

Cours doctoral

Sous l'impulsion de la fédération F2M une série de 6 séances de cours (en 3 demi-journées) est organisée en novembre et décembre 2008. Elle s'adresse à tous les étudiants, ingénieurs et chercheurs et porte sur le thème :

Elements of the Mechanics and Physics of Rubber Elasticity

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Abstract

A short, self-contained series of six lectures will be presented. In an initial approach, basic concepts and results in continuum thermo-mechanics will be reviewed and applied to aspects of the large deformation of elastomeric solids. A complementary approach to constitutive modeling is informed by consideration of macromolecular aspects of elastomeric structure, bonding, and deformation mechanisms, along with microstructural aspects of matrix/filler/void interactions. In a concluding session, we will review recent developments in advanced experimentation and constitutive modeling of rubbers, drawn from a list of topics including strain crystallization, anisotropic hyperelasticity, and elastomer nanocomposites.

Contact: Les personnes intéressées sont priées de contacter Samuel.Forest@ensmp.fr. Une attestation de suivi du cours sera fournie à ceux qui désirent faire valoir ce cours comme cours doctoral, la validation étant laissée à l'appréciation des écoles doctorales concernées.

Dates : 13, 27 novembre, 4 décembre 2008, de 14:00 à 17:00.

Lieu : Ecole des Mines de Paris, 60 Bd Saint-Michel, 75006 Paris. La salle sera indiquée à l'entrée de l'ENSMP en fonction du nombre définitif de participants.

ÉCOLE DES MINES DE PARIS
ELEMENTS OF THE MECHANICS AND PHYSICS OF RUBBER
ELASTICITY
NOTES ON CONTINUUM KINEMATICS

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Material (reference) and deformed (spatial) coordinates:

- position of material point P in reference configuration: $\mathbf{p}(P)$
- position of material point P in deformed configuration: $\mathbf{x}(P; t) = \hat{\mathbf{x}}(\mathbf{p}(P); t)$; a (generally time-dependent) mapping from reference to deformed configurations. For convenience in notation, we will often suppress writing the functional dependence on “time” t .
- the deformation map can be expressed in terms of the displacement vector $\mathbf{u}(\mathbf{p})$ of the ‘material particle’ (or local collection of mass) located, at time $t = t_0$, at position \mathbf{p} in the reference configuration according to

$$\mathbf{x}(\mathbf{p}; t) = \mathbf{p} + \mathbf{u}(\mathbf{p}; t).$$

- the map is invertible: at any time t there exists a reverse mapping $\mathbf{p} = \hat{\mathbf{p}}(\mathbf{x})$ from the instantaneously deformed to the reference configuration
- the maps are assumed to be sufficiently smooth so that (infinitesimally) neighboring points in the reference configuration (there separated by relative position vector $d\mathbf{p}$) map into neighboring positions in the deformed configuration, where they are separated by relative position vector $d\mathbf{x}$.

Deformation gradient tensor

- the (infinitesimal) vectors $d\mathbf{p}$ and $d\mathbf{x}$ are connected by the tensor \mathbf{F} , termed the deformation gradient tensor, according to

$$d\mathbf{x} = \mathbf{F}d\mathbf{p} + o(d\mathbf{p})$$

or, in terms of Cartesian coordinates, and adopting Einstein summation convention on repeated indices, $dx_i = F_{ij} dp_j$.

- the deformation gradient tensor is defined according to

$$\mathbf{F} \equiv \text{Grad } \mathbf{x} = \frac{\partial \mathbf{x}}{\partial \mathbf{p}} = \frac{\partial \mathbf{p}}{\partial \mathbf{p}} + \frac{\partial \mathbf{u}}{\partial \mathbf{p}} = \mathbf{1} + \text{Grad } \mathbf{u} \equiv \mathbf{1} + \mathbf{H},$$

where $\mathbf{1}$ is the identity tensor and \mathbf{H} is the displacement gradient tensor.

- with respect to Cartesian basis vectors \mathbf{e}_i , where the vectors are determined by components according to $\mathbf{p} = p_j \mathbf{e}_j$, $\mathbf{u} = u_i \mathbf{e}_i$, and $\mathbf{x} = x_i \mathbf{e}_i$, the components of $\mathbf{F} = F_{ij} \mathbf{e}_i \otimes \mathbf{e}_j$ are

$$F_{ij} \equiv \mathbf{e}_i \cdot (\mathbf{F} \mathbf{e}_j) = \frac{\partial x_i}{\partial p_j} = \frac{\partial (p_i + u_i)}{\partial p_j} = \delta_{ij} + u_{i,j} = \delta_{ij} + H_{ij},$$

where $H_{ij} = u_{i,j} = \mathbf{e}_i \cdot (\text{Grad } \mathbf{u} \mathbf{e}_j)$

- because the deformation gradient tensor maps an infinitesimal line element from the reference configuration to another in the deformed configuration, it is sometimes referred to as a “two-point” tensor, meaning that the two vectors which it connects via a linear transformation ‘live’ in different domains.
- in general, $\mathbf{F}(\mathbf{p}, t)$ varies from point to point within the reference configuration, as well as with time t ; when \mathbf{F} does not vary with position, the deformation is termed homogeneous.

Local change of shape and orientation from \mathbf{F} :

- reference length of infinitesimal line element $d\mathbf{p} = ds_0 \mathbf{n}_0$ ($dp_i = ds_0 n_{0i}$); \mathbf{n}_0 is unit vector ($\mathbf{n}_0 \cdot \mathbf{n}_0 = |\mathbf{n}_0|^2 = 1$):

$$|d\mathbf{p}| = (d\mathbf{p} \cdot d\mathbf{p})^{1/2} = ((ds_0)^2 \mathbf{n}_0 \cdot \mathbf{n}_0)^{1/2} = ds_0$$

- deformed length of infinitesimal line element $d\mathbf{x} = ds \mathbf{n}$ (\mathbf{n} is unit vector):

$$|d\mathbf{x}| = (d\mathbf{x} \cdot d\mathbf{x})^{1/2} = (ds \mathbf{n} \cdot ds \mathbf{n})^{1/2} = ((ds)^2 \mathbf{n} \cdot \mathbf{n})^{1/2} = ds$$

- alternative expression for ds in terms of \mathbf{F} :

$$ds = |d\mathbf{x}| = ((\mathbf{F}d\mathbf{p}) \cdot (\mathbf{F}d\mathbf{p}))^{1/2} = (d\mathbf{p} \cdot ((\mathbf{F}^T \mathbf{F}) d\mathbf{p}))^{1/2}.$$

Subscript notation can also help here:

$$ds = (dx_i dx_i)^{1/2} = (F_{ij} dp_j F_{ik} dp_k)^{1/2} = (dp_j F_{ij} F_{ik} dp_k)^{1/2} = (dp_j F_{ji}^T F_{ik} dp_k)^{1/2}$$

- The symmetric tensor $\mathbf{C} \equiv \mathbf{F}^T \mathbf{F}$ (Note: $\mathbf{C}^T = (\mathbf{F}^T \mathbf{F})^T = \mathbf{F}^T (\mathbf{F}^T)^T = \mathbf{F}^T \mathbf{F} = \mathbf{C}$) is termed the right Cauchy-Green tensor, and quantifies the local stretch ratio, λ , of a reference line element initially parallel to \mathbf{n}_0 according to

$$\lambda(\mathbf{n}_0) \equiv \frac{ds}{ds_0} = \frac{(d\mathbf{p} \cdot (\mathbf{C} d\mathbf{p}))^{1/2}}{ds_0} = \frac{(ds_0 \mathbf{n}_0 \cdot (\mathbf{C} ds_0 \mathbf{n}_0))^{1/2}}{ds_0} = (\mathbf{n}_0 \cdot (\mathbf{C} \mathbf{n}_0))^{1/2} > 0$$

- because the stretch $\lambda > 0$ for any reference direction \mathbf{n}_0 , the tensor \mathbf{C} is positive-definite, and $\det \mathbf{C} = \det(\mathbf{F}^T \mathbf{F}) = J^2$. Here, use is made of the definition $J \equiv \det \mathbf{F}$ and the identities $\det(\mathbf{A}\mathbf{B}) = (\det \mathbf{A})(\det \mathbf{B})$ and $\det \mathbf{A} = \det \mathbf{A}^T$.
- Cartesian components of the right Cauchy-Green tensor are $C_{ij} = F_{ik}^T F_{kj}$
- The positive-definite symmetric tensor \mathbf{C} can be written as the product of another symmetric, positive-definite tensor, \mathbf{U} , termed the right stretch tensor, with itself:

$$\mathbf{C} = \mathbf{U}\mathbf{U} \equiv \mathbf{U}^2.$$

Transformation of oriented material area elements

- An oriented (vector-valued) infinitesimal material area in the reference configuration can be formed from 2 non-colinear vectors $d\mathbf{p} = ds_0 \mathbf{n}_0$ and $\delta\mathbf{p} = \delta s_0 \mathbf{m}_0$ according to

$$d\mathbf{a}_0 = da_0 \mathbf{r}_0 \equiv d\mathbf{p} \times \delta\mathbf{p},$$

where

$$da_0 = |d\mathbf{p} \times \delta\mathbf{p}| = |d\mathbf{p}| |\delta\mathbf{p}| \sin(\mathbf{n}_0, \mathbf{m}_0) = ds_0 \delta s_0 \sin(\mathbf{n}_0, \mathbf{m}_0)$$

and the reference unit normal to the area is

$$\mathbf{r}_0 = \frac{\mathbf{n}_0 \times \mathbf{m}_0}{|\mathbf{n}_0 \times \mathbf{m}_0|}.$$

- Under the deformation, the line elements $d\mathbf{p}$ and $\delta\mathbf{p}$ are mapped into corresponding vectors $d\mathbf{x} = \mathbf{F}d\mathbf{p} = ds \mathbf{n}$ and $\delta\mathbf{x} = \mathbf{F}\delta\mathbf{p} = \delta s \mathbf{m}$, which generate the deformed material area vector

$$d\mathbf{a} = da \mathbf{r} \equiv d\mathbf{x} \times \delta\mathbf{x},$$

with

$$da = |d\mathbf{x} \times \delta\mathbf{x}| = |d\mathbf{x}| |\delta\mathbf{x}| \sin(\mathbf{n}, \mathbf{m}) = ds \delta s \sin(\mathbf{n}, \mathbf{m}),$$

and deformed unit normal direction

$$\mathbf{r} = \frac{\mathbf{n} \times \mathbf{m}}{|\mathbf{n} \times \mathbf{m}|}.$$

- The relation between reference and deformed elemental areas, termed Nanson's relation, is

$$d\mathbf{a} = (\det \mathbf{F}) \mathbf{F}^{-T} d\mathbf{a}_0,$$

or

$$da \mathbf{r} = (\det \mathbf{F}) \mathbf{F}^{-T} da_0 \mathbf{r}_0.$$

This can be derived, using Cartesian subscript notation, in the following way:

$$r_i da = \epsilon_{ijk} dx_j \delta x_k = \epsilon_{ijk} (F_{jm} dp_m) (F_{kp} \delta p_p).$$

This can be multiplied from the left, on both sides of the equation, by \mathbf{F}^T (Cartesian components: $F_{iq} = F_{qi}^T$) to give

$$F_{qi}^T r_i da = \epsilon_{ijk} F_{iq} F_{jm} F_{kp} dp_m \delta p_p.$$

The determinant of the matrix $[F_{ij}]$ satisfies the matrix identity

$$\det[F] \epsilon_{qmp} = \epsilon_{ijk} F_{iq} F_{jm} F_{kp},$$

so that

$$F_{qi}^T r_i da = \epsilon_{ijk} F_{iq} F_{jm} F_{kp} dp_m \delta p_p = \det[F] \epsilon_{qmp} dp_m \delta p_p = \det[F] da_0 r_{0q},$$

or, in coordinate-free notation,

$$\mathbf{F}^T d\mathbf{a} = (\det \mathbf{F}) d\mathbf{a}_0.$$

On multiplying through by the inverse of \mathbf{F}^T ($\mathbf{F}^{-T} \equiv (\mathbf{F}^T)^{-1}$), one finally obtains

$$d\mathbf{a} = (\det \mathbf{F}) \mathbf{F}^{-T} d\mathbf{a}_0.$$

Changes in angle between infinitesimal line elements

- consider again the 2 reference line elements $d\mathbf{p} = ds_0 \mathbf{n}_0$ and $\delta\mathbf{p} = \delta s_0 \mathbf{m}_0$. In the reference configuration, the dot product of these two vectors is

$$d\mathbf{p} \cdot \delta\mathbf{p} = ds_0 \delta s_0 \cos(\Theta),$$

where Θ is the angle between the unit vectors \mathbf{n}_0 and \mathbf{m}_0 : $\cos(\Theta) = \cos(\mathbf{n}_0, \mathbf{m}_0) = \mathbf{n}_0 \cdot \mathbf{m}_0$.

- In the deformed configuration, the respective images of these vectors are

$$d\mathbf{x} = \mathbf{F}d\mathbf{p} = ds \mathbf{n};$$

$$\delta\mathbf{x} = \mathbf{F}\delta\mathbf{p} = \delta s \mathbf{m}.$$

- The dot product of these two vectors in the deformed configuration provides

$$d\mathbf{x} \cdot \delta\mathbf{x} = ds \delta s \cos(\theta),$$

where θ is the angle between the unit vectors \mathbf{n} and \mathbf{m} : $\cos(\theta) = \cos(\mathbf{n}, \mathbf{m}) = \mathbf{n} \cdot \mathbf{m}$.

- Using the reference-configuration-based definitions of the deformed line elements, the dot product can also be expressed as

$$\begin{aligned} d\mathbf{x} \cdot \delta\mathbf{x} &= ds \delta s \cos(\theta) \\ &= (\mathbf{F}d\mathbf{p}) \cdot (\mathbf{F}\delta\mathbf{p}) \\ &= d\mathbf{p} \cdot (\mathbf{F}^T \mathbf{F}) \delta\mathbf{p} \\ &= ds_0 \delta s_0 \mathbf{n}_0 \cdot (\mathbf{C}\mathbf{m}_0). \end{aligned}$$

- Combining the last three equations,

$$\cos(\theta) = \frac{\mathbf{n}_0 \cdot (\mathbf{C}\mathbf{m}_0)}{\lambda(\mathbf{n}_0) \lambda(\mathbf{m}_0)},$$

where the stretch ratios are $\lambda(\mathbf{n}_0) = ds/ds_0$ and $\lambda(\mathbf{m}_0) = \delta s/\delta s_0$ are given by, e.g., $\lambda(\mathbf{n}_0) = (\mathbf{n}_0 \cdot (\mathbf{C}\mathbf{n}_0))^{1/2}$, etc.

- Noting that $\mathbf{C} = \mathbf{1} + 2\mathbf{E}$ (look ahead to p. 9 of these notes), we see that

$$\cos(\theta) = \frac{\cos(\Theta) + 2\mathbf{n}_0 \cdot (\mathbf{E}\mathbf{m}_0)}{\lambda(\mathbf{n}_0) \lambda(\mathbf{m}_0)};$$

when the two line elements are orthogonal in the reference configuration ($\mathbf{n}_0 \cdot \mathbf{m}_0 = 0 \Rightarrow \Theta = \pi/2$), and on expressing the shear (γ) by $\theta = \Theta - \gamma = \pi/2 - \gamma$, then $\cos(\theta) = \sin(\gamma)$ and

$$\sin(\gamma) = \frac{2\mathbf{n}_0 \cdot (\mathbf{E}\mathbf{m}_0)}{\lambda(\mathbf{n}_0) \lambda(\mathbf{m}_0)}.$$

Transformation of material volume elements

- the determinant of the deformation gradient relates a material volume element of size dv_0 in the reference configuration to size dv in the deformed configuration according to

$$dv = (\det \mathbf{F}) dv_0 = J dv_0.$$

- in the limit of *small displacement gradients*, when $\|\mathbf{H}\| = O(\epsilon)$, the linearized kinematics provides

$$dv = (\det \mathbf{F}) dv_0 = \det[\delta_{ij} + u_{i,j}] dv_0 = (1 + u_{i,i} + O(\epsilon)) dv_0.$$

so that the small strain dilatation (or fractional volume change) e is given by

$$e \equiv \frac{dv - dv_0}{dv_0} = u_{i,i},$$

or $e = \nabla \cdot \mathbf{u} \equiv \text{Div} \mathbf{u}$.

- A proof of the volume transformation can be performed by identifying the elemental reference volume, dv_0 , determined by a reference oriented surface area element, $d\mathbf{a}_0 = da_0 \mathbf{r}_0 \equiv d\mathbf{p} \times \delta\mathbf{p}$, and a third, linearly independent reference line element $\Delta\mathbf{p} \equiv \Delta s_0 \mathbf{q}_0$, according to

$$dv_0 \equiv \Delta\mathbf{p} \cdot d\mathbf{a}_0$$

and then evaluating the volume of the mapped volume element as

$$dv \equiv \Delta\mathbf{x} \cdot d\mathbf{a},$$

where $\Delta\mathbf{x} \equiv \mathbf{F} \Delta\mathbf{p}$.

