E-\frac{1}{2}\ln\gamma'=-\ln\alpha E+s', \quad \Delta=\Delta',$$

$$I_1=-3\ln\alpha+I'_1, k_n=k'_n. \tag{17}$$

However, it hence follows at once that all mechanical tests (for the purpose of determining elastic properties) of samples under pressure should involve measurement of the real changes in the real linear dimensions, which give the values of the elastic coefficients under pressure (for detailed explanations see Sec. 5).

More specifically, the stress tensor (10) is written by virtue of (17) in the form

$$\sigma=-p'E+2\mu'\Delta'+\nu'\Delta', \tag{18}$$

where the functions $p$, $\mu$, and $\nu$ marked with primes refer to the point $\{-3\ln\alpha+I'_1, k'_2, k'_3\}$ and can be expanded in the vicinity of the hydrostatic strain $s_0=-E\ \ln\alpha$ in powers of the invariants of the primed (i.e., observed under pressure as a result of the application of an additional load) strain.

The material presented shows that in the natural-strain representation the shear and the isotropic compression are completely separated (more precisely, their mutual influence is manifested only through the equilibrium equation). This cannot be said for the nonlinear strain tensor $u$: the magnitude of the shear component for the latter is directly dependent on the magnitude of the isotropic compression.

In addition, if the hydrostatic equation of state is known, $\alpha$ (whose value is not needed when measurements are performed) can be determined, in principle, from the known pressure $P$ using either of the relations [see (11)]

$$q(P,\alpha^3\rho_0,t)=0, \quad p_0(-3\ \ln\alpha)=P. \tag{19}$$

## 5. UNIAXIAL EXTENSION OF A SOLID BODY

Let us consider the problem of the uniaxial extension of a sample under the pressure $P$ as an example. Since we shall henceforth encounter only values of all the dimensions, increments of dimensions, and tensors specifying strains under pressure, we shall omit the primes on them [like those used in (16)–(18)], bearing in mind only the need to add $-E\ \ln\alpha$ to the total strain. The $z$ axis is parallel to the axis of the sample.

The tensors $\beta$, $\gamma$, $s$, and $\sigma$, are clearly diagonal; therefore, we shall mark their components with one subscript: for example, $\sigma_{zz}=\sigma_z$ etc. In the spirit of the theory formulated in Euler variables, the strain is defined as the ratio of the linear displacement to the current length:

$$\beta_x=\Delta L_x/L_x, \quad \beta_z=\Delta L_z/L_z, \tag{20}$$

however, experimentalists usually use the "Lagrange" values

$$\varepsilon_x=\Delta L_x/L_x^0, \quad \varepsilon_z=\Delta L_z/L_z^0, \tag{20a}$$

(the quotation marks refer to the fact that the zero lengths are the lengths measured under pressure before the beginning of uniaxial deformation, rather than the initial lengths). The relationship between them is quite obvious:

$$(1-\beta_i)(1+\varepsilon_i)=1. \tag{20b}$$

It is understood from (4) that the tensor $s$ has the form[1)]

$$s=-\begin{bmatrix}\ln(1-\beta_x) & 0 & 0\\ 0 & \ln(1-\beta_x) & 0\\ 0 & 0 & \ln(1-\beta_z)\end{bmatrix}$$

$$=\begin{bmatrix}\ln(1+\varepsilon_x) & 0 & 0\\ 0 & \ln(1+\varepsilon_x) & 0\\ 0 & 0 & \ln(1+\varepsilon_z)\end{bmatrix}, \tag{21}$$

whence, since

$$I_1=2\ln(1+\varepsilon_x)+\ln(1+\varepsilon_z)=2\omega+3\kappa \tag{22}$$

[$\kappa=\ln(1+\varepsilon_z)$, and the definition of $\omega$ is given below], it follows from (7) that

$$\Delta=\frac{1}{3}\begin{bmatrix}\omega & 0 & 0\\ 0 & \omega & 0\\ 0 & 0 & -2\omega\end{bmatrix}, \tag{21a}$$

where $\omega=\ln[(1+\varepsilon_x)/(1+\varepsilon_z)]$, and that [see (A1a)]

$$k_2=\omega^2/3, \quad k_3=-2\omega^3/27, \tag{22a}$$

and from (9) it follows that

$$\Delta_2=\frac{1}{9}\begin{bmatrix}-\omega^2 & 0 & 0\\ 0 & -\omega^2 & 0\\ 0 & 0 & 2\omega^2\end{bmatrix}. \tag{21b}$$

Now it is clear that since

$$\sigma_x=-p+(2\mu/3)\omega-(\nu/9)\omega^2=-P, \tag{23}$$

substitution of the value of $p$ hence obtained into

$$\sigma_z=-P+t=-p-(4\mu/3)\omega+(2\nu/9)\omega^2 \tag{23a}$$

($t$ is the tensile stress) gives

$$t=-2\mu\omega+(\nu/3)\omega^2. \tag{24}$$

The functions $p$, $\mu$, and $\nu$ must still be expanded in the vicinity of $\{-3\ \ln\alpha,0,0\}$ with the required accuracy, and $\varepsilon_x$ from (23) must be expressed in terms of $\varepsilon_z$ and substituted into (24) to obtain the dependence of $\varepsilon_z$ (and thus of $\varepsilon_x$) on the tensile stress $t$. We perform the corresponding calculations to the second order with respect to the strain in (23) and (24):

$$p(-3\ \ln\alpha+I_1,k_2,k_3)=P-KI_1-\frac{1}{2}K'I_1^2-2(\mu+\mu')k_2+\dots,$$

$$\mu(-3\ \ln\alpha+I_1,k_2,k_3)=\mu+\mu'I_1+\dots, \tag{25}$$

$$\nu(-3\ \ln\alpha+I_1,k_2,k_3)=\nu+\dots,$$

where the values of the moduli were taken at the point $\Gamma=\{-3\ \ln\alpha,0,0\}$, and the prime denotes the derivatives of the respective quantities with respect to $I_1$ at that point. For example:

$$K=-\left.\frac{\partial p}{\partial I_1}\right|_\Gamma, \quad \mu'=\left.\frac{\partial\mu}{\partial I_1}\right|_\Gamma=-\left.\frac{K\partial\mu}{\partial p}\right|_P. \tag{25a}$$

Also, it was taken into account in (25) that $\partial p/\partial k_2=-2(\mu+\mu')$ (this is a consequence of the equality of the cross derivatives of the free energy with respect to $I_1$ and $k_2$; see Ref. 1).

We note that we were forced to resort to an expansion different from (13)–(13c) in (25), because Tr $s$ is not a fixed quantity in the case of uniaxial deformation.

