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**The scientific work  
of Bernard D. Coleman**

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Bernard D. Coleman was an extraordinary figure of the 20th century continuum mechanics and thermodynamics. He made a number of deep and permanent contributions that changed the way these sciences are now understood, presented, and applied. Many of his results are now standard parts of textbooks, monographs and research papers.

His initial inspiration came mainly from Clifford Truesdell, and many of his most influential papers from the “golden era” of his career were written in collaboration with Walter Noll. Work in continuum mechanics and thermodynamics before their time was typically characterized by the absence of precisely formulated general principles and a lack mathematical rigor. The present-day clarity and efficiency of these sciences owes much to the efforts of Truesdell, Coleman, Noll and others. In 1963 Coleman was one of the founding members of the Society for Natural Philosophy, which fosters high quality in scientific research in continuum mechanics and thermodynamics, and he was a long-standing member of the editorial board of the *Archive for Rational Mechanics and Analysis*.

His research interests were wide. Apart from general questions of continuum mechanics and thermodynamics (especially thermodynamics of materials with fading memory), they included elasticity, wave propagation, stability, viscoelasticity,

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nonlocal materials, birefringence, electromagnetism, population dynamics, polymer physics, theory of second sound, physical chemistry, neural networks, and biophysics related to the properties of DNA. His research was supported by powerful mathematical skills that included functional analysis and partial differential equations.

His written work was generally superior to his public lectures. The former are well organized and presented with striking clarity. In contrast, he would often fall into too much detail in his lectures at the expense of the substance of the matter. He was notorious for exceeding his allotted time in talks and lectures, and he was well known at conferences for turning his question for the speaker into a “mini-talk”. These qualities caught many a session chairperson off guard.



B. D. COLEMAN

In 1954 Coleman received his doctorate in chemistry at Yale with two theses - one under the guidance of Kirkwood, the other, of Fuoss. The former concerned theory and experiment on dilute polymer solutions. In 1954–1957 Coleman was a research chemist at the du Pont Company. He came to be regarded an expert on the strength of artificial fibres. He developed a theory of the dependence of lifetimes of bundles on the strength of the individual fibres. Although ignored at the time, the model was taken up in industry many years later. In 1957 he was appointed as a senior research fellow at the Mellon Institute. At Carnegie Mellon University he became Professor of Mathematics in 1967, Professor of Biology in 1974, and Professor of Chemistry in 1974. In 1988 he moved to Rutgers with the splendid and long-deserved title of J. Willard Gibbs Professor of Thermomechanics as well as Professor of Mathematics. In 1991 he was nominated a Graduate Director, Program in Mechanics, Rutgers Uni-

versity, and in 1997 Member of the Center for Molecular Biophysics and Biophysical Chemistry.

B. D. Coleman received many awards. We mention: Bingham Medal of the Society of Rheology (1984), Fourth Annual Aris Phillips Memorial Lecture, Yale University (1991), Honorary Doctorate (Laurea Honoris Causa in Mechanica Arte), University of Rome Tor Vergata (1993), Elected to the College of Fellows of the American Institute for Medical and Biological Engineering (AIBME) (2002), Honorary Member of the International Society for the Interaction of Mathematics with Mechanics (ISIMM) “in recognition of outstanding achievements in the field of Applied Mathematics and Thermodynamics” (2002), and Fellow of the Society of Rheology (2016).

We now present a selection of some of his results in their simplified form.

**Mechanical breakdown phenomena** At the beginning of his career, he worked in the area of stochastic-process models for mechanical breakdown phenomena. Perhaps the culmination of that work is his 1963 paper with T. Fox, General theory of stationary random sequences with applications to the tacticity of polymers. This paper was selected in 1996 for reprinting in the *J. Polymer Science* with commentaries as one of the “most important and influential” articles to appear in the *Journal* during its first 50 years.