Eigenvalue problems

- Tensors have special directions, termed eigenvectors (principal, or ‘characteristic’ vectors), such that the operation of the tensor on the eigenvector gives a multiple of the eigenvector itself. Restricting attention to unit vectors, the magnitude (and units) of the multiplying factor are termed eigenvalues (or principal values) of the tensor. For the stretch tensor \mathbf{C} , the eigenvalue problem can be posed as finding a unit direction \mathbf{n} and corresponding eigenvalue S such that

$$\mathbf{C}\mathbf{n} = S\mathbf{n} = S\mathbf{1}\mathbf{n}; \quad \text{or} \quad (\mathbf{C} - S\mathbf{1})\mathbf{n} = \mathbf{0},$$

for $\mathbf{n} \neq \mathbf{0}$. In terms of Cartesian components, this is equivalent to the matrix eigenvalue problem

$$\begin{bmatrix} C_{11} - S & C_{12} & C_{13} \\ C_{21} & C_{22} - S & C_{23} \\ C_{31} & C_{32} & C_{33} - S \end{bmatrix} \begin{Bmatrix} n_1 \\ n_2 \\ n_3 \end{Bmatrix} = \begin{Bmatrix} 0 \\ 0 \\ 0 \end{Bmatrix}.$$

- the matrix eigenvalue problem has non-trivial solutions only when the determinant of the matrix vanishes. This leads to a cubic equation in the (sought-for) eigenvalue itself:

$$0 = \det(\mathbf{C} - S\mathbf{1}) = -S^3 + I_1S^2 - I_2S + I_3 = -(S - S_1)(S - S_2)(S - S_3),$$

where $I_i(\mathbf{C})$; $i = 1, 2, 3$, are the scalar invariants of \mathbf{C} , defined by

$$\begin{aligned} I_1(\mathbf{C}) &\equiv \text{tr } \mathbf{C} = C_{ii} = S_1 + S_2 + S_3 \\ I_2(\mathbf{C}) &\equiv \frac{1}{2} [(\text{tr } \mathbf{C})^2 - \text{tr}(\mathbf{C}^2)] = \frac{1}{2} (C_{ii}C_{jj} - C_{ji}C_{ij}) = S_1S_2 + S_2S_3 + S_3S_1 \\ I_3(\mathbf{C}) &\equiv \det \mathbf{C} = \epsilon_{ijk}C_{1i}C_{2j}C_{3k} = S_1S_2S_3 \end{aligned}$$

The parameters S_i , $i = 1, 2, 3$ in the factorization of the characteristic polynomial are the sought-for roots, or eigenvalues.

- Every real-valued (as opposed to complex-valued = real + i imaginary) tensor has at least one real eigenvalue (the characteristic cubic polynomial must cross the zero axis somewhere in $-\infty < S < \infty$!); symmetric real tensors have 3 real eigenvalues, S_1 , S_2 , and S_3 , with corresponding unit eigenvectors \mathbf{n}_i , $i = 1, 2, 3$. The set of eigenvalues is the spectrum of the tensor.
- When the 3 eigenvalues are distinct, the 3 eigenvectors are orthogonal: $\mathbf{n}_i \cdot \mathbf{n}_j = \delta_{ij}$. If two eigenvalues coincide, but differ from the remaining one (e.g., if $S_2 = S_3 = "S" \neq S_1$, then the eigenvectors $\mathbf{n}(S)$ corresponding to [both] S_2 and S_3 are not uniquely defined, but they must both be in a plane perpendicular to the (unique!) eigenvector \mathbf{n}_1 corresponding to the (unique) eigenvalue S_1 : $\mathbf{n}(S) \cdot \mathbf{n}_1 = 0$. For convenience, we chose \mathbf{n}_2 as any unit vector in this plane, then make \mathbf{n}_3 orthogonal to both the others via $\mathbf{n}_3 = \mathbf{n}_1 \times \mathbf{n}_2$.

- When all three eigenvalues are the same (say, $S_1 = S_2 = S_3 \equiv S$), then the tensor is that multiple of the identity tensor, $\mathbf{C} = S \mathbf{1}$, and every direction \mathbf{n} is an eigenvector of the tensor, with corresponding eigenvalue S .
- Every tensor \mathbf{C} solves its own characteristic polynomial equation:

$$\mathbf{0} = -\mathbf{C}^3 + I_1 \mathbf{C}^2 - I_2 \mathbf{C} + I_3 \mathbf{1} = -(\mathbf{C} - S_1 \mathbf{1})(\mathbf{C} - S_2 \mathbf{1})(\mathbf{C} - S_3 \mathbf{1});$$

this is the Cayley-Hamilton theorem.

Spectral representation of \mathbf{C} and \mathbf{U} ; polar decomposition

- Based on the eigenvalues and eigenvectors of the symmetric tensor \mathbf{C} , it can be expressed as (using “circle-cross” notation for dyadics)

$$\mathbf{C} = (\lambda_1)^2 \mathbf{n}_1 \otimes \mathbf{n}_1 + (\lambda_2)^2 \mathbf{n}_2 \otimes \mathbf{n}_2 + (\lambda_3)^2 \mathbf{n}_3 \otimes \mathbf{n}_3,$$

or, on using Gibbs’ notation, with no ‘ \otimes ’ between dyad vector pairs, as

$$\mathbf{C} = (\lambda_1)^2 \mathbf{n}_1 \mathbf{n}_1 + (\lambda_2)^2 \mathbf{n}_2 \mathbf{n}_2 + (\lambda_3)^2 \mathbf{n}_3 \mathbf{n}_3;$$

the stretch tensor \mathbf{U} admits the related representations

$$\mathbf{U} = \lambda_1 \mathbf{n}_1 \otimes \mathbf{n}_1 + \lambda_2 \mathbf{n}_2 \otimes \mathbf{n}_2 + \lambda_3 \mathbf{n}_3 \otimes \mathbf{n}_3$$

- The deformation gradient can be factored into the product of an orthogonal tensor, \mathbf{R} , termed the rotation tensor, and the symmetric positive-definite stretch tensor \mathbf{U} according to

$$\mathbf{F} = \mathbf{R}\mathbf{U}.$$

This factorization is termed the polar decomposition of the tensor \mathbf{F} .

Recall that a (proper) orthogonal tensor \mathbf{R} has its transpose as its inverse, so that $\mathbf{R}\mathbf{R}^T = \mathbf{R}^T\mathbf{R} = \mathbf{1}$, and $\det \mathbf{R} = 1$.

Note: $\mathbf{C} \equiv \mathbf{F}^T\mathbf{F} = (\mathbf{R}\mathbf{U})^T(\mathbf{R}\mathbf{U}) = \mathbf{U}^T(\mathbf{R}^T\mathbf{R})\mathbf{U} = \mathbf{U}^T\mathbf{U} = \mathbf{U}\mathbf{U} = \mathbf{U}^2$ is independent of the rigid-body rotation associated with \mathbf{R} .

- the polar decomposition of \mathbf{F} can also be expressed as

$$\mathbf{F} = \mathbf{V}\mathbf{R},$$

where \mathbf{R} is the same orthogonal tensor as before, and the symmetric, positive-definite tensor \mathbf{V} is termed the left stretch tensor.

- the left Cauchy-Green strain tensor is $\mathbf{B} \equiv \mathbf{F}\mathbf{F}^T = \mathbf{V}^2$.
- The left and right stretch tensors are connected via the transformations

$$\mathbf{V} = \mathbf{R}\mathbf{U}\mathbf{R}^T;$$

$$\mathbf{U} = \mathbf{R}^T\mathbf{V}\mathbf{R};$$

- Show that $\mathbf{B} = \mathbf{R}\mathbf{C}\mathbf{R}^T$.

[Referential, or ‘Material’] Strain tensors

- The Green-Lagrange strain tensor \mathbf{E} is defined by

$$\mathbf{E} \equiv \frac{1}{2} (\mathbf{C} - \mathbf{1}).$$

- The spectral representation of the Green-Lagrange strain tensor is

$$\mathbf{E} = \frac{1}{2}((\lambda_1)^2 - 1) \mathbf{n}_1 \otimes \mathbf{n}_1 + \frac{1}{2}((\lambda_2)^2 - 1) \mathbf{n}_2 \otimes \mathbf{n}_2 + \frac{1}{2}((\lambda_3)^2 - 1) \mathbf{n}_3 \otimes \mathbf{n}_3;$$

- When there is no deformation (every direction has stretch of unity), but only rigid-body rotation, then $\mathbf{U} = \mathbf{1}$ and $\mathbf{F} = \mathbf{R}$; under these conditions, $\mathbf{C} = \mathbf{1}$, and the Green-Lagrange strain tensor vanishes: $\mathbf{E} = \mathbf{0}$.

- Cartesian components of the Green-Lagrange strain tensor are

$$\begin{aligned} E_{ij} &= \frac{1}{2} (C_{ij} - \delta_{ij}) = \frac{1}{2} (F_{ik}^T F_{kj} - \delta_{ij}) = \frac{1}{2} ((\delta_{ik} + H_{ik})^T (\delta_{kj} + H_{kj}) - \delta_{ij}) \\ &= \frac{1}{2} (H_{ij} + H_{ji} + H_{ik}^T H_{kj}) = \frac{1}{2} (u_{i,j} + u_{j,i} + u_{k,i} u_{k,j}). \end{aligned}$$

- Our customary definition of (small) extensional “strain” is that of (small) change in length divided by initial length; in mathematical terms, the extensional strain measure “ e ” associated with a given direction can be considered as a function of the stretch λ , in that direction,

$$e = f(\lambda),$$

providing the function f satisfies the following two restrictions for small stretches, or for $|\lambda - 1| \ll 1$:

1. $f(\lambda) \rightarrow 0$ as $|\lambda - 1| \rightarrow 0$
2. $f'(\lambda) = df(\lambda)/d\lambda \rightarrow 1$ as $|\lambda - 1| \rightarrow 0$

- In the Green-Lagrange measure of stretch, the chosen function is

$$f(\lambda) = \frac{1}{2} (\lambda^2 - 1) = \frac{1}{2} (\lambda + 1)(\lambda - 1);$$

clearly, as $\lambda \rightarrow 1$, both requirements are fulfilled. Other functions satisfying the requirements of a proper strain definition include $f = \lambda - 1$ (nominal strain) and $f = \ln(\lambda)$ (logarithmic, or ‘true’ strain).

- Corresponding tensor measures of strain can be generated from applying the respective functions to the stretch tensor \mathbf{U} ; e.g., $\mathbf{E} = f(\mathbf{U}) = (1/2)(\mathbf{U}^2 - \mathbf{1})$. Spectral representations for the other strain-measure tensors, \mathbf{E}_f , follow:

$$\mathbf{E}_f = f(\mathbf{U}) = f(\lambda_1) \mathbf{n}_1 \otimes \mathbf{n}_1 + f(\lambda_2) \mathbf{n}_2 \otimes \mathbf{n}_2 + f(\lambda_3) \mathbf{n}_3 \otimes \mathbf{n}_3;$$

- In the limit of small displacement gradients, where $\|\mathbf{H}\| = O(\epsilon) \ll 1$, the Green-Lagrange strain tensor \mathbf{E} (and, indeed, all the strain measures \mathbf{E}_f) approach a common limit, termed the small strain tensor, $\boldsymbol{\epsilon}$, where

$$\boldsymbol{\epsilon} = \frac{1}{2} (\text{Grad } \mathbf{u} + (\text{Grad } \mathbf{u})^T);$$

Cartesian components of the small strain tensor are

$$\epsilon_{ij} = \mathbf{e}_i \cdot (\boldsymbol{\epsilon} \cdot \mathbf{e}_j) = \frac{1}{2} (u_{i,j} + u_{j,i}).$$

Motions, velocities, spatial descriptions, and rate kinematics

- when the displacement is time-dependent, the material time derivative of position of the particle originally at \mathbf{p} , and instantaneously at \mathbf{x} , is

$$\dot{\mathbf{x}}(\mathbf{p}, t) = \dot{\mathbf{u}}(\mathbf{p}, t) = \frac{\partial \mathbf{x}(\mathbf{p}, t)}{\partial t} = \frac{\partial \mathbf{u}(\mathbf{p}, t)}{\partial t}.$$

- the corresponding material time derivative of the deformation gradient is

$$\dot{\mathbf{F}} = \dot{\mathbf{H}} = \frac{\partial \dot{\mathbf{u}}}{\partial \mathbf{p}} = \text{Grad} \dot{\mathbf{u}}.$$

- the spatial description of any field f expresses how the entity f instantaneously depends on the current deformed position in the body, \mathbf{x} , and time, t :

$$f_s = \hat{f}(\mathbf{x}, t).$$

If we wish to construct a map of the instantaneous material time derivative of f , or \dot{f} , we must be sure that we are referring to the time-varying f -history of a particular particle. This is most readily accomplished by “pulling back” the spatial description of \mathbf{x} , and hence of f , to the time-invariant reference frame, using the known material map of the motion, $\mathbf{x} = \hat{\mathbf{x}}(\mathbf{p}, t)$, and its implicit inverse, namely

$$\mathbf{p} = \hat{\mathbf{p}}(\mathbf{x}, t).$$

In words, this means that the inverse function $\hat{\mathbf{p}}$ “pulls back” the particle that is located at position \mathbf{x} at time t , and maps it back to its reference location \mathbf{p} at the reference value of the time parameter. Alternatively, the [forward] time-dependent mapping $\hat{\mathbf{x}}$ “pushes forward” the location of the particle originally at \mathbf{p} to instantaneously deformed position \mathbf{x} .

- Now we are in a position to describe the field corresponding to the spatial description of particle velocity, $\mathbf{v}(\mathbf{x}, t)$, in terms of the reference description of velocity:

$$\dot{\mathbf{u}}(\mathbf{p}, t) = \dot{\mathbf{u}}(\hat{\mathbf{p}}(\mathbf{x}, t), t) \equiv \mathbf{v}(\mathbf{x}, t).$$

- This structure permits definition of the spatial description of the material time derivative of any field f , denoted as $\dot{f}(\mathbf{x}, t)$, by

$$\begin{aligned} \dot{f}(\mathbf{x}, t) &= \frac{Df(\mathbf{x}, t)}{Dt} \\ &= \left(\frac{\partial f(\mathbf{x}; t)}{\partial t} \right) \Big|_{\mathbf{x}} + \left(\frac{\partial f(\mathbf{x}; t)}{\partial \mathbf{x}} \right) \Big|_t \left(\frac{\partial \mathbf{x}(\mathbf{p}, t)}{\partial t} \right) \Big|_{\mathbf{p}=\hat{\mathbf{p}}(\mathbf{x}, t)} \\ &= \left(\frac{\partial f(\mathbf{x}, t)}{\partial t} \right) + \text{grad } f(\mathbf{x}, t) \cdot \mathbf{v}(\mathbf{x}, t) \end{aligned}$$

This can also be formally expressed, using cartesian coordinates, by

$$\dot{f} = \frac{\partial f}{\partial t} + \frac{\partial f}{\partial x_i} v_i.$$

- The spatial field corresponding to the spatial gradient of \mathbf{v} , denoted $\mathbf{L}(\mathbf{x}, t)$, is termed the velocity gradient field:

$$\mathbf{L} = \text{grad} \mathbf{v} = \mathbf{D} + \mathbf{W},$$

where $\mathbf{D} = \mathbf{D}^T = (\mathbf{L} + \mathbf{L}^T) / 2$ is the stretching and $\mathbf{W} = -\mathbf{W}^T = (\mathbf{L} - \mathbf{L}^T) / 2$ is the spin.