The substitution of (25) into (23) gives the relationship between $\omega$ and $\kappa$:

$$A\omega^2+2B\omega+C=0, \tag{26}$$

where

$$A=2\mu/3-\nu/9+2(\mu'+K'),$$

$$B=K+\mu/3+(\mu'+3K')\kappa, \tag{26a}$$

$$C=3(K+3K'\kappa/2)\kappa,$$

whence

$$\omega=-\frac{3K\kappa}{2(K+\mu/3)}-D\kappa^2+\dots. \tag{27}$$

Here

$$D=\frac{[6(\mu+\mu')+\nu]K^2+2\mu(K'\mu-2K\mu')}{8(K+\mu/3)^3}. \tag{27a}$$

Now substitution into (24) gives

$$t=\frac{3K\mu\kappa}{K+\mu/3}+F\kappa^2+\dots \tag{28}$$

with

$$F=\frac{3K^2[2\mu(\mu+\mu')+K\nu]-2\mu^2(2K\mu'-\mu K')}{4(K+\mu/3)^3}. \tag{28a}$$

In the linear theory (see Ref. 4) $\lim(t/\varepsilon_z)$ as $\varepsilon_z\to 0$ is called Young's modulus $Y$. It is seen from (28) and (22) that, as expected, within the measurement procedure chosen

$$Y(P)=\frac{9K\mu}{3K+\mu}. \tag{29}$$

Equation (28) expressed in terms of $\varepsilon_z$ [see (22)] has the form

$$t=Y\varepsilon_z+(F-Y/2)\varepsilon_z^2+\dots. \tag{28b}$$

The tensor equation of state also specifies $s_x$ (due to the equalities $\sigma_x=\sigma_y=0$), and now we can write

$$\varphi=-\frac{s_x}{s_z}=\frac{\ln(L_x^0/L_x)}{\ln(L_z/L_z^0)}=-\frac{\kappa+\omega}{\kappa}=\sigma_p+D\kappa+\dots, \tag{30}$$

where $D$ is the same coefficient as in (27a), and

$$\sigma_p(P)=\frac{3K-2\mu}{2(3K+\mu)} \tag{30a}$$

has the meaning of the Poisson constant under pressure.

The measurement of $\Delta V/V_0$ and, therefore, of $K(P)$ and $\partial K/\partial P$ (although, perhaps, with insufficient accuracy) is a fairly routine matter in high-pressure physics. The shear

TABLE I. Approximate values of the second shear modulus $\nu$ (according to published data).

| Material | $K$, GPa | $\partial K/\partial p$ | $\mu$, GPa | $\partial \mu/\partial p$ | $\Delta_y$, % | $b$ | $\nu/K$ | $\nu$, GPa |
|---|---|---|---|---|---|---|---|---|
| Steel | 166 | 6.5 | 82.1 | 1.96 | 5.5 | 17.7 | −19.6 | −3250 |
| Copper | 138 | 5.74 | 46.84 | 1.39 | −2.3 | 23.7 | −17.3 | −2380 |
| Cu (single) | 137 | 5.84 | 47.34 | 1.37 | −1.42 | 23.7 | −17.6 | −2420 |
| Copper (s) | 137 | 5.84 | 47.34 | 1.37 | 7.91 | 185 | −156 | −21 400 |
| Ag (single) | 104 | 6.18 | 29.7 | 1.39 | −4.17 | 9.79 | −4.43 | −461 |

modulus $\mu$ and its derivative $\partial\mu/\partial P$ can be found from ultrasonic experiments (this is also true for $K$) or from measurements of Young's modulus $Y(P)$ using Eq. (29):

$$\mu(P)=\frac{3KY}{9K-Y}, \tag{31}$$

and knowledge of $F$ (or $D$) makes it possible to determine the second shear modulus $\nu(P)$ (here $\eta=\mu/3K$):

$$\frac{\nu}{k}=\frac{4F(1+\eta)^3}{3K}+6\eta(1-2\eta)\frac{\partial\mu}{\partial p}-18\eta^2\left(1-\eta\frac{\partial K}{\partial p}\right)$$
$$=18\eta\left(1+\eta\frac{\partial K}{\partial p}\right)-8D(1+\eta)^3-6(1-2\eta)\frac{\partial\mu}{\partial p}. \tag{32}$$

To avoid any misunderstanding we recall that $K=K(P)$ etc. denote the values of the modulus etc. under hydrostatic compression, i.e., at the point $\Gamma$ [see (25)].

Considering a phase which does not exist under a zero load, we must bear in mind that the strain in it should be measured from the intrinsic zero corresponding to its unloaded state, whose position can, in principle, be restored after experimentally studying the equation of state. As this can be done in the particular case of uniaxial deformation, it is illustrated in Appendix B, which is also of interest in itself.

## 6. APPROXIMATE EVALUATIONS OF THE SECOND SHEAR MODULUS

It would be of interest to evaluate $\nu$ in materials for which there are more or less adequate experimental results.

For this purpose it must, first of all, be taken into account that a lack of data on the transverse compression in extension forced most experimentalists to express (as a function of either the nominal or the natural strain) the nominal stress, which we denote by $\tilde{t}$:

$$\tilde{t}=F/S_0=tS/S_0=t(1+\varepsilon_x)^2. \tag{33}$$

Next, we call the quantity $\tilde{Y}(p,\varepsilon_z)=d\tilde{t}/d\varepsilon_z$ under any (elastic) strain $\varepsilon_z$ the tangential Young's modulus to distinguish it from the modulus $Y$ of the linear theory, which we can call the initial modulus.

Grüneisen (for further details, see Ref. 6) obtained very accurate values of $Y$ for several materials using an interference technique for measuring small strains (from $1.7\times10^{-6}$ to $7\times10^{-6}$ with an accuracy of $2\times10^{-8}$). Then, utilizing the results of other investigators for large strains, he used Hartig's formula for Young's modulus $\tilde{Y}$ expressed in terms of $\tilde{t}$

$$\tilde{Y}=Y-b\tilde{t}, \tag{34}$$

to obtain the values of $b$ for cast iron (GK3 and A15), soft copper (with matching to Carl Bach's results), copper, bronze, silver, and steel (with matching to J. O. Thompson's results).