**Nonlinear viscoelastic fluids** In a series of papers—in part with Noll but also single-authored – Coleman deals with the important topic of the analytic determination of the velocity field and stress tensor in steady laminar shear flows of incompressible simple fluids (Newtonian, non-Newtonian, or viscoelastic), without neglect of inertia. In the paper written with W. Noll, *On Certain Steady Flows of General Fluids*, they showed by simple methods that the exact analytical solutions available for the Rivlin-Ericksen fluids can be extended to all incompressible simple fluids. This class is characterized by the equation for the Cauchy stress  $\mathbf{T}(t)$  of the form

$$\mathbf{T}(t) = -p(t)\mathbf{I} + \mathbf{T}^\circ(t)$$

where  $p(t)$  the undetermined pressure and  $\mathbf{T}^\circ(t)$  the constitutive part of stress, determined by the constitutive equation

$$\mathbf{T}^\circ(t) = \mathfrak{T}^\circ(\mathbf{F}^t). \quad (1)$$

Here  $\mathbf{F}^t$  is the history of the deformation gradient  $\mathbf{F}$  up to time  $t$ , which is the function of the elapsed time  $s \geq 0$ , given by

$$\mathbf{F}^t(s) = \mathbf{F}(t - s), \quad (2)$$

and  $\mathfrak{T}^\circ$  is a functional characterizing the fluid. By the incompressibility we have the constraint that  $\mathbf{F}(t)$  be unimodular (i.e.,  $\det \mathbf{F}(t) = 1$ ) for all  $t$ ; we impose the normalization condition  $\text{tr} \mathbf{T}^\circ(t) = 0$ . Equation (1) states that the present value of  $\mathbf{T}^\circ$  is determined by the values of the deformation gradient at all times  $t - s$  in the past; thus the class of fluids may account for hereditary effects including stress relaxation. The functional  $\mathfrak{T}^\circ$  is defined on a specified set  $\mathcal{H}$  of unimodular histories  $\mathbf{H}$ , i.e., functions defined on  $[0, \infty)$  with values in the set of all unimodular second-order tensors. It has to satisfy two basic requirements: the principle of material frame indifference

$$\mathfrak{T}^\circ(\mathbf{QH}) = \mathbf{Q}(0)\mathfrak{T}^\circ(\mathbf{H})\mathbf{Q}^\text{T}(0) \quad (3)$$

for every history  $\mathbf{H} \in \mathcal{H}$  and every history  $\mathbf{Q}$  of proper orthogonal tensors, and the relation that  $\mathfrak{T}^\circ$  describes a simple fluid in the sense of W. Noll, i.e.,

$$\mathfrak{T}^\circ(\mathbf{H}\mathbf{U}) = \mathfrak{T}^\circ(\mathbf{H}) \quad (4)$$

for every history  $\mathbf{H} \in \mathcal{H}$  and every constant unimodular tensor  $\mathbf{U}$ .

The paper deals with flows for which the velocity field has the form

$$(v^1, v^2, v^3) = (0, v(x_1), 0) \quad (5)$$

in some appropriate curvilinear orthogonal coordinate system  $x^1, x^2, x^3$  in which the metric tensor  $\mathbf{g}$  is diagonal and independent of  $x^2$ . Calculating the deformation gradient  $\mathbf{F}$  corresponding to the flow (5), inserting the result into (1), and using the properties (3) and (4) of  $\mathfrak{T}^\circ$ , one finds that  $\mathbf{T}^\circ$  has the form

$$\mathbf{T}^\circ(t) = \begin{bmatrix} t_{11} & t_{12} & 0 \\ t_{21} & t_{22} & 0 \\ 0 & 0 & t_{33} \end{bmatrix} \quad (6)$$

where  $t_{ij}$  are some functions of the shear rate  $\varkappa = v'(x_1)$ . By the normalization  $\text{tr} \mathbf{T}^\circ = 0$  and the symmetry of stress only three of the five elements of the above matrix are independent, and thus the behavior of the fluid in this class of flows is determined by only three material functions, called viscometric functions, viz.,

$$\tau(\varkappa) = t_{12}, \quad \sigma_1(\varkappa) = t_{11} - t_{33}, \quad \sigma_1(\varkappa) = t_{22} - t_{33}. \quad (7)$$

The class (5) covers: flow through a channel; helical flow between concentric cylinders in relative rotation and relative axial motion; flow through a tube of circular cross-section; flows between cone (or plate) and plate in relative rotation. In each case, Equation (6) and the viscometric functions (7) enable to determine the measurable torques, forces, or pressure distributions.