- We can express the material description of a spatial field $\mathbf{a}(\mathbf{x}, t)$ as

$$\mathbf{a}_m(\mathbf{p}, t) = \mathbf{a}(\mathbf{x}(\mathbf{p}, t), t).$$

Material (referential) gradients of a material description of a spatial field are evaluated using the chain rule as

$$\text{Grad} \mathbf{a}_m(\mathbf{p}, t) \equiv \frac{\partial \mathbf{a}_m(\mathbf{p}, t)}{\partial \mathbf{p}} = \left(\frac{\partial \mathbf{a}(\mathbf{x}(\mathbf{p}, t), t)}{\partial \mathbf{x}} \right) \left(\frac{\partial \mathbf{x}(\mathbf{p}, t)}{\partial \mathbf{p}} \right) = (\text{grad} \mathbf{a})_m \mathbf{F}(\mathbf{p}, t).$$

- The material time derivative of the deformation gradient can be expressed as

$$\dot{\mathbf{F}} = \mathbf{L}_m \mathbf{F}.$$

This is shown by noting that

$$\dot{\mathbf{F}}(\mathbf{p}, t) = \frac{\partial \text{Grad} \mathbf{x}(\mathbf{p}, t)}{\partial t} = \text{Grad} \dot{\mathbf{x}}(\mathbf{p}, t) = \text{Grad} \mathbf{v}_m(\mathbf{p}, t) = (\text{grad} \mathbf{v})_m \mathbf{F}(\mathbf{p}, t) = \mathbf{L}_m \mathbf{F}.$$

ÉCOLE DES MINES DE PARIS
 ELEMENTS OF THE MECHANICS AND PHYSICS OF RUBBER
 ELASTICITY
 NOTES ON STRESS AND EQUILIBRIUM

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Nominal and “true” stress tensors

- In conjunction with the deformation-induced change in oriented material surface elements leading to Nanson’s relation, we followed an infinitesimal vector-valued area element $d\mathbf{a}_0 = da_0 \mathbf{n}_0$, centered at \mathbf{p} in the reference configuration, of magnitude $da_0 = |d\mathbf{a}_0|$ and with reference unit normal vector \mathbf{n}_0 . Under the deformation gradient \mathbf{F} , this material area element is mapped into (deformed/re-oriented) area element $d\mathbf{a} = da \mathbf{n}$, centered at \mathbf{x} . The two area element vectors are related by (Nanson) as:

$$d\mathbf{a} = (\det \mathbf{F}) \mathbf{F}^{-T} d\mathbf{a}_0.$$

- As the surfaces under consideration are ‘imagined’, they may be (a) on the boundary of the body, (b) at a distinguished internal interface within the body (e.g., a material interface; a grain boundary, etc.), or (c) a ‘generic’ point internal internal to the body. In any event, there are 2 sides (or faces) to the surface. We let the 2 sides be denoted “+” and “-”, respectively, with the understanding that both \mathbf{n}_0 and \mathbf{n} point from the “-”-side to the “+”-side.
- We understand that, in the deformed (“loaded”) configuration, there will be mechanical interaction across the surface element. This interaction consists of an elemental force vector, $d\mathbf{f}$, applied by some mass/material element on the “+”-side, to the mass/material point on the “-”-side: force is a mechanical transaction between elements of mass, in this case transpiring across an interface. We relate this elemental force vector to the stress tensors and elemental areas in two ways:

$$d\mathbf{f} = \mathbf{T} d\mathbf{a} = \mathbf{t}(\mathbf{n}) da;$$

$$d\mathbf{f} = \mathbf{P} d\mathbf{a}_0 = \mathbf{t}_0(\mathbf{n}_0) da_0.$$

- Here \mathbf{T} is the Cauchy (or “true”) stress tensor, at location \mathbf{x} of the deformed configuration, and \mathbf{P} is the first Piola-Kirchhoff (or “nominal”) stress tensor, “at” \mathbf{p} of the reference configuration. Strictly speaking, the reference configuration was, at its time of definition, most likely not supporting traction (although the reference configuration could be supporting initial stress). Instead the traction was induced by mechanical

interactions associated with the deformation itself; deformation which, evidently, had not yet occurred at the time/place of the reference configuration. In this sense, then,, we can view the nominal stress tensor as (a) a mechanics “bookkeeping” device (a description often used by Professor A. S. Argon), or (b) more formally, as a “pull-back” of the Cauchy stress tensor. Without prejudice, we will find that the introduction of the nominal stress tensor provides certain advantages in general solid mechanics formulations, which we will exploit. A further notation sometimes introduced for \mathbf{P} is “ \mathbf{P}^{PK1} ”, indicating the first Piola-Kirchhoff stress tensor. Note that the nominal stress tensor is not symmetric, in general (see page 9 of current notes).

- We can define a stress-dimensional traction vector as the limit, as dimensions tend to zero, of the ratio of the force vector to the magnitude of the area element. Using definitions of the area elements and to the tensor operation,

$$\mathbf{t}(\mathbf{x}, \mathbf{n}) \equiv \lim_{da \rightarrow 0} \frac{d\mathbf{f}}{da} = \mathbf{T}(\mathbf{x})\mathbf{n}.$$

- The traction vectors associated with a given direction, \mathbf{n} , and its negative direction, $-\mathbf{n}$, are equal and opposite (Cauchy’s relation):

$$\mathbf{T}\mathbf{n} = \mathbf{t}(\mathbf{n}) = -\mathbf{t}(-\mathbf{n}) = -\mathbf{T} \cdot (-\mathbf{n}) = \mathbf{T}\mathbf{n}.$$

- Likewise, a nominal traction vector can be defined as

$$\mathbf{t}_0(\mathbf{p}, \mathbf{r}_0) \equiv \lim_{da_0 \rightarrow 0} \frac{d\mathbf{f}}{da_0} = \mathbf{P}(\mathbf{p})\mathbf{n}_0.$$

- The nominal stress tensor \mathbf{P} reckons the force (in the deformed configuration) per unit oriented area in the reference configuration. We can use Nanson’s relation to connect \mathbf{T} , \mathbf{P} , and \mathbf{F} :

$$d\mathbf{f} = \mathbf{P}d\mathbf{a}_0 = \mathbf{T}d\mathbf{a} = \mathbf{T}(\det \mathbf{F} \mathbf{F}^{-T})d\mathbf{a}_0,$$

or, on rearranging the second and last parts of the equation,

$$(\mathbf{P} - (\det \mathbf{F})\mathbf{T}\mathbf{F}^{-T}) d\mathbf{a}_0 = \mathbf{0}.$$

- Since the area element $d\mathbf{a}_0$ is arbitrary, the tensor within parentheses must be the zero tensor, identically. Alternatively,

$$\mathbf{P} = (\det \mathbf{F})\mathbf{T}\mathbf{F}^{-T} = J \mathbf{T}\mathbf{F}^{-T},$$

or

$$\mathbf{T} = (\det \mathbf{F})^{-1}\mathbf{P}\mathbf{F}^T = J^{-1} \mathbf{P}\mathbf{F}^T.$$

- Note: the notation used here for nominal stress is the transpose of the definition of nominal stress found in certain publications. Be careful, because similar convention disagreements on notation abound in the applied mechanics literature...

- **Power conjugate stress measures.** In the derivation above, we connected the measure-dependent stress tensors \mathbf{T} and \mathbf{P} by application of a traction rule for arbitrary orientations. While the results we obtained are correct, another path to connect stress measures comes from power conjugacy. Briefly, the stress-working power in an elemental mass having deformed volume dv , and supporting Cauchy stress \mathbf{T} , and undergoing the velocity gradient $\mathbf{L} = \text{grad } \mathbf{v} = \dot{\mathbf{F}}\mathbf{F}^{-1}$ is

$$d\mathcal{P} = \mathbf{T} \cdot \mathbf{D} dv$$

where the stretching $\mathbf{D} = 1/2 (\mathbf{L} + \mathbf{L}^T)$, and the generic tensor scalar product operation $\mathbf{A} \cdot \mathbf{B} \equiv \text{tr}(\mathbf{A}\mathbf{B}^T) = A_{ij}B_{ji}^T = A_{ij}B_{ij}$. We can ask that this same power be obtained as the tensor scalar product of stress measure \mathbf{P}^* (to be determined) with the time rate of change of deformation gradient, $\dot{\mathbf{F}}$, according to

$$d\mathcal{P} = \mathbf{P}^* \cdot \dot{\mathbf{F}} dv_0.$$

Using $dv = J dv_0$ and the fact that Cauchy stress is symmetric ($\mathbf{T} = \mathbf{T}^T$), we can show that

$$d\mathcal{P} = J \mathbf{T} \cdot \mathbf{L} dv_0 = J \mathbf{T} \cdot (\dot{\mathbf{F}}\mathbf{F}^{-1}) dv_0,$$

or $d\mathcal{P} = J T_{ij} \dot{F}_{jk} F_{ki} dv_0$. It is straightforward to equate the two measures of stress-working power, re-arrange the expression for the tensor scalar product, and show that

$$0 = dv_0 (\mathbf{P}^* - J \mathbf{T}\mathbf{F}^{-T}) \cdot \dot{\mathbf{F}},$$

which, on invoking $dv_0 \neq 0$ and arbitrary $\dot{\mathbf{F}}$ again provides $\mathbf{P} = J \mathbf{T}\mathbf{F}^{-T}$.

- **Example problem.** The time rate of change of the Green-Lagrange strain tensor is $2\dot{\mathbf{E}} = \dot{\mathbf{C}} = d(\mathbf{F}^T\mathbf{F})/dt = \dot{\mathbf{F}}^T\mathbf{F} + \mathbf{F}^T\dot{\mathbf{F}}$. It can be shown that $\dot{\mathbf{C}} = 2\mathbf{F}^T\mathbf{D}\mathbf{F}$:

$$\begin{aligned} \dot{\mathbf{C}} &= \dot{\mathbf{F}}^T\mathbf{F} + \mathbf{F}^T\dot{\mathbf{F}} \\ &= \mathbf{F}^T\mathbf{F}^{-T}\dot{\mathbf{F}}^T\mathbf{F} + \mathbf{F}^T\dot{\mathbf{F}}\mathbf{F}^{-1}\mathbf{F} \\ &= \mathbf{F}^T \left(\mathbf{F}^{-T}\dot{\mathbf{F}}^T + \dot{\mathbf{F}}\mathbf{F}^{-1} \right) \mathbf{F} \\ &= \mathbf{F}^T \left(\left(\dot{\mathbf{F}}\mathbf{F}^{-1} \right)^T + \dot{\mathbf{F}}\mathbf{F}^{-1} \right) \mathbf{F} \\ &= \mathbf{F}^T (\mathbf{L}^T + \mathbf{L}) \mathbf{F} = 2\mathbf{F}^T\mathbf{D}\mathbf{F}. \end{aligned}$$

By requiring the stress measure \mathbf{S} (to be determined) to satisfy the stress working power relation

$$d\mathcal{P} = \mathbf{S} \cdot \dot{\mathbf{E}} dv_0,$$

for arbitrary conditions, show that

$$\mathbf{S} = J \mathbf{F}^{-1}\mathbf{T}\mathbf{F}^{-T} = \mathbf{F}^{-1}\mathbf{P}.$$

Solution:

By hypothesis,

$$d\mathcal{P} = \mathbf{S} \cdot \dot{\mathbf{E}} dv_0 = \frac{1}{2} \mathbf{S} \cdot \dot{\mathbf{C}} dv_0 = \mathbf{S} \cdot (\mathbf{F}^T \mathbf{D} \mathbf{F}) dv_0,$$

while also $d\mathcal{P} = \mathbf{T} \cdot \mathbf{D} dv$. Equating these and using $dv = J dv_0$ gives

$$J \mathbf{T} \cdot \mathbf{D} = \mathbf{S} \cdot (\mathbf{F}^T \mathbf{D} \mathbf{F}),$$

which can be re-arranged into

$$(J \mathbf{T} - \mathbf{F} \mathbf{S} \mathbf{F}^T) \cdot \mathbf{D} = 0,$$

giving

$$\begin{aligned} \mathbf{T} &= J^{-1} \mathbf{F} \mathbf{S} \mathbf{F}^T; \\ \mathbf{S} &= J \mathbf{F}^{-1} \mathbf{T} \mathbf{F}^{-T} = \mathbf{F}^{-1} (J \mathbf{T} \mathbf{F}^{-T}) = \mathbf{F}^{-1} \mathbf{P}. \end{aligned}$$

The stress tensor \mathbf{S} which is power-conjugate to the time rate of change of the Green-Lagrange strain is termed the **second Piola-Kirchhoff stress tensor**.

The stress tensor $\mathbf{S} = \mathbf{S}^T$ is symmetric, by inspection, but the symmetry of $\dot{\mathbf{E}}$ itself in the work-conjugacy condition guarantees that the skew part of \mathbf{S} , should it exist, would in any event have no stress working through $\dot{\mathbf{E}}$.

Balance of linear momentum

- The total external force transmitted to a deformed body of material, currently occupying region R_t at time t , through its (deformed) surface area ∂R_t , by means of external (outward-pointing) traction vectors is

$$\mathbf{f}_{(\text{surface-traction})} = \int_{R_t} d\mathbf{f} = \int_{R_t} \mathbf{t} da = \int_{R_t} \mathbf{T}\mathbf{n} da.$$

- Neglecting body forces (distributed forces per unit mass; e.g., gravity; magnetic attraction, etc.) and acceleration (no change of linear momentum), the total external force applied to any body, in this case, that force resultant transmitted to the body via surface tractions, must vanish: $\mathbf{f}_{(\text{total})} = \mathbf{f}_{(\text{surface-traction})} = \mathbf{0}$.
- For sufficiently smooth scalar, vector, or tensor functions “(...)”, the Cartesian subscript form of the divergence theorem of vector calculus can be written as

$$\int_{\partial R_t} (\dots) n_i da = \int_{R_t} \frac{\partial(\dots)}{\partial x_i} dv.$$

This means that the arbitrary (but smooth) field (...) may have any set of Cartesian indices, providing that the expression makes sense when multiplied by n_i , or differentiated with respect to x_i .

Note: If the field “(...)” is not sufficiently smooth for the indicated differentiation operator to make sense on some internal surface (e.g., the field (...) exhibits a jump discontinuity of magnitude “[...]” $\equiv (\dots)^{(+)} - (\dots)^{(-)}$ across surface Σ_t , having normal $n_i^{(+)} = -n_i^{(-)}$ directed from its (+)-side towards its (-)-side, then a modified version of the divergence theorem is constructed by adding both sides of Σ to the generalized boundary, and restricting the volume integral to those portions of R_t where the differentiation can be performed, resulting in

$$\int_{\partial R_t} (\dots) n_i da = \int_{R_t} \frac{\partial(\dots)}{\partial x_i} dv - \int_{\Sigma_t} [\dots] n_i^{(+)} da.$$

- The i th Cartesian component of the surface traction is $t_i = T_{ij}n_j$. Thus the equilibrium condition is

$$f_{(\text{total})i} = 0_i = \int_{\partial R_t} T_{ij}n_j da = \int_{R_t} \frac{\partial T_{ij}}{\partial x_j} dv \equiv \int_{R_t} (\text{div } \mathbf{T})_i dv.$$

Here the vector-valued function “div \mathbf{T} ” is implicitly defined by its indicated Cartesian components as sums of certain partial derivatives of the tensor components themselves:

$$\begin{aligned} \text{div } \mathbf{T} &= \left(\frac{\partial T_{11}}{\partial x_1} + \frac{\partial T_{12}}{\partial x_2} + \frac{\partial T_{13}}{\partial x_3} \right) \mathbf{e}_1 \\ &+ \left(\frac{\partial T_{21}}{\partial x_1} + \frac{\partial T_{22}}{\partial x_2} + \frac{\partial T_{23}}{\partial x_3} \right) \mathbf{e}_2 \\ &+ \left(\frac{\partial T_{31}}{\partial x_1} + \frac{\partial T_{32}}{\partial x_2} + \frac{\partial T_{33}}{\partial x_3} \right) \mathbf{e}_3 \end{aligned}$$

- We use the fact that, for no body force or accelerations, the zero value for external force applies for all deformed regions R_t having instantaneous surface areas ∂R_t . If we could find a place where $\text{div } \mathbf{T} \neq \mathbf{0}$, we could chose the region R_t to include only regions where the (assumed non-zero) value of the vector function had components of one sign. Then, as the limit of $R_t \rightarrow 0$ was taken at that point, it is clear that it would at some point not be possible for the volume integral of the divergence to give zero total. Thus we conclude that the vector $\text{div } \mathbf{T}$ must therefore vanish identically everywhere: $\text{div } \mathbf{T} = \mathbf{0}$.

- Had a body force vector per unit mass of magnitude \mathbf{b} been present, the total body force would be

$$\mathbf{f}_{(\text{body-force})} = \int \mathbf{b} \, \text{dm} = \int_{R_t} \mathbf{b} \rho \, dv,$$

where $\rho = \text{dm}/dv$ is the mass per unit deformed volume.

- The linear momentum of the material within R_t is given by

$$\mathbf{l}(t) \equiv \int_{R_t} \rho \mathbf{v} \, dv,$$

where it is understood that $\mathbf{v} = \dot{\mathbf{x}}$ is the particle velocity, measured in an inertial frame, based on the material time derivative of that particle's position.