To utilize his results, we take into account that, as is clear from (30),

$$\tilde{t}=t\exp[2(\omega+\kappa)]=t\exp(-2\varphi\kappa), \tag{33a}$$

after which the substitution of $\varphi$ from (30) and $t$ from (28b) gives

$$\tilde{t}\approx Y\varepsilon_z+(F-Y/2-2Y\sigma_p)\varepsilon_z^2, \tag{33b}$$

whence

$$\tilde{Y}\approx Y-\tilde{t}[Y(1+4\sigma_p)-2F]/Y, \tag{34a}$$

so that, in accordance with (34),

$$b=[Y(1+4\sigma_p)-2F]/Y, \tag{34b}$$

and from (32) we obtain

$$\frac{\nu}{K}=18\eta\left[1-\eta-\eta^2\left(1-\frac{\partial K}{\partial p}\right)\right]$$
$$+6\eta\left[(1-2\eta)\frac{\partial\mu}{\partial p}-(1+\eta)^2b\right]. \tag{32a}$$

We use this equation to evaluate $\nu$ at zero pressure, but since measurements of all the parameters required by Eq. (32a) have not yet been performed on a single sample, the values of the moduli and their derivatives must be extracted from existing publications, for which purpose we used Ref. 7. Unfortunately, the parameters of construction materials depend strongly on the technology used to manufacture them; therefore, it is difficult to require even simple reproducibility of their properties. As for other materials, their properties also depend, although not strongly, on the history of the sample, and such dependences can be important in precision measurements (see the discussion of these questions in Ref. 6).

This means that only an attempt can be made to find some correspondence in Ref. 7 to the materials described by Grüneisen, but it is sufficient for an approximate evaluation. The degree of correspondence can be assessed in some sense using $\Delta_Y$:

$$\Delta_Y=100(Y_{[7]}-Y_{[6]})/Y_{[7]},$$

where $Y_{[7]}$ is obtained from the values of $K$ and $\mu$ in Table I, and $Y_{[6]}$ are the values of $Y$ found by Grüneisen in Eq. (34).

The values of $K$, $\mu$, and their derivatives in Table I were taken from Ref. 7. The values for the materials followed by the word "single" were adjusted to a polycrystal (by the method proposed in Ref. 8) from experimental data for cubic Cu and Ag single crystals, the row labeled "Copper (s)" refers to soft copper, and the remaining materials are ordinary polycrystals.

Table I needs no additional commentary apart from the fact that the result for soft copper is the least reliable.[2)] The negative values of $\nu$, as can be seen in the calculation employing Eq. (32a), are a consequence mainly of the large values of $b$, i.e., the excessive decrease in the tangential Young's modulus with increasing extension.

It would be useful to perform experiments not only with determination of all the parameters listed in Table I on a single sample, but also with simultaneous measurement of its transverse strain and to compare the results for $\nu$ obtained from $D$ and $F$. In fact, in a strict sense the proposed theory applies to a completely isotropic substance, and only glass can probably be considered such when there are no gradients of the properties in it. In single crystals any of the parameters can be expanded in powers of the strain tensor with increasing rank of the tensor coefficients, which are averaged differently in polycrystals, and for this reason there must be no dependence between moduli like (34), which would act as a criterion of amorphousness in this light.

An expansion up to terms of higher order with respect to $\kappa$, unfortunately, is relatively uninformative, since the appearance of a continually increasing number of derivatives of the moduli with respect to the invariants $s$ permits making any adjustments due to a lack of experimental data which would make it possible to compare the results of measurements under different types of loading.

## 7. MURNAGHAN'S AND RIVLIN'S FORMULATIONS OF THE THEORY OF FINITE STRAINS

In Ref. 1 it was noted that Murnaghan's equation of state[9] in Birch's form[10] is obtained, if the invariants $K_n^\gamma$ are chosen as the independent variables in $f$ [see Appendix A and (4)], since, as was shown therein,

$$\partial/\partial s=-2\gamma\partial/\partial\gamma, \tag{35}$$

so that (6) with consideration of (4) gives

$$\sigma/\rho=-2\gamma(\partial f/\partial\gamma)=(E-2u)(\partial f/\partial u)_T, \tag{35a}$$

which implies, of course, a transition to the invariants of $u$ using the formulas

$$J_1^\gamma=\mathrm{Tr}(E-2u)=3-2J_1^u,$$

$$J_2^\gamma=\mathrm{Tr}(E-2u)^2=\mathrm{Tr}(E-4\mu+4\mu^2)=3-4J_1^u+4J_2^u\ldots,$$

etc.

As was noted in Ref. 1, the choice of $u$ (or, more precisely, $\gamma$) as the variable in the free energy is useful in calculations of the equilibrium state of a stressed body.

More specifically, if $X_1=0.5\ln I_3^\gamma$, $X_2=0.5\ln I_1^\gamma$, and $X_3=0.5K_2^\gamma$ are chosen as the variables in $f$, we can avoid the tedious and cumbersome need to express $\gamma^3$ in terms of the lower powers of $\gamma$ from the Hamilton–Kelly equation, since, as is clear from (35) and (A7),

$$\begin{aligned}-\sigma/\rho&=\gamma\left(\gamma^{-1}\frac{\partial f}{\partial X_1}+E\frac{\partial f}{\partial X_2}+\gamma\frac{\partial f}{\partial X_3}\right)\\&=E\frac{\partial f}{\partial X_1}+\gamma\frac{\partial f}{\partial X_2}+\gamma^2\frac{\partial f}{\partial X_3},\end{aligned} \tag{36}$$

and since it follows from (8) that

$$\rho=\rho_0\exp(-I_1^s)=\rho_0\sqrt{I_3^\gamma}, \tag{36a}$$

the stress tensor $\sigma$ is completely specified in terms of $\gamma$ and can be substituted into the equilibrium equations (2a), which must be supplemented by compatibility conditions of the Saint-Venant type. Since $\gamma$ can be treated as a metric tensor in a curvilinear coordinate system parametrized by the Cartesian coordinates of points in the loaded state or, stated differently, in a coordinate grid obtained from a Cartesian grid after removal of the load (see Refs. 4 and 1), the compatibility conditions are the conditions for a Euclidean space written in that coordinate system, i.e., the vanishing of all the components of the curvature tensor [or the Ricci tensor $R_{ij}$ (see Ref. 1)]. In a three-dimensional space their number equals 6, as does the number of Saint-Venant relations.

We shall discuss Rivlin's theory[11] in greater detail, since it has been used to describe physically interesting results of large-strain experiments with rubber.