This research is concisely and lucidly summarized in the monograph *Viscometric Flows of Non-Newtonian Fluids; Theory and Experiment*, by B. D. Coleman, Markovitz & W. Noll, Springer 1966. The book is accessible to a wide audience.

**Viscoelasticity, fading memory** One of the motivations for Coleman's works comes from his research on the properties of polymers, especially their viscoelastic and rheological properties. The paper, co-authored by Walter Noll, *An Approximation Theorem for Functionals, with Applications in Continuum Mechanics*, is the first systematic approach to materials with fading memory. It starts the ground-breaking series of papers, some written with Noll, on materials with fading memory. This paper was featured in a 1986 issue of *Current Contents* by the Institute for Scientific Information as "citation classic". Another article with Noll, *Foundations of linear viscoelasticity*, (1961) was listed as among the 100 most cited papers in the Review of Modern Physics for the period 1955–1986.

The paper *An Approximation Theorem for Functionals, with Applications in Continuum Mechanics* analyzes the relationship

$$\mathbf{S}(t) = \mathfrak{G}(\mathbf{F}^t) \quad (8)$$

expressing the present value of the stress (or any other physical quantity) as a functional of the history  $\mathbf{F}^t$  of the deformation gradient up to some  $t$ , see (2). In many

physical situations, the value  $\mathbf{S}$  in (8) will be more sensitive to the values of  $\mathbf{F}$  for small  $s$  than for large  $s$ . Intuitively speaking, the “memory” of the system will “fade away” in time. An example is a functional given by

$$\mathbf{S}(t) = \int_0^{\infty} \mathbf{k}(s) \mathbf{F}^t(s) ds,$$

where  $\mathbf{k}$  is some kernel function which approaches  $\mathbf{0}$  rapidly as  $s \rightarrow \infty$ . In contrast to the previous work, Coleman & Noll do not postulate any concrete form of the functional  $\mathfrak{S}$ . Rather, they introduce a norm  $\|\cdot\|$  in the space  $\mathcal{H}$  of histories  $\mathbf{H}$  given by

$$\|\mathbf{H}\| = \left( \int_0^{\infty} (|\mathbf{H}(s)|h(s))^p ds \right)^{1/p} \quad (9)$$

where  $p$  is a fixed number  $1 \leq p < \infty$  and  $h(s)$ , called an influence function, is a nonnegative-valued function which approaches zero rapidly as  $s \rightarrow \infty$ . Thus the norm  $\|\mathbf{H}\|$  we assigns a greater influence to the values of  $\mathbf{H}$  for small  $s$  (recent past) than for very large  $s$  (distant past). Both  $p$  and  $h$  are parts of the specification of the constitutive structure. That the stress response fades away is expressed by requirement of continuity of the functional  $\mathfrak{S}$  on the Banach space of histories  $\mathbf{H}$  with finite norm  $\|\cdot\|$ .

It is well-known that for slow processes in viscoelastic materials the relationship between stress and strain simplifies: the present value of stress  $\mathbf{S}(t)$  is determined approximately by the present values of the deformation gradient and its time derivatives. The main result of the paper *An Approximation Theorem for Functionals, with Applications in Continuum Mechanics* is the proof that for processes that are slow in a precisely defined sense and for sufficiently Fréchet differentiable functionals  $\mathfrak{S}$ , the constitutive equation (8) can be replaced, with explicitly determined accuracy, by an approximate relation

$$\mathbf{S}(t) \approx \mathfrak{s}(\mathbf{F}^{(0)}(t), \dots, \mathbf{F}^{(k)}(t)), \quad (10)$$

where

$$\mathbf{F}^{(m)}(t) = \frac{d^m \mathbf{F}(t)}{dt^m}, \quad m = 0, \dots, k,$$

and  $\mathfrak{s}$  is a function completely determined by  $\mathfrak{S}$  and its derivatives.