- Had the material points (with velocity \mathbf{v}) been accelerating, the total change in linear momentum for the body would be

$$\frac{\mathcal{D}\mathbf{l}(t)}{\mathcal{D}t} \equiv \frac{\mathcal{D}}{\mathcal{D}t} \int_{R_t} \rho \mathbf{v} \, dv = \int_{R_0} \dot{\mathbf{v}} \rho_0 \, dv_0 = \int_{R_t} \rho \dot{\mathbf{v}} \, dv.$$

Here we have pulled back the integral over the time-dependent deformed region, R_t , to an equivalent integral over the time-independent reference region, R_0 , with a time-independent reference mass density field $\rho_0(\mathbf{p})$. The “dot” notation is short hand for material time derivative, and the operation of integration of a tensor-valued function (such as \mathbf{v} or $\dot{\mathbf{v}}$) with respect to mass can be straightforwardly pulled-back/pushed-forward to equivalent integrals, as shown.

- The most general case of balance of linear momentum (Newton's law!) results in

$$\begin{aligned} \mathbf{f}_{(\text{total})} &= \mathbf{f}_{(\text{surface-traction})} + \mathbf{f}_{(\text{body-force})} = \frac{\mathcal{D}\mathbf{l}(t)}{\mathcal{D}t} \Rightarrow \\ \mathbf{0} &= \int_{R_t} (\text{div} \mathbf{T} + \rho \mathbf{b} - \rho \dot{\mathbf{v}}) \, dv \end{aligned}$$

for any deformed volume (region) R_t , so the integrand must vanish identically:

$$\text{div } \mathbf{T} + \rho \mathbf{b} = \rho \dot{\mathbf{v}}.$$

- We can also frame the force balance relation in terms of the nominal stress tensor \mathbf{P} , the nominal traction vector $\mathbf{t}_0 = \mathbf{P}\mathbf{n}_0$, and a material divergence operator “Div” according to

$$\mathbf{f}_{(\text{surface-traction})} = \int_{\partial R_0} d\mathbf{f} = \int_{\partial R_0} \mathbf{t}_0 da_0 = \int_{\partial R_0} \mathbf{P}\mathbf{n}_0 da_0 = \int_{R_0} (\text{Div } \mathbf{P}) dv_0,$$

where

$$\begin{aligned} \text{Div } \mathbf{P} &= \left(\frac{\partial P_{11}}{\partial p_1} + \frac{\partial P_{12}}{\partial p_2} + \frac{\partial P_{13}}{\partial p_3} \right) \mathbf{e}_1 \\ &+ \left(\frac{\partial P_{21}}{\partial p_1} + \frac{\partial P_{22}}{\partial p_2} + \frac{\partial P_{23}}{\partial p_3} \right) \mathbf{e}_2 \\ &+ \left(\frac{\partial P_{31}}{\partial p_1} + \frac{\partial P_{32}}{\partial p_2} + \frac{\partial P_{33}}{\partial p_3} \right) \mathbf{e}_3 \end{aligned}$$

- Note that the spatial divergence operator, div , involved spatial differentiation with respect to the deformed coordinates x_i , while the reference divergence operator, Div involves corresponding derivatives with respect to reference Cartesian coordinates, p_j .
- Again, the arbitrariness of the reference region R_0 means that $\text{Div } \mathbf{P} = \mathbf{0}$ everywhere, in the absence of body force and acceleration. The body forces and accelerations can be “added” to the momentum balance, referential formulation, in a straightforward manner, resulting, when localized to an arbitrary reference volume element, in

$$\text{Div } \mathbf{P} + \rho_0 \mathbf{b}_0 = \rho_0 \dot{\mathbf{v}} = \rho_0 \ddot{\mathbf{x}}.$$

Balance of angular momentum

- Neglecting the possibility of distributed couples (moments; torques) in the limit of infinitesimal surface areas and volumes, the only source for a resultant moment about the origin (an arbitrary, but convenient point for summing moments), the total moment created by the surface tractions and body forces is

$$\mathbf{m}_0(t) = \int_{\partial R_t} \mathbf{x} \times \mathbf{t} \, da + \int_{R_t} \mathbf{x} \times \rho \mathbf{b} \, dv;$$

here the vector cross-product is indicated. Using the stress/traction relation and the divergence theorem, the surface integral contribution can be transformed into

$$\int_{\partial R_t} \mathbf{x} \times \mathbf{t} \, da = \int_{\partial R_t} \mathbf{x} \times (\mathbf{T}\mathbf{n}) \, da.$$

- Using Cartesian subscripts for convenience, this becomes

$$\begin{aligned} (\mathbf{m}_0(t))_i &= \int_{\partial R_t} \epsilon_{ijk} x_j (T_{km} n_m) \, da + \int_{R_t} \epsilon_{ijk} x_j (\rho b_k) \, dv \\ &= \int_{R_t} \epsilon_{ijk} [(x_j T_{km})_{,m} + x_j \rho b_k] \, dv \\ &= \int_{R_t} \epsilon_{ijk} [(x_j T_{km,m} + \delta_{jm} T_{km}) + x_j \rho b_k] \, dv \\ &= \int_{R_t} [\epsilon_{ijk} x_j (T_{km,m} + \rho b_k) + \epsilon_{ijk} T_{jk}] \, dv. \end{aligned}$$

- The angular momentum about the origin is defined by

$$\mathbf{h}_0(t) = \int_{R_t} \mathbf{x} \times \rho \mathbf{v} \, dv;$$

its time rate of change is

$$\frac{\mathcal{D}\mathbf{h}_0(t)}{\mathcal{D}t} = \frac{\mathcal{D}}{\mathcal{D}t} \int_{R_t} \mathbf{x} \times \rho \mathbf{v} \, dv = \frac{\mathcal{D}}{\mathcal{D}t} \int_{R_0} \mathbf{x} \times \rho_0 \mathbf{v} \, dv_0 = \frac{\mathcal{D}}{\mathcal{D}t} \int_{R_0} [\dot{\mathbf{x}} \times \rho_0 \mathbf{v} + \mathbf{x} \times \rho_0 \dot{\mathbf{v}}] \, dv_0.$$

However, since $\dot{\mathbf{x}} = \mathbf{v}$, the first vector cross product vanishes, and the remaining term can be brought back to an integral over the deformed configuration as

$$\frac{\mathcal{D}\mathbf{h}_0(t)}{\mathcal{D}t} = \int_{R_t} \mathbf{x} \times \rho \dot{\mathbf{v}} \, dv.$$

- The balance of angular momentum states that $\mathbf{m}_0(t) = \mathcal{D}\mathbf{h}_0(t)/\mathcal{D}t$, resulting, after re-arrangement, in

$$0_i = \int_{R_t} [\epsilon_{ijk} T_{jk} + \epsilon_{ijk} x_j (T_{km,m} + \rho b_k - \rho \dot{v}_k)] dv.$$

At this point, we recognize the vector in parentheses as the zero-valued form of the linear momentum balance equations, so only the term $\epsilon_{ijk} T_{jk}$ remains as an integrand in an integral over an arbitrary domain, which must, in any event, vanish; thus, it is necessary that

$$\epsilon_{ijk} T_{jk} = 0_i.$$

Since we are summing on repeated indices j and k , and since the alternating tensor is, by definition, antisymmetric with respect to permutation of any 2 indices, we conclude that the stress tensor must necessarily be symmetric: $T_{jk} = T_{kj}$, or else its possibly non-zero skew part would give a non-zero contribution when summed with ϵ_{ijk} . The upshot of all this is that $\mathbf{T} = \mathbf{T}^T$, Cauchy stress tensor is symmetric, on account of the balance of angular momentum.

- The stress tensor \mathbf{T} is symmetric: $\mathbf{T} = \mathbf{T}^T$ (angular momentum balance). Although neither \mathbf{F} or \mathbf{P} need be symmetric, the following condition must be satisfied:

$$\mathbf{P}\mathbf{F}^T = \mathbf{F}\mathbf{P}^T.$$

This result also follows from a consistent pull-back of the angular momentum balance equations to the (arbitrary) reference configuration, R_0 .

Balance of mass

- An element of mass dm is conserved during deformation. It can be expressed as the product of (reference) mass density per unit reference volume, ρ_0 , and reference elemental volume, dv_0 , and as the product of (deformed) mass density per unit deformed volume, ρ , and the deformed elemental volume, dV :

$$dm = \rho_0 dv_0 = \rho dV.$$

- Using the volume ratio $dV/dv_0 = \det \mathbf{F} = J$ along with conservation of mass gives

$$\rho = \rho_0 J^{-1}.$$

ÉCOLE DES MINES DE PARIS
ELEMENTS OF THE MECHANICS AND PHYSICS OF RUBBER
ELASTICITY
NOTES ON POLYMER NETWORK MODELS

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Polymer “chains”

- In cross-linked rubbers, the molecular kinetic freedom associated with ‘entropic’ elasticity is primarily confined to those portions of the macromolecular network between kinematic restraints such as chemical cross-links or mechanical entanglements. To a first approximation, the spatial locations of such end-points define an end-to-end **chain vector** $\mathbf{r} = \mathbf{r}_1 + \mathbf{r}_2 + \dots + \mathbf{r}_n$, where \mathbf{r}_ν is the position vector connecting the atoms defining the ν th **link** along the chain backbone.
- The chains are taken to have \sim fixed chain vectors in both a reference configuration of the solid (\mathbf{r}_0) and in a deformed configuration (\mathbf{r}), with respective end-to-end distances $r_0 = |\mathbf{r}_0|$ and $r = |\mathbf{r}|$.
- The high degree of molecular kinematic freedom within an isolated chain generally permits many possible sequences of segment-to-segment vectors \mathbf{r}_i which add vectorially to provide a given chain vector $\mathbf{r} = \sum \mathbf{r}_i$. The geometric uncertainty (or lack of complete information) associated with the multiplicity of chain configurations connecting to give a given chain vector \mathbf{r} constitutes (in the sense of Shannon, for example), a **configurational entropy** of the chain. As a chain of a fixed number of chain segments is stretched in length from r_0 to $r > r_0$, the number of possible connecting sequences, and hence the associated uncertainty, decreases.
- The configurational entropy of chain ν is denoted $g_c(\nu)$, the change in chain configurational entropy associated with the deformation-induced change in end-to-end chain vector is

$$\Delta g_c(\nu) = g_c(\mathbf{r}(\nu)) - g_c(\mathbf{r}_0(\nu)),$$

and the isothermal change in continuum thermomechanical entropy per unit reference volume, $\Delta\eta$, is represented by an appropriate sum/integral of the changes in chain configurational entropies:

$$\Delta\eta = \Delta g = \sum_{\nu} \Delta g_c(\nu).$$

- As was shown in the thermomechanical derivations for rubbers, the principal source of deformation-induced changes in Helmholtz free energy per unit reference volume,

$\psi = e - \theta\eta$, where e is internal energy per unit reference volume and θ is absolute temperature, is due to deformation-induced changes in the entropy. Thus, a central concept of network-based models of elastomeric solids is to reckon deformation-induced changes in the configurational entropies of the network's chains.

Idealizations of network modeling

- Real molecular networks have high three-dimensional spatial complexity, as well as complex temporal kinetics, so models of such networks must adopt many simplifying idealizations. Among the difficult issues to consider are network topology, bond length and bond-angle “energetic constraints”, and three-dimensional self-avoidance and density packing of the chains, and the enormous numbers of atomic constituents (of order 10^{23}) comprising a macroscopic macromolecular solid.
- Note that, *en principe*, many of these details can be accurately addressed through the use of modern computer-intensive molecular dynamics and/or molecular statics modeling of deformable networks, albeit perhaps at the cost of certain insights afforded by simpler models.
- Among the “traditional” idealizations of polymer networks, the **freely-jointed chain** model offers a good compromise of physical fidelity and tractable analytical insight. In this model, each chain segment link length is constrained to $r_i = |\mathbf{r}_i| = \ell$, while the (spherical) angle between adjacent links is taken to be a random variable having a uniform probability density.
- The probability of a chain of ν links resulting in end-to-end chain vector \mathbf{r} is denoted $p(\mathbf{r})$, and constitutes the basis for defining a chain entropy through the associated Boltzmann relation $g_c(\mathbf{r}(\nu)) = k_B \log(p(\mathbf{r}))$, where k_B is Boltzmann's constant.

ASIDE: Probability convolution integrals

- In one coordinate dimension, suppose that coordinate position $y = x_1 + x_2$ is the sum of two random variables, x_1 and x_2 , which have respective probability distributions $p_1(x_1)$ and $p_2(x_2)$ in the regions $-\infty \leq x_i \leq \infty$, with each probability distribution being properly normalized by

$$1 = \int_{-\infty}^{\infty} p_i(x_i) dx_i \quad (\text{no sum on index } i).$$

What is the cumulative probability distribution $p(y)$? Evidently, since $x_2 = y - x_1$, and, for fixed x_1 , $dy = dx_2$, the probability density satisfies

$$p(y) dy = \left(\int_{-\infty}^{\infty} p_1(x_1) p_2(y - x_1) dx_1 \right) dy$$

so that

$$p(y) = \int_{-\infty}^{\infty} p_1(x_1) p_2(y - x_1) dx_1$$

is a **convolution integral** of the respective probabilities.

- In the context of infinite-domain convolution integrals, recall the utility of the **Fourier transform** $P(\xi)$ of the probability function $p(y)$ defined by

$$P(\xi) \equiv \int_{-\infty}^{\infty} e^{-iy\xi} p(y) dy,$$

with **inverse Fourier transform**

$$p(y) \equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{+iy\xi} P(\xi) d\xi.$$

- We associate the probability transform functions P_i and p_i ; the convolution property of the Fourier transform provides in the present case the simple multiplicative relation

$$P(\xi) = P_1(\xi) P_2(\xi),$$

which can be generalized to n steps by

$$P(\xi) = \prod_{j=1}^n P_j(\xi).$$

- If each of the n probability functions P_j is identical to the first one, say, P_1 , then

$$P(\xi) = [P_1(\xi)]^n.$$

Return to the freely-jointed chain

- We can form the three-dimensional Fourier transform of the chain end-to-end vector probability function $p(\mathbf{r})$ by

$$P(\boldsymbol{\rho}) \equiv \int_{R_3} e^{-i\mathbf{r}\cdot\boldsymbol{\rho}} p(\mathbf{r}) d^3\mathbf{r},$$

along with the inverse Fourier transform relation

$$p(\mathbf{r}) \equiv \frac{1}{(2\pi)^3} \int_{R_3} e^{+i\mathbf{r}\cdot\boldsymbol{\rho}} P(\boldsymbol{\rho}) d^3\boldsymbol{\rho}.$$

- Let $\mathbf{r} = \sum_{j=1}^n \mathbf{r}_j$, where the probability distribution of each link vector \mathbf{r}_i is identical and can be expressed for any argument \mathbf{r} as $p_1(\mathbf{r})$, with corresponding Fourier transform $P_1(\boldsymbol{\rho})$. From the convolution relation, the transformed probability function for n links is simply $P(\boldsymbol{\rho}) = [P_1(\boldsymbol{\rho})]^n$, so that

$$p(\mathbf{r}) \equiv \frac{1}{(2\pi)^3} \int_{R_3} e^{+i\mathbf{r}\cdot\boldsymbol{\rho}} [P_1(\boldsymbol{\rho})]^n d^3\boldsymbol{\rho}.$$

- In the freely-jointed chain model, the probability function for a single link vector of length ℓ can be expressed as

$$p_1(\mathbf{r}) = \frac{1}{4\pi\ell^2} \delta(r - \ell); \quad r \equiv |\mathbf{r}|.$$

Physically, this requires the next atom position on the chain to be chosen at random from a location on a sphere of radius $r = |\mathbf{r}| = \ell$ centered at the prior atom of the chain, and the normalizing factor $4\pi\ell^2$ corresponds to the surface area of such a sphere.

- Using spherical coordinates, it is easy to demonstrate that this probability function is properly normalized:

$$\int_{R_3} p_1(\mathbf{r}) d^3\mathbf{r} = \frac{1}{4\pi\ell^2} \int_0^\pi \sin(\Theta) d\Theta \int_0^{2\pi} d\phi \int_0^\infty \delta(r - \ell) r^2 dr = 1.$$

- The Fourier transform $P_1(\boldsymbol{\rho})$ of $p_1(\mathbf{r})$ can likewise be constructed using a spherical coordinate system according to

$$\begin{aligned} P_1(\boldsymbol{\rho}) &= \frac{1}{4\pi\ell^2} \int_{R_3} e^{-i\mathbf{r}\cdot\boldsymbol{\rho}} \delta(|\mathbf{r}| - \ell) d^3\mathbf{r} \\ &= \frac{1}{4\pi\ell^2} \int_0^{2\pi} d\phi \int_0^\infty \delta(r - \ell) r^2 dr \int_0^\pi e^{-ir\rho\cos(\Theta)} \sin(\Theta) d\Theta \\ &= \frac{\sin \rho\ell}{\rho\ell}, \end{aligned}$$

where $\rho = |\boldsymbol{\rho}|$ and $\mathbf{r} \cdot \boldsymbol{\rho} = r\rho\cos(\Theta)$.