Referring the reader to the work just cited, we point out only that the independent variables or invariants chosen by Rivlin have the following forms in our notation:

$$\tilde{I}_1=\frac{\gamma_1\gamma_2+\gamma_1\gamma_3+\gamma_2\gamma_3}{\gamma_1\gamma_2\gamma_3}=\frac{I_2^\gamma}{I_3^\gamma},\quad \tilde{I}_2=\frac{I_1^\gamma}{I_3^\gamma},\quad \tilde{I}_3=\frac{1}{I_3^\gamma}. \tag{37}$$

If we introduce the notation $\alpha=\exp(-2x)$ and $\beta=\exp(-2y)$ ($x$ and $y$ are the eigenvalues $\Delta_1$ and $\Delta_2$, respectively), then, since $\gamma=\exp(-2s)$ [see (4)], it is clear from (C7a) that

$$a_2=\alpha+\beta+1/\alpha\beta, \tag{38}$$

and it follows from (C1) and (C6) that (the invariants of the natural strain tensor $s$ are written, as always, without indices)

$$I_1^\gamma=a_2\exp(-2I_1/3). \tag{39}$$

Also, since

$$J_2^\gamma=\mathrm{Tr}\gamma^2=\mathrm{Tr}\exp(-4s)=a_4\exp(-4I_1/3), \tag{39a}$$

it follows from (1.5) that

$$I_2^\gamma=\frac{a_2^2-a_4}{2}\exp\left(-\frac{4I_1}{3}\right), \tag{39b}$$

and a direct calculation with consideration of (C7a) gives

$$\frac{a_2^2-a_4}{2}=\frac{1}{\alpha}+\frac{1}{\beta}+\alpha\beta=a_{-2}, \tag{40}$$

so that Rivlin's variables expressed in terms of the natural strain tensor have the form

$$\tilde{I}_1=a_{-2}\exp(2I_1/3),\quad \tilde{I}_2=a_2\exp(4I_1/3),$$

$$\tilde{I}_3=\exp(2I_1). \tag{37a}$$

It is more convenient, however, to choose a slightly different set of independent variables, viz.,

$$X_1=a_{-2},\quad X_2=a_2,\quad X_3=\tilde{I}_3=\exp(2I_1), \tag{41}$$

whose use permits isolation of the dependence on the density in a separate argument and thereby simplification of the calculations along with greater transparency of the equations.

Introducing the notation $f_k=\partial f/\partial X_k$, from (10a) and (C6b) we have

$$\begin{aligned}-p/\rho&=2X_3\partial f/\partial X_3=2f_3\exp(2I_1),\\ 2\mu/\rho&=2f_1b_{-2}-2f_2b_2,\\ \nu/\rho&=2f_1c_{-2}-2f_2c_2,\end{aligned} \tag{42}$$

or, with consideration of (C7a),

$$\begin{aligned}2\mu/\rho&=2f_1[x\omega_1(1/\alpha-\alpha\beta)+y\omega_2(1/\beta-\alpha\beta)]\\ &\quad+2f_2[x\omega_1(1/\alpha\beta-\alpha)+y\omega_2(1/\alpha\beta-\beta)],\\ \nu/\rho&=2f_1[\omega_1(1/\alpha-\alpha\beta)+\omega_2(1/\beta-\alpha\beta)]\\ &\quad+2f_2[\omega_1(1/\alpha\beta-\alpha)+\omega_2(1/\alpha\beta-\beta)].\end{aligned} \tag{43}$$

The bulk compressibility modulus is obtained, if the first of the equalities (42) is differentiated with respect to $I_1$ after recalling that $\rho=\rho_0\exp(-I_1)$ [see (8)]:

$$K=-\partial p/\partial I_1=2\rho_0f_3\exp(I_1)+4\rho_0f_{33}\exp(3I_1) \tag{44}$$

or, alternatively[3)]

$$K/\rho_0=2(\rho_0/\rho)f_3+4(\rho_0/\rho)^3f_{33}. \tag{44a}$$

Since it follows from (41) and (C8) that

$$X_2=3+4k_2+\dots, \tag{41a}$$

under small shearing strains, (C8a) and (43) give

$$\begin{aligned}2\mu/\rho&=4(f_1^0+f_2^0)+8Qk_2+\dots,\\ \nu/\rho&=4(f_1^0-f_2^0)+4Rk_2+\dots\end{aligned} \tag{43a}$$

with the coefficients

$$\begin{aligned}Q&=(f_1^0+f_2^0)/3+2f_{22}^0,\\ R&=(f_1^0-f_2^0)/3-4f_{22}^0,\end{aligned} \tag{43b}$$

where the functions with the superscript 0 have the arguments $\{3,3,\exp(2I_1)\}$.

The behavior of the moduli in the vicinity of $\Delta=0$ is thus determined by the signs of $A$ and $R$, and when the deviator $\Delta$ increases and its value (i.e., $\sqrt{\mathrm{Tr}\Delta^2}=\sqrt{k_2}$) exceeds unity, as is clear from (C7) and (C7b), $X_1$, $X_2$, and their derivatives with respect to $k_2$ and $k_3$ increase exponentially; therefore, $\mu$ and $\nu$ should increase only if $f_1$ and $f_2$ do not decrease more rapidly than $\exp(-2\sqrt{k_2})$.

## 8. DISCUSSION OF THE RESULTS OF EXPERIMENTS ON THE DEFORMATION OF RUBBER

The variables (37) and (37a) were used in Ref. 12 to interpret the results of experiments on the deformation of various types of crude rubber and unfilled vulcanized rubber under the assumption that the volume is invariant ($I_1=0$). A relation of the form

$$f=A(\tilde{I}_1-3)+\chi(\tilde{I}_2-3), \tag{45}$$

where $A$ is a constant and the function $\chi$ was studied by Rivlin and Saunders[12] (and was also presented in Rivlin's review[11]), was obtained for the free energy at not excessively large values of $\tilde{I}_2$ (see below). In the variables (41), which faithfully describe the experiment, since they simply coincide with the variables (37a) when $I_1\equiv 0$ ($I_3^\gamma=1$), it can be assumed that

$$f=A(X_1-3)+\chi(X_2-3). \tag{45a}$$

After the transformation mentioned in the footnote to Eq. (D1), from (43a) and (43b) with the values of the constants indicated in Appendix D we obtain

$$\begin{aligned}&2\mu_{\Delta=0}=9.6\ \text{kgf/cm}^2,\quad \nu|_{\Delta=0}=4\ \text{kgf/cm}^2,\\ &Q=-1.6\ \text{kgf/cm}^2,\quad R=9.32\ \text{kgf/cm}^2.\end{aligned} \tag{43c}$$

An analysis of the graphical form of the dependences (43) on the eigenvalues of the deviator of $\Delta$ (see Appendix C) reveals that in the region (D2) studied by Rivlin and Saunders [with $f$ of form (42a) and $\chi'$ from (D1)], as expected [see the remark after (43b)], $\mu$ has a maximum at zero [see (43c)], which is surrounded by a "trench" at a distance of $\sim 0.3$ with a maximum depth (relative to the maximum) equal to about 0.38 kg/cm$^2$ at the point $x=y\approx 0.23$, and $\nu$ has a minimum, which is also specified by (43c).

## 9. UNIAXIAL EXTENSION OF RUBBER

Let us directly compare the equations of Rivlin's theory and the natural-strain equations for the case of uniaxial extension under zero pressure in the same notation and geometry as in Sec. 5.

Going to the limit $y\to x$ in (44), we obtain

$$\begin{aligned}2\mu/\rho&=f_1[4/3\alpha+4(1/\alpha-\alpha^2)/9x]\\ &\quad+f_2[4\alpha/3+4(1/\alpha^2-\alpha)/9x],\\ \nu/\rho&=f_1[4/3\alpha x-2(1/\alpha-\alpha^2)/9x^2]\\ &\quad+f_2[4\alpha/3x-2(1/\alpha^2-\alpha)/9x^2],\end{aligned} \tag{46}$$

and then, recalling that $x=\omega/3=-\kappa/2$ [see (28a) and (24)], after some simple calculations we arrive at the expression

$$\begin{aligned}t/\rho&=-(2\mu/\rho)3x+(\nu/\rho)3x^2\\ &=4\sinh(3\kappa/2)[f_1\exp(\kappa/2)+f_2\exp(-\kappa/2)]\end{aligned} \tag{47}$$

with the following arguments for $f_k$:

$$\begin{aligned}X_1&=2\alpha+1/\alpha^2=2e^{-\kappa}+e^{2\kappa}\\ &=3+4\sinh^2(\kappa/2)(2+e^{-\kappa}),\\ X_2&=3+4\sinh^2(\kappa/2)(2+e^{-\kappa}),\end{aligned} \tag{48}$$

$X_3=1.$

The appearance of the third relation here is due to the absence of compressibility, which also permits writing the dependences (48) with a single argument, since [see (22)]

$$I_1=2\omega+3\kappa=0. \tag{48a}$$

We now perform the calculations in the Murnaghan–Rivlin theory [we combine them because of the use of the ordinary nonlinear strain tensor $u$; see (4)].

For the comparison we must use the variables (41a) for $f$ expressed in terms of $\gamma$:

$$X_1=I_2^\gamma/(I_3^\gamma)^{2/3},\quad X_2=I_1^\gamma/(I_3^\gamma)^{1/3},\quad X_3=1/I_3^\gamma. \tag{41b}$$

Using (38), from (6) we obtain

$$\frac{\sigma}{\rho}=-2\gamma\left(f_1\frac{\partial X_1}{\partial\gamma}+f_2\frac{\partial X_2}{\partial\gamma}+f_3\frac{\partial X_3}{\partial\gamma}\right). \tag{49}$$

The derivatives are calculated as explained at the end of Appendix A. Then, with consideration of (1.7), as can easily be proved, we obtain

$$\gamma\frac{\partial X_1}{\partial\gamma}=-\frac{\gamma^2-I_1^\gamma\gamma+2I_2^\gamma E/3}{(I_3^\gamma)^{2/3}},$$

$$\gamma\frac{\partial X_2}{\partial\gamma}=\frac{\gamma-I_1^\gamma E/3}{(I_3^\gamma)^{1/3}}, \tag{50}$$

$$\gamma\frac{\partial X_3}{\partial\gamma}=-\frac{E}{I_3^\gamma}.$$

Substitution of these expressions into (49) gives the following relation in the principal axes:

$$\frac{\sigma_k}{\rho}=2\left[\frac{f_1(\gamma_k^2-I_1^\gamma\gamma_k+2I_2^\gamma/3}{(I_3^\gamma)^{2/3}}-\frac{f_2(\gamma_k-I_1^\gamma/3)}{(I_3^\gamma)^{1/3}}-\frac{f_3}{I_3^\gamma}\right]. \tag{49a}$$

After expressing $f_3/I_3^\gamma$ from the equation $\sigma_x=0$ and substituting it into $\sigma_z$, we obtain

$$\frac{\sigma_z}{\rho}=2\left\{\frac{f_1[\gamma_z^2-\gamma_x^2-I_1^\gamma(\gamma_z-\gamma_x)]}{(I_3^\gamma)^{2/3}}-\frac{f_2(\gamma_z-\gamma_x)}{(I_3^\gamma)^{1/3}}\right\}. \tag{49b}$$

Under the assumption of incompressibility we have $\gamma_x\gamma_y\gamma_z=1$, whence $\gamma_z=1/\gamma_x^2$, and since

$$X_1=I_2^\gamma=\gamma_x^2+2\gamma_x\gamma_z=\gamma_x^2+2/\gamma_x,$$

$$X_2=I_1^\gamma=2\gamma_x+\gamma_z=2\gamma_x+1/\gamma_x^2, X_3=I_3^\gamma=1, \tag{41c}$$

we now obtain

$$t/2\rho_0=2f_1[1/\gamma_x^4-\gamma_x^2-(2\gamma_z+1/\gamma_x^2)(1/\gamma_x^2-\gamma_x)]$$
$$-f_2(1/\gamma_x^2-\gamma_x)=-2(1/\gamma_x-\gamma_x^2)(f_1+f_2/\gamma_x). \tag{47a}$$

Since [see (4), (20b), (22), (21a), and (48a)]

$$\gamma_x=(1-\beta_x)^2=1/(1+\varepsilon_x)^2=1/\alpha=e^{-2\omega/3}=e^\kappa=1+\varepsilon_z, \tag{51}$$

we can easily prove that (47a) coincides with (47).

Any of the dependences $t(s_z)$, $t(\varepsilon_z)$, $\tilde{t}(s_z)$, and $\tilde{t}(\varepsilon_z)$ constructed using an expression for $f_2=\chi'$ as a function of $X_2$ like (D1) has a slope $Y\approx3\mu=14.4$ kgf/cm$^2$ at zero, as it should when $K\gg\mu$. The first of these dependences is a concave function at zero, and the others are convex. Also, the first dependence deviates least strongly from the $14.4x$ straight line, and the last dependence deviates least strongly (in the permissible range $X_2\leqslant5.5$, which corresponds to the range $-0.532\leqslant\varepsilon_x\leqslant1.68$ or, in natural strains, $-0.759\leqslant s_z\leqslant0.986$).

## 10. CONCLUSIONS

The results of this work can be summarized in the following manner.

1) When the theory of finite strains is formulated in terms of the natural strain tensor, the values of the shear and the isotropic compression at an individual point in a body are independent of one another.

2) The absolute value of the second shear modulus $\nu$ of a solid body is of the order of the elastic moduli $K$ and $\mu$ from the linear theory, but it can take either sign.

3) When elastic moduli are determined under pressure, correct values of the relative strains under the action of additional (apart from the pressure) loads are obtained, if the increments of the linear dimensions are measured and their ratios to the current (under pressure) values are taken.