- From the convolution property, then,

$$P(\boldsymbol{\rho}) = [P_1(\boldsymbol{\rho})]^n = \left[\frac{\sin \rho\ell}{\rho\ell} \right]^n.$$

- Using the inverse Fourier transform, the probability function $p(\mathbf{r})$ can be evaluated as

$$\begin{aligned} p(\mathbf{r}) &= \frac{1}{(2\pi)^3} \int_{R_3} e^{+i\mathbf{r}\cdot\boldsymbol{\rho}} \left(\frac{\sin \rho\ell}{\rho\ell} \right)^n d^3\boldsymbol{\rho} \\ &= \frac{1}{2\pi^2 r} \int_0^\infty \sin(\rho r) \left[\frac{\sin \rho\ell}{\rho\ell} \right]^n \rho d\rho \\ &= \hat{p}(r = |\mathbf{r}|). \end{aligned}$$

Thus, the probability function $p(\mathbf{r})$ for the freely-jointed chain model depends only on $r = |\mathbf{r}|$, the end-to-end length of the n -link chain. This last result was attributed in the Wiener text as being originally due to Rayleigh. Wiener gives closed-form expressions

for the result for small integers $n = 2, 3, 4, \dots$ using trigonometric identities for n -th powers of the sine function; for large values of n , these results become problematically tedious (but can Mathematica help here?) so other methods and approximations have been adopted for evaluation.

- Weiner offers the formal evaluation of $p(\mathbf{r})$ in the limit $n \rightarrow \infty$ based on the change of variables $\rho = y\ell n^{-1/2}$; $\rho\ell = yn^{-1/2}$; leading to

$$p(\mathbf{r}) = \frac{1}{2\pi^2 r n \ell^2} \int_0^\infty \sin(yr\ell n^{-1/2}) \left[\frac{\sin(yn^{-1/2})}{yn^{-1/2}} \right]^n y dy,$$

and noting that

$$\left[\frac{\sin(yn^{-1/2})}{yn^{-1/2}} \right]^n = \left[1 - \frac{y^2}{3!n} (1 + O(1)) \right]^n \sim e^{-y^2/6},$$

the stage is set for obtaining a Gaussian probability distribution function from the model in the limit $n \rightarrow \infty$:

$$p(r) \rightarrow \left(\frac{3}{2\pi n \ell^2} \right)^{3/2} \exp \left(\frac{-3r^2}{2n\ell^2} \right).$$

- The **expectation value** for the square of the end-to-end chain length, denoted $\langle r^2 \rangle$, is defined by

$$\langle r^2 \rangle \equiv \int_{R_3} r^2 p(\mathbf{r}) d^3 \mathbf{r} \rightarrow 4\pi \int_0^\infty r^4 p(r) dr,$$

where the last representation follows from the functional dependence $p(\mathbf{r}) = \hat{p}(r)$. For the Gaussian probability distribution, $\langle r^2 \rangle = n\ell^2$, so the Gaussian probability distribution can also be written as

$$p(r) = \left(\frac{3}{2\pi \langle r^2 \rangle} \right)^{3/2} \exp \left(\frac{-3r^2}{2 \langle r^2 \rangle} \right).$$

- In the Gaussian limit, the configurational chain entropy of chain ν , containing n_ν links, can be expressed as

$$\begin{aligned} g_c(\mathbf{r}(\nu)) &\equiv k_B \log(p(\mathbf{r}(\nu))) \\ &\rightarrow k_B \log \left[\left(\frac{3}{2\pi n \ell^2} \right)^{3/2} \exp \left(\frac{-3r(\nu)^2}{2n\ell^2} \right) \right] \\ &= \frac{3k_B}{2} \log \left(\frac{3}{2\pi n_\nu \ell^2} \right) - \frac{3k_B r(\nu)^2}{2n_\nu \ell^2} \\ &= \text{constant} - \frac{3k_B r(\nu)^2}{2n_\nu \ell^2}. \end{aligned}$$

Clearly, the constant is inessential to the definition of the deformation-induced changes in chain entropy, and may be neglected.

- Thus, if the reference length of the chain is $r_0(\nu) = |\mathbf{r}_0(\nu)|$, while the deformed chain length is $r(\nu) = |\mathbf{r}(\nu)|$, the change in chain entropy, in the Gaussian limit, is

$$\Delta g_c(\nu) = \frac{-3k_B}{2n_\nu \ell^2} (r(\nu)^2 - r_0(\nu)^2).$$

Connecting continuum deformation to changes in chain configurational entropy: the Gaussian limit

- The traditional routes to obtaining the deformation-induced changes in chain configurational entropy rely on an assumption of (continuum-scale) **affine motion** of the junctions defining the chain ends. That is, if the continuum deformation gradient is \mathbf{F} , it is assumed that the microscopic-scale chain vectors in the reference and deformed configurations are connected by

$$\mathbf{r}(\nu) = \mathbf{F}\mathbf{r}_0(\nu),$$

so that

$$r(\nu)^2 - r_0(\nu)^2 = \mathbf{r}_0(\nu) \cdot 2\mathbf{E}\mathbf{r}_0(\nu) = \mathbf{r}_0(\nu) \cdot (\mathbf{C} - \mathbf{1})\mathbf{r}_0(\nu),$$

where $\mathbf{E} = 1/2(\mathbf{C} - \mathbf{1}) = 1/2(\mathbf{F}^T\mathbf{F} - \mathbf{1})$ is the Green-Lagrange strain tensor.

- The total change in configurational entropy of a unit reference volume containing N chains is then

$$\begin{aligned} \Delta\eta(\mathbf{E}) &= \sum_{\nu=1}^N \Delta g_c(\nu) \\ &= -\frac{3k_B}{2\ell^2} (2\mathbf{E}) \cdot \left(\sum_{\nu=1}^N \frac{1}{n_\nu} \mathbf{r}_0(\nu) \otimes \mathbf{r}_0(\nu) \right) \\ &= -k_B \mathbf{E} \cdot \mathbf{M}, \end{aligned}$$

where the structure tensor

$$\mathbf{M} \equiv \frac{3}{\ell^2} \sum_{\nu=1}^N \frac{1}{n_\nu} \mathbf{r}_0(\nu) \otimes \mathbf{r}_0(\nu)$$

is a property of the undeformed network.

- If the undeformed network is macroscopically homogeneous and isotropic, we conclude that \mathbf{M} must be a multiple of the identity tensor:

$$\mathbf{M} = M \mathbf{1},$$

where

$$M = \frac{1}{3} \text{tr}\mathbf{M} = \frac{1}{\ell^2} \sum_{\nu=1}^N \frac{1}{n_\nu} \mathbf{r}_0(\nu) \cdot \mathbf{r}_0(\nu) = \frac{1}{\ell^2} \sum_{\nu=1}^N \frac{1}{n_\nu} r_0(\nu)^2.$$

- The value of M can be conceptually evaluated by considering the chains to have been formed by “instantaneous” cross-linking at a moment when the non-cross-linked network was in a statistically-representative configuration, resulting in a distribution of m groups of chains, each containing c_α chains of n_α links, where $\alpha = 1, \dots, m$, and having end-to-end distance $r_0(q, \alpha)$, $q = 1, \dots, c_\alpha$: in this case

$$N = \sum_{\alpha=1}^m c_\alpha \quad \text{and}$$

$$M = \frac{1}{\ell^2} \sum_{\alpha=1}^m n_\alpha^{-1} \sum_{q=1}^{c_\alpha} r_0^2(q, \alpha)^2.$$

The values of $r_0(q, \alpha)^2$ would be drawn from a Gaussian distribution having variance $n_\alpha \ell^2$, suggesting

$$\sum_{q=1}^{c_\alpha} r_0^2(q, \alpha)^2 = c_\alpha n_\alpha \ell^2,$$

resulting in $M = N$. In this Gaussian limit, then, the change in configurational entropy becomes

$$\Delta\eta = \Delta g = -k_B M \mathbf{E} \cdot \mathbf{1} = -k_B N \text{tr} \mathbf{E} = -\frac{Nk_B}{2} \text{tr}(\mathbf{C} - \mathbf{1}) = -\frac{Nk_B}{2} (I_{1\mathbf{C}} - 3).$$

An alternative connection of continuum deformation to changes in chain configurational entropy

- Anand suggested an alternative approach to obtain the deformation-induced change in a Gaussian network’s configurational entropy. As a starting point, consider the expression

$$\begin{aligned} \Delta g_c(\nu) &\equiv g_c(\mathbf{r}(\nu)) - g_c(\mathbf{r}_0(\nu)) \\ &= \frac{-3k_B}{2n_\nu \ell^2} [r(\nu)^2 - r_0(\nu)^2] \\ &= \frac{-3k_B r_0(\nu)^2}{2n_\nu \ell^2} \left[\frac{r(\nu)^2}{r_0(\nu)^2} - 1 \right] \\ &\equiv \frac{-3k_B r_0(\nu)^2}{2n_\nu \ell^2} [\lambda_c(\nu)^2 - 1], \end{aligned}$$

where the stretch of the chain is introduced as $\lambda_c(\nu)$.

- We have noted above that in the Gaussian regime $\langle r_0(\nu)^2 \rangle = n\ell^2$, which equivalently and effectively defines the average chain link number n , and if we further assume that,

in the chain entropy change expression, a. $r_0(\nu)^2$ can be replaced with $\langle r_0(\nu)^2 \rangle = n\ell^2$, and b. we can replace n_ν with n for each chain, then

$$\Delta g_c(\nu) = \frac{-3k_B}{2} [\lambda_c(\nu)^2 - 1] = \frac{-3k_B}{2} \lambda_c(\nu)^2 + \text{constant},$$

where the resulting constant is independent of deformation.

- Finally, Anand suggests that the junctions defining the chain ends can be assumed to deform in such a manner that the local chain stretch, $\lambda_c(\nu)$, and be taken as equal to the macroscopically-defined constant $\bar{\lambda}$, where

$$\bar{\lambda} \equiv \sqrt{\frac{I_{1\mathbf{C}}}{3}} = \sqrt{\frac{\text{tr } \mathbf{C}}{3}} = \sqrt{\frac{\lambda_1^2 + \lambda_2^2 + \lambda_3^2}{3}}$$

becomes an “effective stretch” measure for the network. It is straightforward then to see that a total chain entropy change can be represented, apart from a constant independent of the deformation, by

$$\Delta g = N\Delta g_c(\nu) \rightarrow N \times \left(\frac{-3k_B\bar{\lambda}^2}{2} \right) = -\frac{Nk_B}{2} \text{tr } \mathbf{C}.$$

Clearly, this final result is equivalent to that derived above, albeit based on a slightly different set of assumptions.

Back to the continuum: Gaussian chain statistics lead to the “Neo-hookean” constitutive model.

- The idealized continuum thermomechanics modeling of rubber elasticity was based on a Helmholtz free energy per unit reference volume given by $\psi = e - \theta\eta$, where e is internal energy per unit reference volume, θ is absolute temperature, and η is the entropy per unit reference volume.
- Using the energy balance equation and the entropy inequality, we were led to the constitutive relations

$$\frac{\partial \psi}{\partial \mathbf{E}} = \mathbf{S}; \quad \frac{\partial \psi}{\partial \theta} = -\eta,$$

where \mathbf{S} , the second Piola-Kirchhoff stress tensor, is work-conjugate (per unit reference volume) to the Green-Lagrange strain \mathbf{E} . Note that other work-conjugate stress and strain pairs could also be adopted (e.g.; $\mathbf{P} = \partial\psi/\partial\mathbf{F}$), as well as noting the factor of 2 appearing in chain-rule derivatives with respect to \mathbf{C} :

$$\frac{\partial \psi}{\partial \mathbf{C}} = \frac{\partial \psi}{\partial \mathbf{E}} \cdot \frac{\partial \mathbf{E}}{\partial \mathbf{C}} = \frac{1}{2} \mathbf{S}.$$

- In (incompressible) elastomers, to a first approximation, the internal energy is mainly a function of temperature only: $e = \hat{e}(\theta)$. Defining the specific heat at constant deformation as

$$c(\theta) \equiv \frac{\partial e(\theta)}{\partial \theta} = \frac{\partial \psi}{\partial \theta} + \eta + \theta \frac{\partial \eta}{\partial \theta} = \theta \frac{\partial \eta}{\partial \theta},$$

since the first 2 terms on the right-hand side of the equation cancel via the adopted constitutive definition of η .

- Re-arranging this special form of the constitutive relationship provides a differential equation for the entropy:

$$\frac{\partial \eta(\theta; \mathbf{E})}{\partial \theta} = \frac{c(\theta)}{\theta},$$

whose solution can be expressed in the separable form

$$\eta(\theta; \mathbf{E}) = f(\theta) + g(\mathbf{E}),$$

where the temperature-dependent function f satisfies the differential equation

$$\frac{df(\theta)}{d\theta} = \frac{c(\theta)}{\theta},$$

and the “geometric” contribution to the entropy, $g(\mathbf{E})$, depends on the deformation from the reference configuration as measured by the strain \mathbf{E} . By introducing a reference temperature θ_0 , and a reference values of $e(\theta_0)$ and $f(\theta_0)$, the general forms for the special case of *constant* c become

$$e(\theta) = e(\theta_0) + c(\theta - \theta_0);$$

$$f(\theta) = f(\theta_0) + c \log(\theta/\theta_0).$$

- Under these circumstances, the free energy becomes

$$\begin{aligned} \psi(\theta, \mathbf{E}) &= e(\theta) - \theta \eta(\theta, \mathbf{E}) \\ &= [e(\theta_0) + c(\theta - \theta_0)] - \theta [f(\theta_0) + c \log(\theta/\theta_0) + g(\mathbf{E})], \end{aligned}$$

leading to the constitutive relationship for the stress as

$$\mathbf{S}(\theta, \mathbf{E}) = \frac{\partial \psi(\theta, \mathbf{E})}{\partial \mathbf{E}} = -\theta \frac{\partial g(\mathbf{E})}{\partial \mathbf{E}}.$$

- Recall that the relationship which was used to derive the relationship $\mathbf{S} = \partial \psi / \partial \mathbf{E}$ was based on identically satisfying the (isothermal) power relationship

$$\left(\mathbf{S} - \frac{\partial \psi}{\partial \mathbf{E}} \right) \cdot \dot{\mathbf{E}} = 0$$

for “arbitrary” values of the strain-rate, $\dot{\mathbf{E}}$. However, in the case of a kinematic constraint on deformation, such as, for example, incompressibility, we know that $h(\mathbf{C}) = \det\mathbf{C} - 1 = 0$ for all admissible deformations, so that the time rate of change of this constraint is also workless:

$$0 = \frac{\partial h(\mathbf{C})}{\partial \mathbf{C}} \cdot \dot{\mathbf{C}} = \frac{\partial(\det\mathbf{C})}{\partial \mathbf{C}} \cdot \dot{\mathbf{C}} = (\det\mathbf{C})\mathbf{C}^{-T} \cdot \dot{\mathbf{C}} = 2\mathbf{C}^{-1} \cdot \dot{\mathbf{E}},$$

on using the value of the incompressibility constraint and the symmetry of \mathbf{C} (and its inverse). We can see, then, that any **reaction stress** component given by

$$\mathbf{S}_R = \lambda^* \mathbf{C}^{-1}$$

can be added to \mathbf{S} without changing the power balance since $\mathbf{S}_R \cdot \dot{\mathbf{E}} = 0$. Thus, in the presence of the incompressibility constraint, we define the stress measure \mathbf{S} by

$$\mathbf{S} = \frac{\partial \psi}{\partial \mathbf{E}} + \mathbf{S}_R = \frac{\partial \psi}{\partial \mathbf{E}} + \lambda^* \mathbf{C}^{-1},$$

with the understanding that the Lagrange multiplier field “ λ^* ” scaling the reaction stress constraint must, in general, be determined from equilibrium considerations.

- The so-called neo-Hookean constitutive model emerges by using the Gaussian network model for entropy (see above) with $g = -Nk_B \text{tr}\mathbf{E}$, resulting in

$$\mathbf{S}(\theta, \mathbf{E}) = \mathbf{S}_R - \theta \frac{\partial g(\mathbf{E})}{\partial \mathbf{E}} = \mathbf{S}_R + Nk_B \theta \frac{\partial \text{tr}\mathbf{E}}{\partial \mathbf{E}} = \lambda^* \mathbf{C}^{-1} + Nk_B \theta \mathbf{1}.$$

- The Cauchy, or “true” stress \mathbf{T} is related to \mathbf{S} by $J\mathbf{T} = \mathbf{F}\mathbf{S}\mathbf{F}^T$, where $J = \det\mathbf{F}$. On inserting the incompressible neo-Hookean expression for $\mathbf{S}(\theta, \mathbf{E})$ into this relationship, the final constitutive form emerges:

$$J\mathbf{T} = \mathbf{F} (\lambda^* \mathbf{C}^{-1} + Nk_B \theta \mathbf{1}) \mathbf{F}^T = \lambda^* \mathbf{F}\mathbf{C}^{-1}\mathbf{F}^T + Nk_B \theta \mathbf{F}\mathbf{F}^T = \lambda^* \mathbf{1} + Nk_B \theta \mathbf{B},$$

where $\mathbf{B} = \mathbf{V}^2$ is the **left Cauchy-Green tensor**. Letting the Lagrange multiplier be re-defined as $\lambda^* \equiv -p^*$ readily identifies its physical significance as being an arbitrary hydrostatic pressure.