4) The second shear modulus $\nu$ can be determined from measurements of the deviations from the linear dependence of the tensile force or the transverse strain on the longitudinal strain (with accuracy to the second order with respect to the strain).

5) Approximate evaluations of $\nu$ for several materials have been performed by comparing the results of different measurements, and it has been found that they do not excessively contradict the physical models and common sense.

6) The formulation of the theory in terms of the natural strain tensor has been compared with the previously proposed versions of the theory of finite strains, and their overall mutual equivalence and methodically prudent areas of application have been ascertained.

We thank G. N. Ermolaev for an informative conversation, which launched this work. It would also have been impossible without the support of the directors of the Institute of High-Pressure Physics.

## APPENDIX A

### System of invariants of a matrix *a*

For an arbitrary matrix $a$ we introduce the invariants

$$J_n^a=\mathrm{Tr}(a^n),\quad K_n^a=J_n^a/n, \tag{A1}$$

and $I_n^a$, which are the coefficients in the equation for the eigenvalues

$$\lambda^3-I_1^a\lambda^2+I_2^a\lambda-I_3^a=0. \tag{A2}$$

Their expressions in terms of several other invariants, viz., the eigenvalues $a_1$, $a_2$, and $a_3$ of the matrix $a$, clearly have the form

$$I_1^a=a_1+a_2+a_3=J_1^a,\quad I_2^a=a_1a_2+a_1a_3+a_2a_3,$$
$$I_3^a=\det|a|=a_1a_2a_3. \tag{A3}$$

After isolating the spherical part of $a$, we obtain

$$a=\Delta^a+EI_1^a/3, \tag{A4}$$

where $\Delta^a$ is the deviator (the traceless part) of the tensor $a$, and then we introduce the following "small" invariants of $a$, which will be useful later on:

$$j_n^a=J_n^\Delta=\mathrm{Tr}(\Delta^n),\quad K_n^a=K_n^\Delta=\mathrm{Tr}(\Delta^n)/n,\quad i_n^a=I_n^\Delta. \tag{A1a}$$

It is obvious that the $i_n^a$ are the coefficients in the secular equation defining the eigenvalues of $\Delta$

$$\lambda^3+i_2^a\lambda-i_3^a=0 \tag{A2a}$$

and are expressed in terms of the eigenvalues of the deviator $\Delta_i=a_i-I_1^a/3$ using formulas similar to (A3):

$$i_2^a=\Delta_1\Delta_2+\Delta_1\Delta_3+\Delta_2\Delta_3=-(\Delta_1^2+\Delta_2^2+\Delta_1\Delta_2),$$
$$i_3^a=\Delta_1\Delta_2\Delta_3=-\Delta_1^2\Delta_2-\Delta_1\Delta_2^2. \tag{A3a}$$

Because the roots of a real symmetric operator are necessarily real (see Ref. 1), the following inequality holds for any values of the deviators:

$$i_3^2/4+i_2^3/27\leq 0. \tag{A3b}$$

Since only three invariants can be independent, there are several relations between them, some of which have already been presented in Ref. 1. Here more of them are needed. For this reason, as well as for reference purposes, we write them all out (invariants of a single matrix are implied; therefore, the index labeling the matrix is omitted):

$$I_1=J_1,\quad I_2=(J_1^2-J_2)/2=i_2+I_1^2/3, \tag{A5}$$
$$I_3=J_3/3-J_1J_2/2+J_1^3/6=i_3+I_1i_2/3+I_1^3/27,$$

$$J_2=I_1^2-2I_2=j_2+I_1^2/3,$$
$$J_3=I_1^3-3I_1I_2+3I_3=j_3+I_1j_2+I_1^3/9, \tag{A5a}$$

$$i_2=-j_2/2=-k_2,\quad i_3=j_3/3=k_3,$$
$$j_2=J_2-J_1^2/3=2I_1^2/3-2I_2, \tag{A5b}$$

$$j_3=J_3-J_1J_2+2J_1^3/9=3I_3-I_1I_2+2I_1^3/9. \tag{A5c}$$

They are obtained by taking the traces of the different powers (A4) and using the matrix equations (A2) and (A2a), in which, in accordance with the Cayley–Hamilton theorem, $\lambda$ is replaced by the actual matrix $a$ (or $\Delta$) (the expressions for the roots $a_i$ in terms of $I_k$ are given by Cardano's equations, which we shall not present here, since they are cumbersome and generally known, but they have been written in our notation in Ref. 1).

The derivatives of any invariant with respect to a matrix [as, for example, (9)] are calculated by expressing it in terms of the powers $J_n$ using (A5)–(A5c), since

$$\partial J_n/\partial a^T=na^{n-1}. \tag{A6}$$

Here we present only a single equation, which is important in applications. Differentiating $I_3$ from (A5), with consideration of the first line of (A5) and after comparison with (A2) we obtain the following expression for $a$:

$$\partial I_3/\partial a=a^2-J_1a+I_2E=I_3a^{-1}. \tag{A7}$$

## APPENDIX B

### Dependence of the strain on the load in Bell's multiple-elasticity theory

J. F. Bell[6] discovered and described a phenomenon, which he called "multiple elasticities" in experiments on testing machines with dead-weight loading (so-called "soft" loading, as opposed to "hard" loading, where the strain is considered given, and the force is measured) with samples of nonconstruction, well annealed materials. Under this phenomenon the uniaxial extension curves clearly exhibit linear segments with different slopes for the dependence of $t$ on $\varepsilon_z$, whose existence Bell attributed to "second-order transitions."[4)] Bell also ascribed the discrepancies which occasionally appeared in the data obtained by different investigators over the course of more than two centuries (beginning with Coulomb's measurements of the shear modulus on a torsion vibration apparatus, which gave an appreciably underestimated value for the modulus for brass) to this phenomenon.

Not wishing to go into a discussion of the possible mechanisms for multiple elasticities (or perhaps, for example, martensitic transformations, reversible twinning, etc.), we shall try to describe the extension diagram (i.e., the $t-\varepsilon$ plot) on a purely phenomenological basis.

If it is assumed that each continuous $i$th segment of this dependence corresponds to its own unstressed state with its own $L_{xi}^0$ and $L_{zi}^0$, then, as can easily be seen from (20) and (20a),

$$s_{xi}=\ln(L_x/L_{xi}^0)=\ln((L_x/L_x^0)(L_x^0/L_{xi}^0))=s_x-s_{xi}^0 \tag{B1}$$

and with respect to $s_x$, which we denoted by $\kappa$ [see (22)],

$$\kappa_i=\kappa-\kappa_i^0. \tag{B1a}$$

Here

$$s_{xi}^0=\ln(L_{xi}^0/L_x^0),\quad \kappa_i^0=s_{xi}^0=\ln(L_{zi}^0/L_z^0), \tag{B1b}$$

since all the strains are measured from the initial state $L_x^0$, $L_z^0$, which, in turn, is one of the unstressed states, for example, the one with $i=1$.