Finite chain length effects: non-Gaussian chains

- The maximum possible end-to-end length for a chain of n rigid links is $r_{\max} = n\ell$, which occurs only when each link element is co-axially aligned. In this case there can be no uncertainty about the position of the chain links, so the entropy of the chain in this case must be at its minimum value. However, the Gaussian probability of finding a chain having end-to-end length $r > r_{\max}$, although exponentially small, is nonetheless non-zero. Clearly the use of Gaussian probability functions in entropy calculations for sufficiently large values of the ratio $r/r_{\max} \leq 1$ is not accurate; in practice, the associated errors are expected to grow rapidly for $r/r_{\max} \geq 0.5$.

- Alternatively, this range of chain lengths can be phrased in terms of chain stretch $\lambda_c(\nu) \sim r(\nu)/\langle r_0(\nu)^2 \rangle^{1/2} = r(\nu)/\sqrt{n\ell^2}$ by introducing a **locking stretch** measure λ_L defined by

$$\lambda_L \equiv \frac{r_{\max}}{\sqrt{n\ell^2}} = \frac{n\ell}{\sqrt{n\ell^2}} = \sqrt{n}.$$

- Returning to the Rayleigh integral definition of the probability function $p(\mathbf{r})$,

$$p(\mathbf{r}) = \frac{1}{2\pi^2 r} \int_0^\infty \sin(\rho r) \left[\frac{\sin \rho \ell}{\rho \ell} \right]^n \rho d\rho,$$

Kuhn and Grun showed that an approximate evaluation of the probability function for “large” values of $r/n\ell$, with n large but finite, is

$$p(\mathbf{r}) \doteq \frac{A^*}{\ell^3} \left[\frac{\sinh x}{x} \right]^n \exp\left(-\frac{xr}{\ell}\right),$$

where A^* is a normalizing constant and the **Langevin function** $\mathcal{L}(x) \equiv \cosh(x) - 1/x = r/(n\ell)$ implicitly defines the parameter x appearing in the expression through the **inverse Langevin function** $x = \hat{x}(r/(n\ell)) = \mathcal{L}^{-1}(r/(n\ell))$.

- Using the Kuhn and Grun approximation and introducing $r = \lambda_c(\nu) \times (\sqrt{n}\ell)$, the argument $r/(n\ell) = \lambda_c(\nu)/\sqrt{n} = \lambda_c(\nu)/\lambda_L$, and the change in chain entropy becomes (again, neglecting an inessential constant not depending on deformation)

$$\begin{aligned} \Delta g_c(\nu) &= k_B \log(p(\mathbf{r})) \\ &\rightarrow -k_B \lambda_L^2 \left[\frac{\lambda_c(\nu)}{\lambda_L} x + \log\left(\frac{x}{\sinh x}\right) \right]. \end{aligned}$$

- The model can again be completed by assuming that $\lambda_c(\nu) = \bar{\lambda} = \sqrt{\text{tr}\mathbf{C}/3}$ for each of the N chains per unit reference volume.
- Following the same series of steps as previously in the Gaussian case, we arrive at an expression for the Cauchy stress that is identical to that given originally by Arruda and Boyce:

$$\mathbf{T} = \mathbf{T}_{\text{A-B}} = \frac{Nk_B\theta}{3} \frac{\sqrt{n}}{\bar{\lambda}} \mathcal{L}^{-1}\left(\frac{\bar{\lambda}}{\sqrt{n}}\right) \mathbf{B} - p^* \mathbf{1}.$$

- It is interesting to note that the inverse Langevin function can be very accurately approximated over its entire domain by the simple Padé approximant

$$\mathcal{L}^{-1}(\xi) \doteq \frac{3\xi}{(1-\xi)}.$$

On using this substitution, the structure of the Arruda-Boyce model becomes clear:

$$\mathbf{T} = \mathbf{T}_{\text{A-B}} \doteq \frac{Nk_B\theta}{[1 - \bar{\lambda}/\sqrt{n}]} \mathbf{B} - p^* \mathbf{1}.$$

At small imposed deformations, when $\bar{\lambda} \ll \sqrt{n}$, the Arruda-Boyce model merges smoothly with the neo-Hookean (Gaussian chain statistics) model derived earlier, while the stress-scaling factor is amplified strongly as $\bar{\lambda}/\sqrt{n}$ grows toward the limiting value 1.

- The simple structure of the Arruda-Boyce model offers many practical advantages in usage, including the fact that only 2 “material constants”, N and n , need be fit to experimental data, the 2 constants are ‘orthogonal’ in the sense that only N governs behavior at small deformation, so that n can be subsequently determined from behavior at large deformations where $\bar{\lambda} \rightarrow \lambda_L = \sqrt{n}$, and the fact that the material stress Jacobian ($\partial \mathbf{T}/\partial \mathbf{E}$, for example) is guaranteed to be positive definite (give or take a small, but finite compressibility), facilitating relatively stable Newton-based iterative procedures in nonlinear finite element analysis.
- Another simple, robust, and easy-to-use 2-constant functional form has been proposed by Gent to address phenomenologically the problems of non-Gaussian chain behavior at large deformations. Gent introduces a “strain energy potential” (in essence, an isothermal Helmholtz free energy function) U_{Gent} according to

$$U_{\text{Gent}} = -\frac{E}{6} \left[1 - \frac{(I_{1\mathbf{C}} - 3)}{J_M} \right],$$

from which Cauchy stress is derived via the now-familiar steps to arrive at

$$\mathbf{T} = \mathbf{T}_{\text{Gent}} = \frac{E}{3} \frac{1}{\left[1 - \frac{(I_{1\mathbf{C}} - 3)}{J_m} \right]} \mathbf{B} - p^* \mathbf{1}.$$

In the incompressible limit, the small-strain tensile (Young’s) modulus E is related to the shear modulus μ by $E = 3\mu$, again bringing the formulation back to the neo-Hookean limit in which $\mu = Nk_B\theta$. Both the Gent and Arruda-Boyce models asymptotically approach the neo-Hookean model at small deformations, and both incorporate a limiting value of the network stretch, reflected in respective limiting values of $I_{1\mathbf{C}}$, although the differing functional forms adopted exhibit modestly different behavior as the limiting network deformation is approached.

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Micromechanical Aspects of Deformation-Induced Crystallization in Elastomers

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Outline

- **Background overview of elastomers**
 - Macromolecular structures and deformation mechanisms
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 - Shape memory metals (e.g., NiTi)
 - TRIP effect in austenitic steels
- **Aspects of continuum modeling**
- **Prospects for further study**



Background overview of elastomers

Macromolecular Notions of Rubber Elasticity

Entropic evidence (pre-thermodynamics)

Gough 1805; Joule 1855

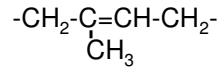
Cross linking (Goodyear, 1839)

Long chain molecular structure: 1900s

Molecular kinetic theory: Meyer, et al., 1930s

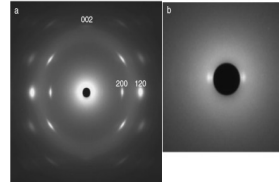
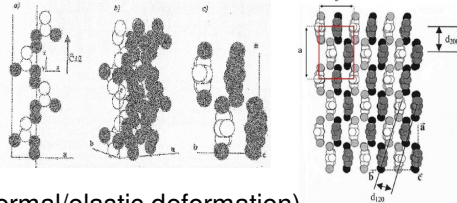
Crystallization in Polyisoprene

isoprene



crystallization issues:

- ~orthorhombic: a/b/c
~ 1.25/0.89/0.81 nm (plus thermal/elastic deformation)
- prominent WAXS peaks: d_{200} , d_{120} , and d_{002}
- Scherrer equation/ peak broadening as estimate of crystallite size
 $\rho_{\text{crystal}}/\rho_{\text{amorphous}} \sim 1.1$
chain-folded; chain-extended;
mechanical properties, etc. etc.



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Chambres d'Hôtes Historiques



Girolles (Bourgogne)



Britannica Online:

"The Frenchman **Georges Bouchardat**, with the aid of hydrogen chloride gas and prolonged distillation, converted isoprene to a rubberlike substance in 1875..."

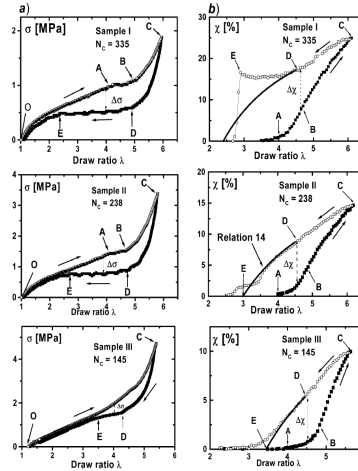
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Mechanical Hysteresis and Strain-Induced Crystallization/Melting in Vulcanized NR

Trabelsi, et al., *Macromol.* (2003)

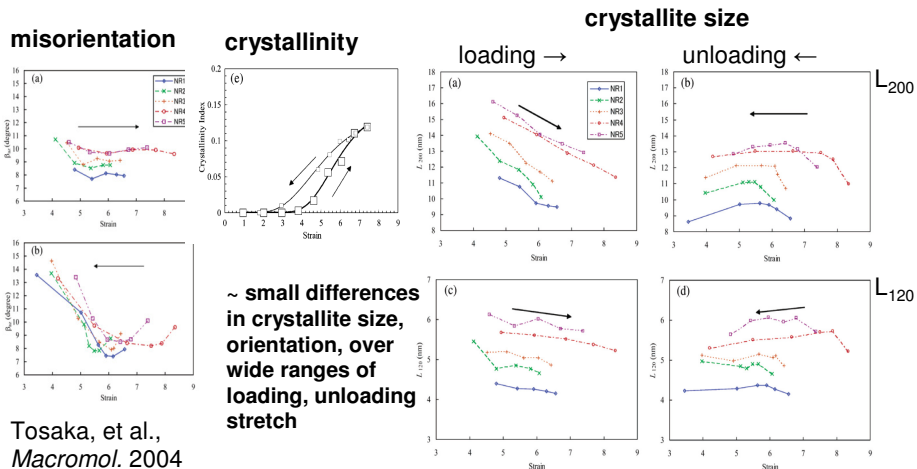
• Simultaneous force and WAXS measurements in cyclic loading show hysteresis at large stretch dominated by supercooling of crystallization with respect to melting

see also, Toki, et al.:
Macromol. (2002);
Polymer (2003)



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Evolution of Crystallite Size and Orientation

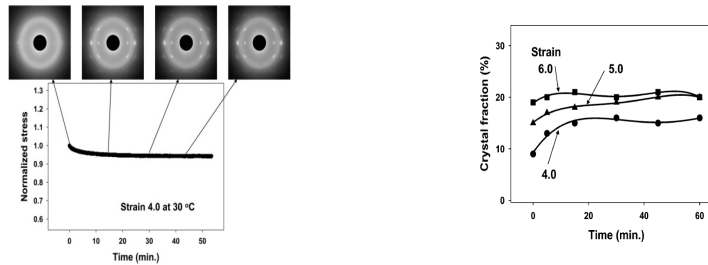


Tosaka, et al.,
Macromol. 2004

 Massachusetts Institute of Technology

Stress Relaxation and Crystallization

Toki, *et al.*,
Macromolecules, Vol. 38, No. 16, 2005

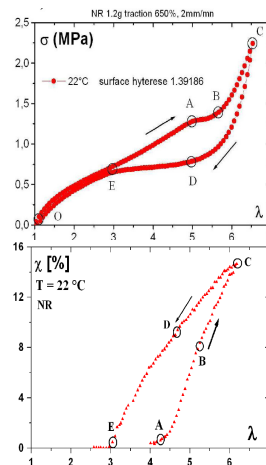


 Massachusetts Institute of Technology

Recent Documentation: Marchal Thèse

Jeanne MARCHAL
 Thèse, U. Paris XI Orsay
 (2006)

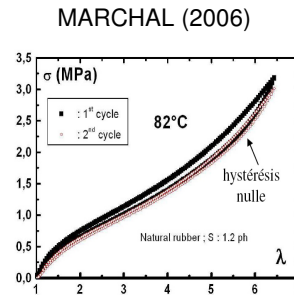
“Cristallization des caoutchoucs chargés et non chargés sous contrainte: Effet sur les chaînes amorphes”



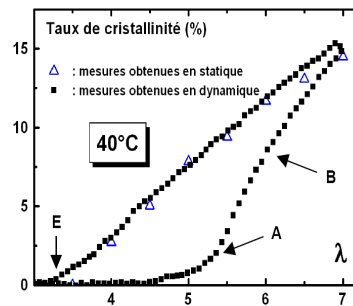
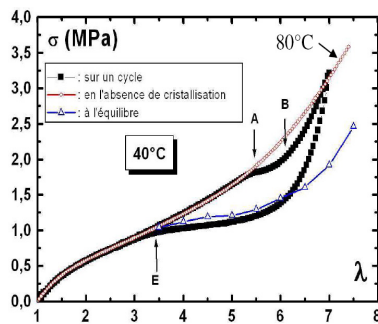
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Elevated Temperatures: No Crystallinity Means ~ No Hysteresis

With no observed crystallization for $\lambda < 6.5$ at 82°C, the hysteresis (2nd cycle) becomes ~negligible in a cross-linked NR (1.2 g S pph)



Unloading curve approaches equilibrium crystallinity

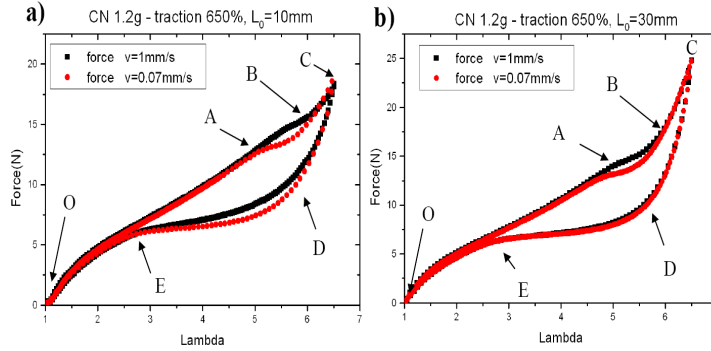


MARCHAL (2006)

Modest rate effects (23C) (especially, unloading)

$$d\lambda/dt=v/L_0=0.007; 0.1/s$$

$$d\lambda/dt=v/L_0=0.0023; 0.033/s$$

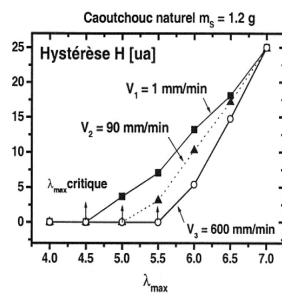


MARCHAL (2006)



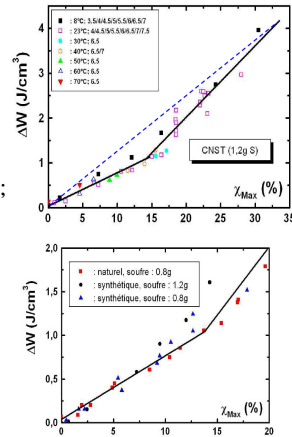
Hysteresis and Induced Crystallinity

S. TRABELSI
Thèse, U. Paris XI
(2002)



Specific dissipation
on loading:
 $d(\text{dissipation}) = f d\chi$
on unloading: $f \sim 0$

MARCHAL (2006)



Hysteresis and Birefringence: Plus ça change...

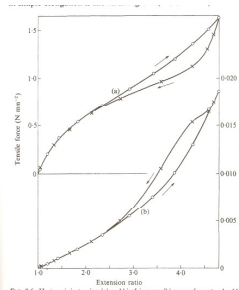
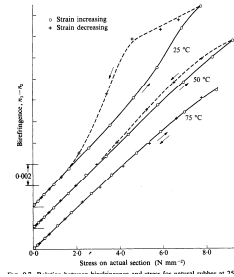


FIG. 5.6. Hysteresis in tension (a) and birefringence (b) curves for natural rubber.



L. R. G. Treloar (1975):

“It is inferred that these hysteresis loops are the result of crystallization, the crystallites themselves being oriented in the direction of the extension and therefore making a specific contribution to the birefringence which is additional to that due to the amorphous network. This supposition is confirmed by experiments at higher temperatures...”