Dividing the semiaxis $\kappa>0$ by the points $q_i(i=1,\dots)$, $q_0=0$ into the intervals of smoothness $Q_i=(q_{i-1},q_i)$, we can write the equation of state in the form

$$\left.\begin{aligned} t&=t_i(\kappa_i)\\ s_x&=\psi_i(\kappa_i)\end{aligned}\right\}\kappa\in Q_i, \tag{B2}$$

where [see (28)]

$$t_i(x)=Y_ix+F_ix^2+\dots, \tag{B2a}$$

and setting $\psi_i(0)=s_{xi}^0$, we can write [see (30)]

$$s_{xi}=s_{xi}^0-\varphi_i(x)x, \tag{B2b}$$

where

$$\varphi_i(x)=\sigma_{pi}+D_i x+\ \ldots. \tag{B2c}$$

In addition, the following continuity conditions must be satisfied on the boundaries between the intervals of smoothness:

$$f_i(q_i-\kappa_i^0)=f_{i+1}(q_i-\kappa_{i+1}^0),$$

$$\psi_i(q_i-\kappa_i^0)=\psi_{i+1}(q_i-\kappa_{i+1}^0).$$

Strictly speaking, this makes it possible to determine $\kappa_i^0$ and $s_{xi}^0$, which are not observed experimentally (only $k_1^0=0$ and $s_{x1}^0=0$ are known).

After this, as is clear from (33) and (21), for $\tilde{t}$ we can write

$$\tilde{t}=t_i\exp(2s_{xi}^0-2\varphi_i x)\approx Y_i(1+2s_{xi}^0)x+(F_i-2\sigma_{pi}Y_i)x^2, \tag{B3}$$

or, taking into account that

$$x=\kappa_i\approx\varepsilon-\varepsilon_i-\varepsilon^2/2+\varepsilon_i^2/2,$$

with accuracy to the second order with respect to $\varepsilon$ and $\varepsilon_i$, we obtain

$$\tilde{t}\approx A_i+\tilde{Y}_i\varepsilon+\tilde{F}_i\varepsilon^2, \tag{B3a}$$

where

$$A_i=[F_i+Y_i(1-4\sigma_{pi})/2]-Y_i(1+2s_{xi}^0),$$

$$\tilde{Y}_i=Y_i(1+2s_{xi}^0)-2(F_i-2\sigma_{pi}Y_i)\varepsilon_i^0, \tag{B3b}$$

$$\tilde{F}_i=F_i-Y_i(1+4\sigma_{pi})/2.$$

Finally, in (B3a) $\varepsilon$ lies in the range

$$\exp q_{i-1}-1<\varepsilon<\exp q_i-1. \tag{B3c}$$

## APPENDIX C

### The matrix-valued function exp($-\lambda a$) of a matrix $a$

Substituting the expression for $a$ in terms of its deviator $\Delta$ into the exponential function, so that $a=I_1E/3+\Delta$ [see (A4)], we obtain

$$\exp(-\lambda a)=\exp(-\lambda I_1/3)\exp(-\lambda\Delta). \tag{C1}$$

Any function $f(\Delta)$ for a case of different eigenvalues $\Delta_k$ of $\Delta$ can be written in the form (see Ref. 13)

$$f(\Delta)=\sum_k f(\Delta_k)Z_k, \tag{C2}$$

where the $Z_k$ are the so-called components of $\Delta$ (or $a$) which do not depend on the form of $f$ (as was pointed out in Ref. 13, the expression for the case of repeated eigenvalues, in which some of the $Z_k$ become meaningless, can be obtained by the corresponding limiting transition).

It was shown in Ref. 1 that [for the definition of the second shear $\Delta_2$ see (9)]

$$Z_k=\partial a_k/\partial a=E/3+\partial\Delta_k/\partial a,\quad \partial\Delta_k/\partial a=\psi_k\Delta+\omega_k\Delta_2. \tag{C3}$$

Substituting $f=1$ into (C2), we can easily prove that

$$\sum_k\psi_k=0,\quad \sum_k\omega_k=0. \tag{C4}$$

Differentiating the characteristic equation for $\Delta$

$$\Delta_k^3=k_2\Delta_k+k_3, \tag{C5}$$

we readily obtain

$$\frac{\partial\Delta_k}{\partial a}=\frac{\Delta_k\Delta+\Delta_2}{3\Delta_k^2-k_2}, \tag{C3a}$$

whence after a comparison with (B3) we conclude that

$$\psi_k=\frac{\partial\Delta_k}{\partial k_2}=\Delta_k\omega_k,\quad \omega_k=\frac{\partial\Delta_k}{\partial k_3}=\frac{1}{3\Delta_k^2-k_2}. \tag{C3b}$$

Therefore, we can write

$$\exp(-\lambda\Delta)=a_\lambda E/3+b_\lambda\Delta+c_\lambda\Delta_2, \tag{C6}$$

where

$$a_\lambda=\sum\exp(-\lambda\Delta_k),\quad b_\lambda=\sum\psi_k\exp(-\lambda\Delta_k),$$
$$c_\lambda=\sum\omega_k\exp(-\lambda\Delta_k), \tag{C6a}$$

and, as can easily be proved,

$$\partial a_\lambda/\partial k_2=-\lambda b_\lambda,\quad \partial a_\lambda/\partial k_3=-\lambda c_\lambda. \tag{C6b}$$

If the notation $x=\Delta_1$ and $y=\Delta_2$ for the eigenvalues of $\Delta$, as well as the notation $\alpha_\lambda=\exp(-\lambda x)$ and $\beta_\lambda=\exp(-\lambda y)$, is introduced, we have

$$k_2=x^2+y^2+xy,m\quad k_3=-xy(x+y), \tag{C7}$$

$$a_\lambda=\alpha_\lambda+\beta_\lambda+1/\alpha_\lambda\beta_\lambda,$$

$$\psi_1=x\omega_1,\quad \psi_2=y\omega_2, \tag{C7a}$$

$$\omega_1=\frac{1}{(x-y)(2x+y)},\quad \omega_2=\frac{1}{(y-x)(2y+x)},$$

and then we can write

$$b_\lambda=x\omega_1(\alpha_\lambda-1/\alpha_\lambda\beta_\lambda)+y\omega_2(\beta_\lambda-1/\alpha_\lambda\beta_\lambda),$$
$$c_\lambda=\omega_1(\alpha_\lambda-1/\alpha_\lambda\beta_\lambda)+\omega_2(\beta_\lambda-1/\alpha_\lambda\beta_\lambda), \tag{C7b}$$

which, after being substituted into (C6), completely solves the problem of interest to us in a parametric form (the parameters are the eigenvalues of the shear tensor $\Delta$).