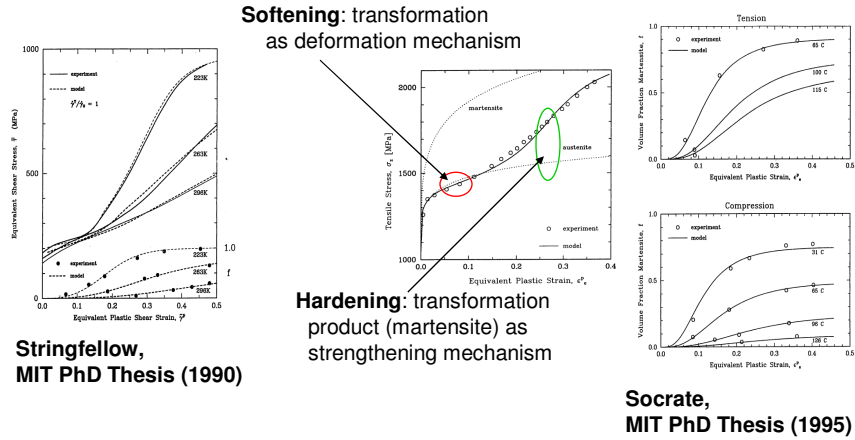
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Analogous Phenomena in Crystalline Materials

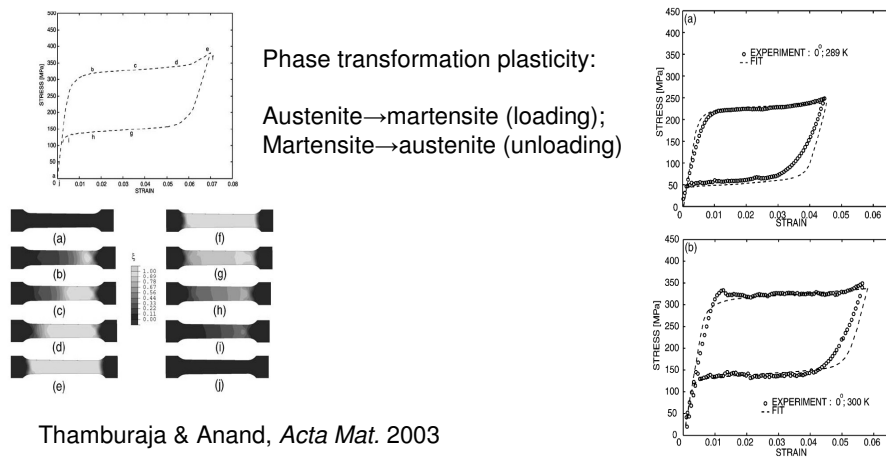
- a. TRIP effect in austenitic steels
- b. Shape-memory metals (e.g., NiTi)

 Massachusetts Institute of Technology

Strain-Induced Transformation Plasticity In Austenitic Steels



Superelasticity of Textured NiTi Sheet



Aspects of continuum modeling

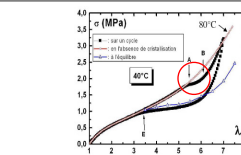
A Micromechanically-Based Framework for Continuum Modeling

•Macro response dominated by entropic elasticity of an amorphous cross-linked macromolecular network
 $\psi(\Lambda; n, N; x) = e^{-\eta\theta}$

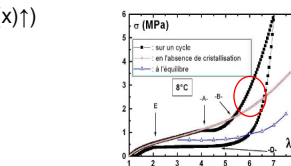
•Crystallization, x , modifies the response of the amorphous network in two opposite ways:

- softening**: local entropy (or chain stretch) is increased by crystallization; opposite for melting
- hardening**: crystallites impose new constraints on the kinetic freedoms permitted by the chains
 - shortened amorphous chain lengths ($n(x) \downarrow$)
 - captured chains increased local chain density ($N(x) \uparrow$)

- Evolution equations: crystallization (dissipative); melting (~ equilibrium)
- General thermodynamic loading conditions
- Tensorial generalization to other deformation modes



Flory model
 $\lambda_a < \lambda$
 $n_a = n_0 - n_c$



Assumed Helmholtz free energy/reference volume

$$\Psi = x \Psi_x(\theta) + (1-\beta x) \Psi_{\text{Lang}}(\theta, \lambda_e; N_0, n_0) + (\beta x) \Psi_{\text{Lang}}(\theta, \lambda_m; N_x, n_x)$$

Effective stretch: $3(\lambda_e)^2 = \text{tr}(\mathbf{C}) = \lambda^2 + 2/\lambda$ (tension)

Crystalline mass fraction: x (~ crystalline volume fraction)

Crystallinity-affected volume fraction of amorphous zone: $(\beta-1)x$

Crystallinity-affected (reduced) effective stretch: $\lambda_m = \lambda_e(\lambda_e; x) \leq \lambda_e$

Langevin-based Helmholtz free energy: Ψ_{Lang}
(Arruda-Boyce "8-chain" model;)

N = chain density /volume

$n = (\lambda_L)^2$: number of links/chain;

λ_L = "locking stretch"

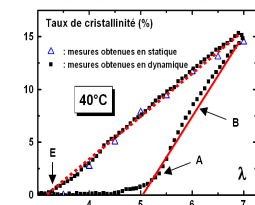
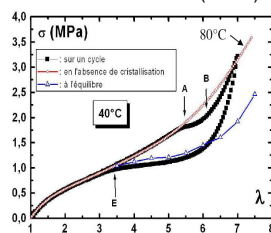
Stretch-stretch: $S = \partial \Psi(\lambda; x; \theta) / \partial \lambda$

Internal variable trajectory: $x = x(\lambda; \eta)$ (should derive from $\partial \Psi(\lambda; x; \theta) / \partial x$)

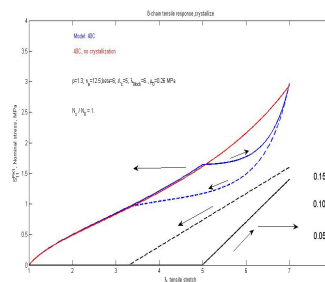


Initial Modeling Steps

MARCHAL (2006)

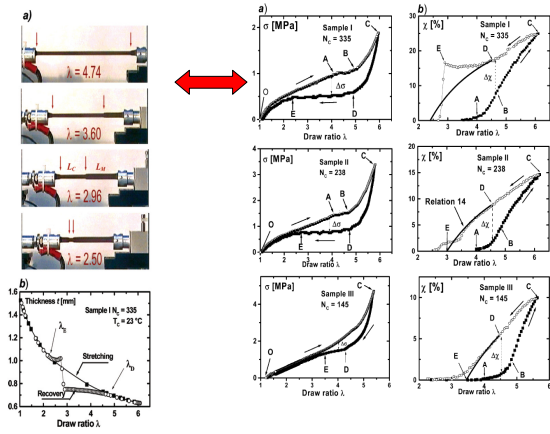


A Recent 1-D Model (40C)



“Inverse Yielding” on de-stretching

Microplasticity **2014**, 2(1), 1051-1070
 “Crystal Orientation and Yielding” Processes by Uniaxial Stretched Nitinol
 Chakrabarti
 N. Bhattacharya, P. Li, S. Li, and J. Wang
 Laboratory of Crystal Orientation (LCO), MIT, 770A, Cambridge, MA 02139, USA
 2014, © MIT, Cambridge, MA
 2014, April 14, 2017



MIT Massachusetts Institute of Technology

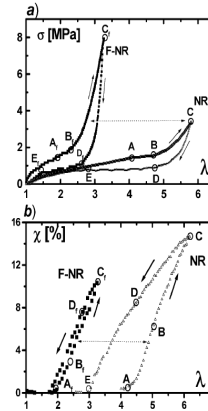
Prospects for further study

MIT Massachusetts Institute of Technology

Crystallization in Filled NRs

Trabelsi, et al., *Macromol.*, 2003

- Strain concentration in filled matrix accentuates strain-induced crystallization in matrix:
 - crystallization at smaller stretch
 - enhanced nucleation at interfaces?
- Filler-reduced chain mobility limits achievable crystallinity
- Elevated hysteresis: elevated dissipative 'driving forces' for crystallization?



 Massachusetts Institute of Technology

Crystallization in Nanoclay-NR

Carretero-Gonzalez, et al., *Macromol.*, 2008

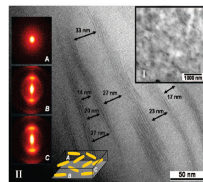
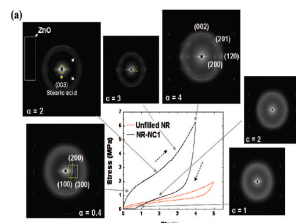
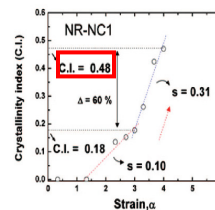
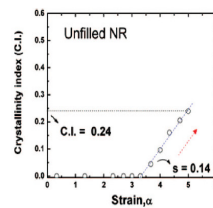


Figure 1. Representative TEM images (I; scale bar 1000 nm; II: scale bar 50 nm) and SAEX patterns (A: face-on view; B and C: edge-on views) of the NR-NC1 nanocomposite.



huge induced crystallinity!



 Massachusetts Institute of Technology

Photoactuation of CNT-based elastomeric nanocomposites

École des Mines de Paris
Centre des Matériaux
December 4, 2008

PHYSICAL REVIEW B 73, 085420 (2006)

Infrared actuation in aligned polymer-nanotube composites

S. V. Ahir, A. M. Squires, A. R. Tajalilolahi, and E. M. Terentjev
Cavendish Laboratory, University of Cambridge, J. J. Thomson Avenue, Cambridge CB3 0HE, United Kingdom
(Received 4 October 2005; revised manuscript received 20 December 2005; published 24 February 2006)

Rubber composites containing multifunctional carbon nanotubes have been irradiated with near-infrared light to study their reversible photo-mechanical actuation response. We demonstrate that the actuation is reproducible across differing polymer systems. The response is directly related to the degree of uniaxial alignment of the nanotubes in the matrix, contracting the samples along the alignment axis. The actuation stroke depends on the specific polymer being tested; however, the general response is universal for all composites tested. We conduct a detailed study of tube alignment induced by stress and propose a model for the reversible actuation behavior based on the orientational averaging of the local response. The single phenomenological parameter of this model describes the response of an individual tube to absorption of low-energy photons; its experimentally determined value may suggest some ideas about such a response.

DOI: 10.1103/PhysRevB.73.085420 PACS number(s): 73.22.Lp, 81.07.-b, 42.70.Gg, 71.35.Gz

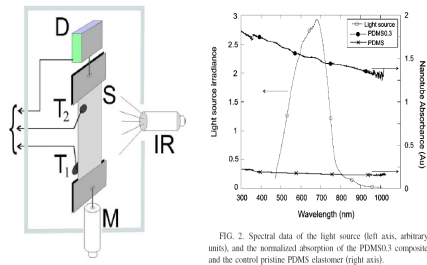


FIG. 2. Spectral data of the light source (left axis, arbitrary units), and the normalized absorption of the PDMS0.3 composite and the control pristine PDMS elastomer (right axis).

“two-way” photo-actuation of Pre-stained PDMS-MWNT nanocomposites

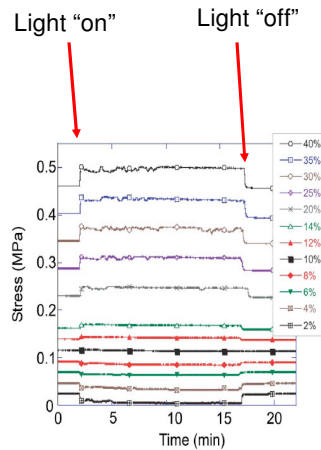


FIG. 7. (Color online) The response of a 1 wt % nanocomposite PDMS1 to IR radiation at different levels of prestrain ϵ . Stress is measured at fixed sample length (different prestrain curves labeled on the plot).

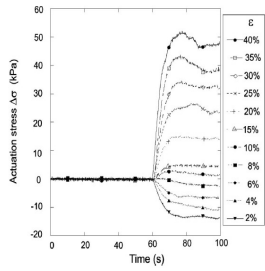


FIG. 8. The speed of actuation response, illustrated by plotting the actuation stress in PDMS3 nanocomposite, $\Delta\sigma$ in kPa, as a function of time for different prestrain values (labeled on the plot).

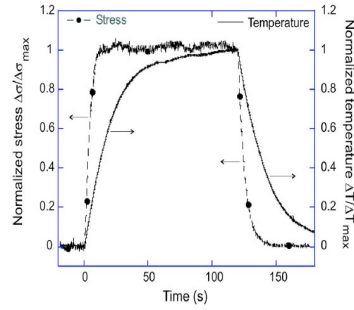


FIG. 9. (Color online) The normalized stress response plotted alongside the normalized change in temperature, as functions of time (PDMS3, prestrain $\epsilon=20\%$); see text for discussion.

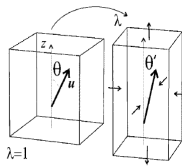


FIG. 6. The scheme of an affine incompressible extension, changing the orientation of an inflexible rod embedded in the medium.

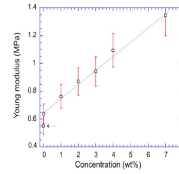


FIG. 4. (Color online) Young modulus, Y for PDMS nanocomposites at increasing MWCNT loading. The arrow points at the value for control PDMS rubber.

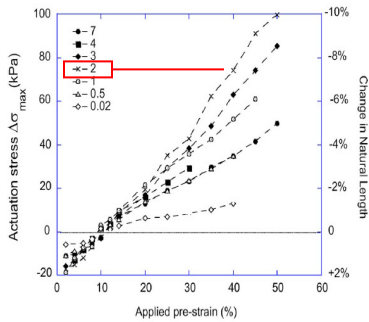


FIG. 10. (Color online) The magnitude (in kPa) of exerted actuation stress (the height of steps in Fig. 7, $\Delta\sigma_{\max}$), as a function of prestrain. Different PDMS composites are labeled on the plot by their wt % value. The right y axis shows the corresponding actuation stroke: the change in natural length L_0 (IR).

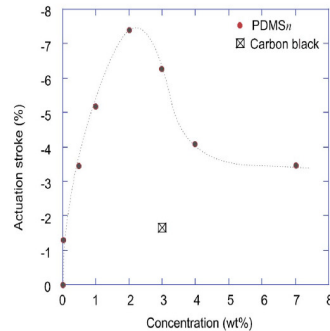


FIG. 11. (Color online) The magnitude of the actuation stroke at $\epsilon=40\%$ as a function of filler concentration n . The maximum of the response at ~ 2 wt% is evident. The single square symbol gives the value for 3 wt% carbon black filler in PDMS.

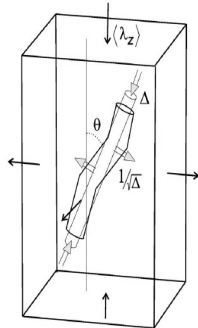


FIG. 13. The scheme illustrating how the distortion (kinking) of an individual tube, lying at an angle θ to the macroscopic alignment axis, projects on the z axis to contribute to the average uniaxial strain, Eq. (10).

Inferred “shortening” of CNTs
under “light on” conditions:
strain-induced orientation of CNTs:
more response at higher pre-strain

Buckling?

cause or effect?

CHEMISTRY

Nanotubes in a Flash—Ignition and Reconstruction

P. M. Ajayan,^{1*} M. Terrones,^{2,3*} A. de la Guardia,¹ V. Huc,⁴
N. Grobert,³ B. Q. Wei,¹ H. Lezec,⁴ G. Ramanath,^{1*}
T. W. Ebbesen^{4*}

Extreme photo-actuation:
ignition

(see also video clip at *Science* web site)

CNTs are highly responsive to near IR photons: thermal response (HOT!);
electrical response
CNTs are excellent thermal conductors (axially)

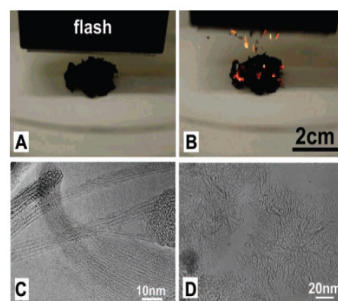


Fig. 1. (A and B) Sequence of burning of SWNT: (A) original sample (about 2 cm outer diameter) showing the flash on top; (B) sample soon after flashing exhibiting the ignited SWNT material with burning red and yellow spots. (C) High-resolution transmission electron microscopy (HRTEM) image of pristine SWNT, in which a cross section of an individual bundle is clearly observed. (D) Typical HRTEM image of remaining carbonaceous material obtained after flashing SWNTs in air; the presence of reconstructed single-walled structures such as nanohorns is noteworthy. See the supplementary material for a movie of the flash and the burning SWNT (17).

“Thermoelastic inversion” (?)

from Treloar (1975)

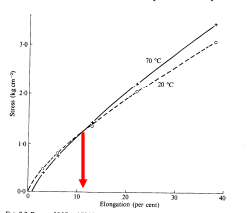


FIG. 2.3. Force at 20 °C and 70 °C plotted against extension calculated on unstrained length at 20 °C. (Ashby, Cocks, and Gubb 1982.)

$$e = L(T;P)/L(T_0;P=0) - 1$$

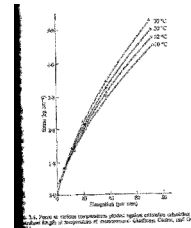


FIG. 2.4. Force at various temperatures plotted against extension calculated on unstrained length at 20 °C. (Ashby, Cocks, and Gubb 1982.)

$$e = L(T;P)/L(T,P=0) - 1$$

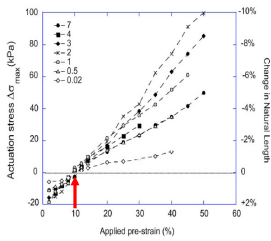


FIG. 10. (Color online) The magnitude (in kPa) of exerted actuation stress (the height of steps in Fig. 7, $\Delta\sigma_{max}$), as a function of pre-strain. Different PDMS composites are labeled on the plot by their wt % value. The right y axis shows the corresponding actuation stroke: the change in natural length $L_0(\Delta R)$.

Both local (near CNT) and global thermal expansion strains likely contribute to the photo-response of the CNT-PDMS nanocomposites

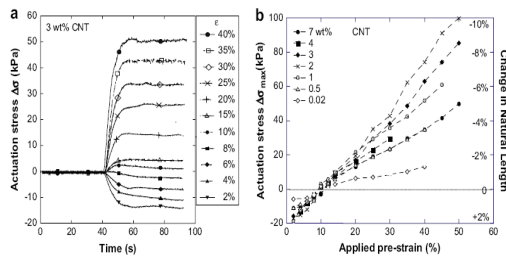


Fig. 6. (a) The actuation stress as a function of time (PDMS elastomer with 3 wt% of MW/CNT). Pre-strain ϵ values (related to the induced tube alignment) are shown in the plot; (b) the maximum, plateau level of actuation stress $\Delta\sigma_{max}$ for different values of pre-strain. The right y-axis shows the corresponding values of actuation stroke representing the change in natural length on irradiation.

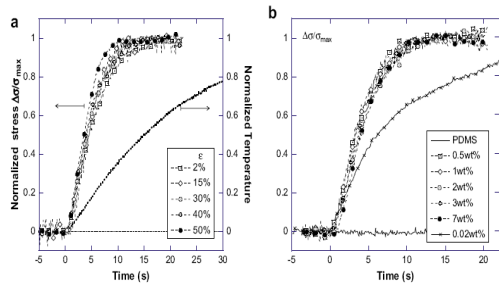


Fig. 8. Normalized stress, $\Delta\sigma/\sigma_{max}$ vs. time, which allows comparison of the response kinetics: (a) the light-on response of 3 wt% PDMS composite at different values of pre-strain ϵ . The right y-axis shows the simultaneously measured, similarly normalized, change in temperature on irradiation; (b) the light-on response of different composites, all at the same 20% pre-strain.

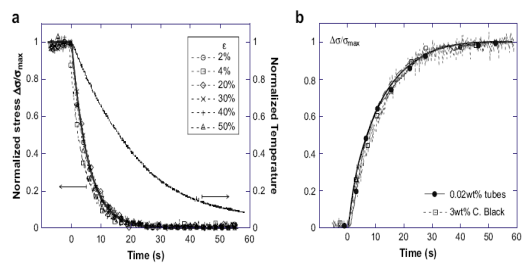


Fig. 10. (a) The normalized stress relaxation of a 3 wt% nanocomposite illuminated at different pre-strain, when the light source is switched off. The right y-axis shows the simultaneously measured, similarly normalized, change in temperature on irradiation; (b) the light-on response of the composite with very low tube loading, and also that of a sample with 3 wt% carbon black, both at $\epsilon = 20\%$. The Debye relaxation is found in both cases, with the fit curve shown by the solid line in both the plots.

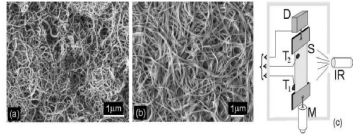


FIG. 1. Networks of carbon nanotubes. (a) SEM image of MWNT mat. (b) SWNT mat, under similar magnification, highlighting the tube bundles. (c) Scheme of the experiment, which controls the temperature (T_1, T_2) and strain via a micrometer (M) and measures the exerted force via a dynamometer (D), in ambient relaxation or on irradiation.

PHYSICAL REVIEW B 76, 165437 (2007)

Thermal fluctuations, stress relaxation, and actuation in carbon nanotube networks

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Department of Electrical and Computer Engineering, University of Delaware, Newark, Delaware 19716, USA

(Received 15 June 2007; revised manuscript received 24 August 2007; published 30 October 2007)

CNT mats: no polymer

SWNTs: evidence of “entropic” stiffening

MWNTs: minute stress increase, then massive relaxation...

The CNTs themselves don't respond as the composite

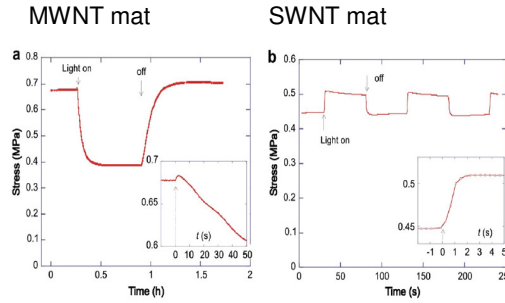


Fig. 13. (a) Photomechanical actuation of MWNT mat recorded at fixed sample length. The inset shows the initial contractive stress response of the film during the first few seconds when the light source is switched on; (b) photomechanical response of SWNT mat, in the same conditions, shows the sample contracting on illumination. The detailed onset kinetics, highlighted in the inset, matches well the compressed-exponential kinetics [63].

PRL 96, 133802 (2006)

PHYSICAL REVIEW LETTERS

week ending 7 APRIL 2006

Fast Relaxation of Carbon Nanotubes in Polymer Composite Actuators

S. V. Ahir and E. M. Terentjev

Cavendish Laboratory, University of Cambridge, J. J. Thomson Avenue, Cambridge CB3 0HE, United Kingdom

(Received 9 January 2006; published 6 April 2006)

Silicone elastomer composites containing individual carbon nanotubes have been irradiated with near-infrared light to study their mechanical actuation response. We show that the speed of the stimulated response is faster than Debye relaxation, instead following a compressed-exponential law. However, the relaxation after switching off the light source follows the simple-exponential relaxation, as does the stimulated response at very low nanotube concentration. We discuss possible models and explanations to account for the fast photomechanical response.

DOI: 10.1103/PhysRevLett.96.133802

PACS numbers: 42.70.Gg; 71.38.-k; 82.35.Np

Light “on” transients

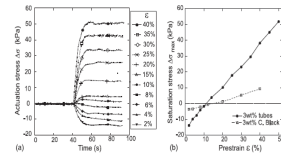


FIG. 1. (a) Typical light-induced stress at different prestrains (ϵ , labeled on plot), corresponding to the increasing tube alignment. The data for a PDMS sample with 3 wt% nanotubes. (b) The dependence of saturation stress $\Delta\sigma_{\max}$ on the degree of tube alignment, represented here by the applied prestrain ϵ . Data for a PDMS sample containing 3 wt% carbon black is also presented for comparison.

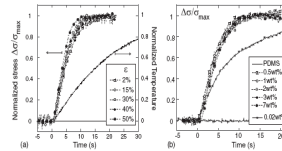


FIG. 2. Normalized stress, $\Delta\sigma/\sigma_{\max}$ vs time, which allows comparison of the response kinetics: (a) The light-on response of 3 wt% composite at different values of prestrain ϵ . The right y axis shows the simultaneously measured, similarly normalized, change in temperature on irradiation. (b) The light-on response of different composites, all measured at the same 20% prestrain.

$$\Delta\sigma/\sigma_{\max} = 1 - \exp(-(t/\tau)^\beta)$$

$$\beta=2; \tau=5s$$

“stretched exponential” transients

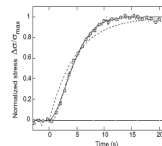
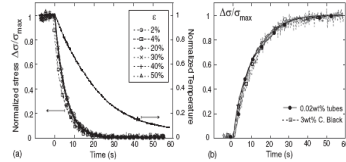


FIG. 3. Illustration of the data fit, for 3 wt% composite at 20% prestrain. Experimental data (\circ) is fitted by the compressed-exponential (solid line) and the simple-exponential (dashed line) functions to demonstrate the discrepancy.

Light "off": CNTs

Light "on": CB; 0.02wt% CNT



$$\Delta\sigma / \sigma_{\max} = 1 - \exp(-t/\tau)$$

$$\tau = 10\text{s}$$

Simple exponential transients:

All specimens, "light off";

3wt% CB: "light on"

0.02wt% CNT: "light on"

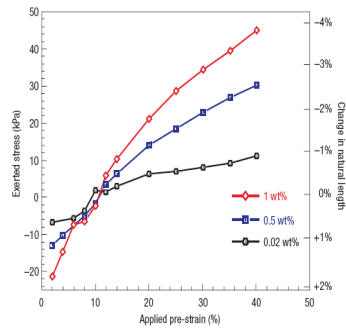
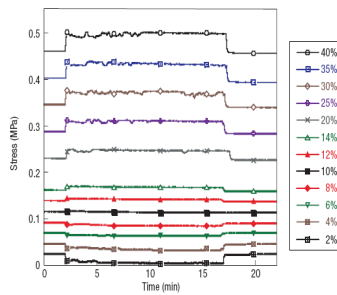
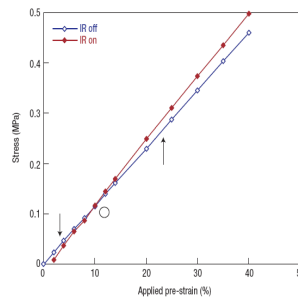
FIG. 4. (a) The normalized stress relaxation of a 3 wt% nano-composite illuminated at different prestrain, when the light source is switched off. The right y axis shows the simultaneously measured, similarly normalized, change in temperature on irradiation. (b) The light-on response of the composite with very low tube loading, and also that of a sample with 3 wt% carbon black, both at $\epsilon = 20\%$. The Debye relaxation is found in both cases, with the fit curve shown by the solid line in both plots.

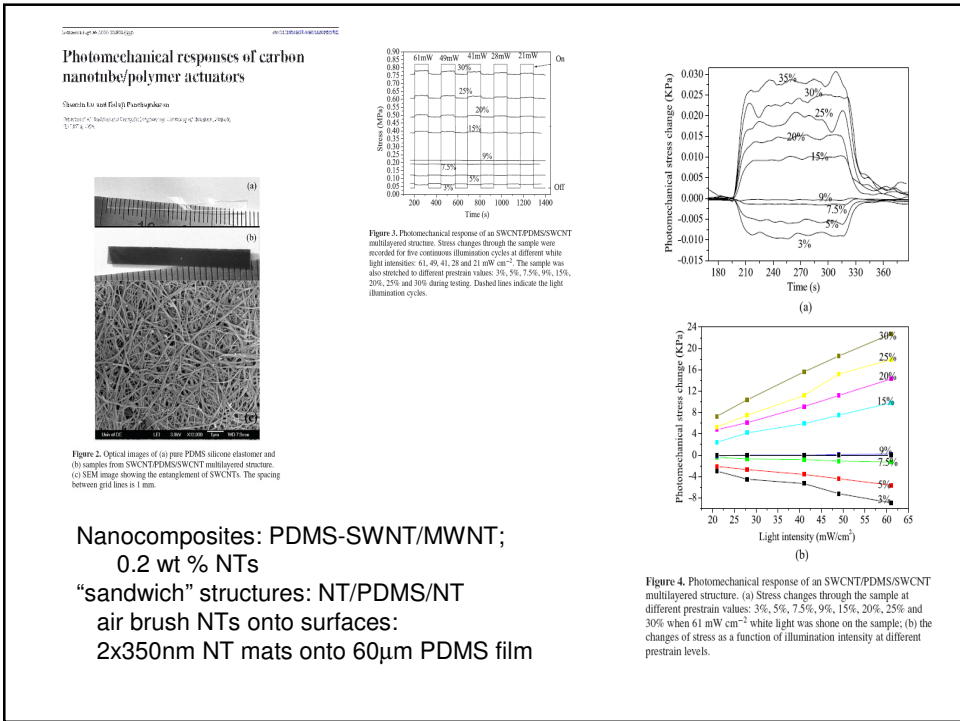
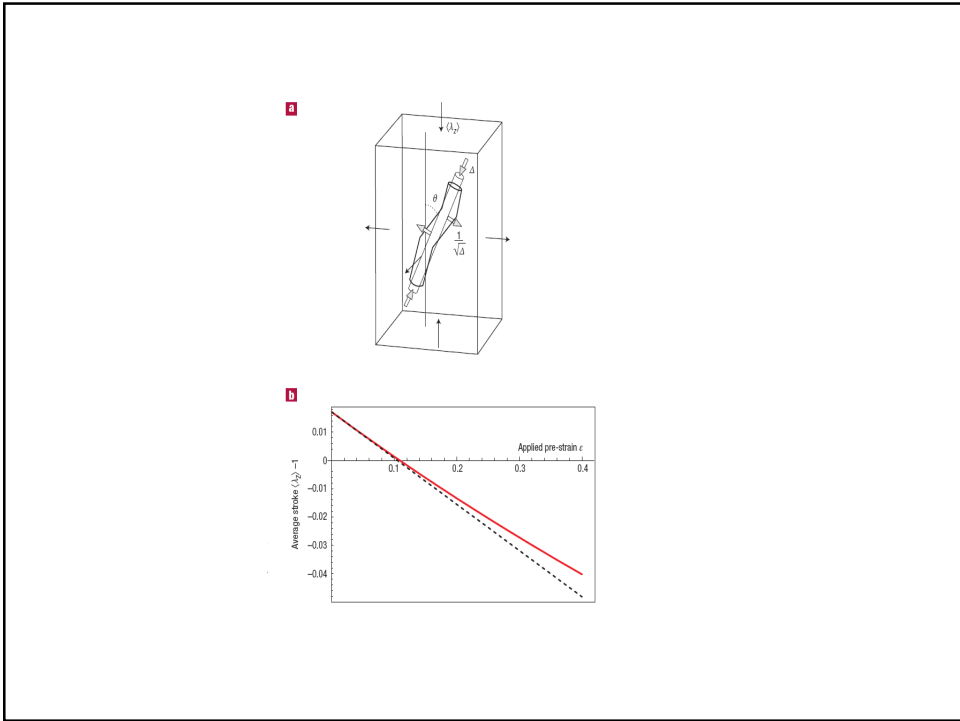
Photomechanical actuation in polymer-nanotube composites

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Macro $\Delta T \sim 15\text{C}$





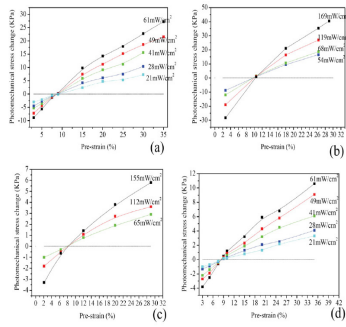


Figure 5. Photomechanical stress as a function of prestrains with light intensity as the third control parameter for (a) SWCNT/PDMS/SWCNT multilayered structure; (b) MWCNT/PDMS/MWCNT multilayered structure; (c) SWCNT-PDMS nanocomposites; (d) MWCNT-PDMS nanocomposites. The dashed lines indicate the zero stress position in each figure. There is a transition point for each sample, where an apparent photomechanical response is observed from the samples. The transition points are (a) ~9%, (b) ~10%, (c) ~8.5%, (d) ~8.5%.

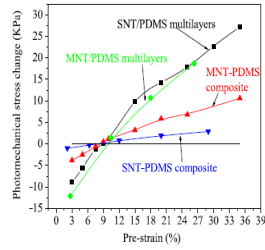


Figure 8. Comparison of photomechanical responses of multilayered and composite samples for both SWCNTs and MWCNTs. The photomechanical stresses versus prestrains under 61 mW cm^{-2} illumination are plotted for all the four samples
 ▲: MWCNT-PDMS composite; ▼: SWCNT-PDMS composite;
 ■: SWCNT/PDMS/SWCNT multilayered structure;
 ◆: MWCNT/PDMS/MWCNT multilayered structure).