For calculations in a solid body, where the deviators are usually small ($\sim\tau_c/\mu$, where $\tau_c$ is the yield point and $\mu$ is the shear modulus), if, of course, for some reason the experimental data are expressed in terms of components of $\gamma$ (or $u$), a direct expansion in the invariants of $a=s$ ($s$ is the natural strain tensor; for the general expansion formula, see Ref. 1) is useful. In our case it has the form

$$a_\lambda=3+\sum_{m+n>0}\left[\frac{(m+n-1)!}{(2m+3n-1)!m!n!}\right](\lambda^2k_2)^m(-\lambda^3k_3)^n$$
$$=3+\lambda^2k_2-\frac{\lambda^3k_3}{2}+\frac{\lambda^4k_2^2}{3!2!}-\frac{\lambda^5k_2k_3}{4!}+\frac{\lambda^6(k_2^3/3-k_3^2/2)}{5!}$$
$$+\ldots, \tag{C8}$$

from which and from (B6b) we obtain

$$b_\lambda=-\frac{1}{\lambda}\frac{\partial a_\lambda}{\partial k_2}=-\lambda-\frac{\lambda^3k_2}{3!}+\frac{\lambda^4k_3}{4!}-\frac{\lambda^5k_2^2}{5!}+\ldots, \tag{C8a}$$

$$c_\lambda=-\frac{1}{\lambda}\frac{\partial a_\lambda}{\partial k_3}=\frac{\lambda^2}{2}+\frac{\lambda^4k_2}{4!}+\ldots.$$

## APPENDIX D

### Required explanations for the graphical representation of elastic moduli and uniaxial tensile forces in rubber

For a graphical representation we set $\rho A=1.7$ kgf/cm$^2$ in (45a), in accordance with the results in Ref. 12[5], and we write the function $\chi'=f_2$ in (42) and (43) in an approximation with the same dimensions for $B$, $D$, and $F$ in the form (with $z=X_2-3$)

$$\rho f_2(z)=\frac{B}{z+C}+\frac{D}{\sqrt{z+E}}+F. \tag{D1}$$

Fixing the values $\rho f_2^0=\rho\chi'(0)=0.7$ kgf/cm$^2$, $\rho f_{22}^0=\rho\chi''(0)=-0.5$ kgf/cm$^2$, and $\rho f_2=0.22$ kgf/cm$^2$, we arrive at a two-parameter problem requiring minimization of the deviations of the values of (D1) from the corresponding values in Ref. 12 by the least-squares method. As a result, we obtain the following set of values for the parameters:

$$C=0.22,\quad E=0.32,\quad B=-0.066,\quad D=0.68,$$
$$F=-0.19, \tag{D1a}$$

which gives an expression that describes the experimental Rivlin–Saunders curve adequately for purposes of graphical representation in the range reliably investigated by them[6]

$$X_2<5.5. \tag{D2}$$

It is not convenient to graphically depict the dependences of the moduli in $X_1$ and $X_2$, since, because of (A3b), the region where any function of the strains is defined in these variables has the form of a beak, which is more conveniently described after displacement in the $(X_1,X_2)$ plane to the point (3.3) and counterclockwise rotation through $\pi/4$, i.e., in the variables

$$\xi=(X_1-3+X_2-3)/\sqrt{2},\quad \eta=(X_2-X_1)/\sqrt{2}, \tag{D3}$$

in which it has the form [after the appropriate substitutions from (A5)]

$$|\eta|\leqslant\eta_+(\xi),\quad \xi>0, \tag{D4}$$

where

$$\eta_+^2(\xi)=108+18\xi\sqrt{2}+\xi^2-4(9+\xi\sqrt{2})^{3/2}, \tag{D4a}$$

so that

$$\eta_+(\xi)\cong\begin{cases}2^{-1/4}(\xi/3)^{3/2}, & \xi\to 0,\\ \xi-2^{7/4}\sqrt{\xi}, & \xi\to\infty.\end{cases} \tag{D4b}$$

In the $(x,y)$ plane of the eigenvalues of the deviator of $x$ introduced in Appendix B the region where (C.2) is defined is bounded by a distorted ellipse with semimajor axis $x+y\cong 0.493$, which is directed downward toward the left along the $x=y$ axis and is confined to the square $-0.759\leqslant x,y\leqslant 1$.

[1] In the case of repeated eigenvalues a function of an arbitrary operator contains another term with its own derivative in the repeated roots, but they vanish identically for the operator of a simple structure, particularly a symmetric structure.

[2] The accuracy of experiments at large $\varepsilon$ (which were used by Grüneisen for matching to his own values of $Y$ using Hartig's formula) must be sufficient for correctly isolating the nonlinearity. However, this means that the experiments cited should have been carried out with an absolute accuracy for a strain measurement no poorer than $10^{-7}$ when $\varepsilon\approx 10^{-3}$ (the accuracy of Thompson's experiments was, in fact, $2\times 10^{-7}$).

[3] The absence of compressibility, i.e, the validity of the equality $I_1=0$, is due to the large value of the bulk compressibility modulus $K$ of rubber, i.e., the large value of $f_{33}$ (which usually ranges from 10 to 100 kbar) compared with the other $f_{ij}=\partial^2f/\partial X_i\partial X_j$, which are three to four orders of magnitude smaller [see Appendix D and (43c)].

[4] In addition, after many years of careful work he found an empirical equation, which gives all the previously measured values of the shear modulus $\mu$ for polycrystals at temperatures above the Debye temperature with good accuracy. They turn out to depend on only one universal parameter (for all materials) and a pair of integers, which are small and more or less definite. This result is remarkable, although it does not rule out the existence of a similar equation substantiated by physical principles in a rigorous theory.

[5] The relationship of $f$ to Rivlin's "stored-energy function" $W$ normalized to the initial volume has the form $f=W/\rho_0$. The dimensions of the coefficients are transformed accordingly, although only their relative values are important for purposes of illustration.

[6] Their measurements covered the region $X_1\leqslant 12, X_2\leqslant 34$, but in a large part of this region the experimental data did not satisfy the requirement of equality between the cross derivatives $\partial^2f/\partial X_1\partial X_2=\partial^2f/\partial X_2\partial X_1$. This may be an indication that the assumption that the materials investigated are isotropic is incorrect.


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