For viscoelastic fluids, when (8) is the stress-strain relation, the first approximation (10) (i.e.,  $k = 1$ ) provides the constitutive equation of compressible Newtonian fluid for the stress tensor  $\mathbf{S}$ :

$$\mathbf{S} = -p(\rho)\mathbf{1} + \lambda(\text{tr} \mathbf{D})\mathbf{1} + 2\mu\mathbf{D}$$

here the rate of deformation tensor  $\mathbf{D}$  is the symmetric part of the velocity gradient tensor;  $p = p(\rho)$  is the hydrostatic pressure the fluid expressed as a function of the density  $\rho$  and  $\lambda, \mu$  are  $\rho$ -dependent viscosity coefficients. Higher-order approximations lead to *nonlinear (polynomial)* dependency of  $\mathbf{S}$  on the Rivlin-Ericksen tensors  $\mathbf{A}_1, \dots, \mathbf{A}_k$ .

Related to the theory of fading memory is Coleman’s paper *On Retardation Theorems* (1971) which deals with spatially nonlocal functionals, where the stress at the given point of the body, say at  $\mathbf{x} = \mathbf{0}$ , depends on the landscape of the deformation  $\phi$

at all points of the body, which is assumed to extend over the entire three-dimensional space. The paper analyses the analog of (8), viz.,

$$S = \mathfrak{F}(\phi), \quad (11)$$

where  $\mathfrak{F}$  is a functional defined on a certain class  $\mathcal{L}$  of maps  $\phi$  from  $\mathbb{R}^3$  into  $\mathbb{R}^3$ . The functional is assumed to have the property that the point close to  $\mathbf{x} = \mathbf{0}$  influence the response at  $\mathbf{x} = \mathbf{0}$  more than the distant ones. Again, this is expressed by the continuity or Fréchet differentiability of the functional  $\mathfrak{F}$  with respect to the norm

$$\|\phi\| = \left( \int_{\mathbb{R}^3} (|\phi(\mathbf{x})| h(\mathbf{x}))^p d\mathbf{x} \right)^{1/p}$$

where  $p$  is a fixed number  $1 \leq p < \infty$  and the nonnegative influence function  $h(\mathbf{x})$  approaches zero rapidly as  $|\mathbf{x}| \rightarrow \infty$ . The spatial version of the retardation theorem deals with “tame” deformations  $\phi$  which vary in space lightly. Under sufficient Fréchet differentiability of the functional  $\mathfrak{F}$ , for tame deformations the response (11) can be approximated by

$$S(\mathbf{x}) \approx \mathfrak{f}(\phi^{[0]}(\mathbf{x}), \dots, \phi^{[k]}(\mathbf{x}))$$

where

$$\phi^{[m]}(\mathbf{x}) = \nabla^m \phi(\mathbf{x}), \quad m = 0, \dots, k$$

and  $\mathfrak{f}$  is a function completely determined by the functional  $\mathfrak{F}$  and its Fréchet derivatives. The author of this review believes that this less known paper by B. D. Coleman of 1971 has new relevancy in view of the current discussion of nonlocal models constructed within the framework of the peridynamic theory.

**Thermodynamics** His research on viscoelasticity and fading memory naturally brought Coleman to thermodynamics. The paper *On the Thermostatistics of Continuous Media*, (1959), written with W. Noll, is a response to Truesdell’s *Hauptproblem of finite elasticity*, as formulated in 1954 and published in 1956. In the *Hauptproblem*, Truesdell pronounces the requirement that it is necessary to determine restrictions on the strain-energy function of nonlinear materials that guarantee reasonable (existence of solutions, stability, reality of wave speeds, uniqueness etc.). These restrictions should be nonlinear counterparts of the well-known inequalities on the Lamé constants  $\lambda$  and  $\mu$  of linear elasticity. In the late fifties, prior to the publications of Coleman and Noll, the situation was not at all clear. Even the position of these (as yet unknown) restrictions was not clear: are they consequences of the (as yet unknown form of) the second law of thermodynamics, or just mathematical conditions? The analyses gradually separated the issues of dissipation from those of stability and restrictions on the stored energy function. The entropy principle alone did not restrict the form of the strain-energy function; the inequalities on the energy functions are related to stability and to other finer properties.

The paper *On the Thermostatistics of Continuous Media* regards thermostatistics as that branch of thermodynamics which deals with bodies which are at rest at the present time and which may be regarded as having been at rest at all times in the past. One is thus led to the thermoelastic response, governed by the constitutive equations for the specific internal energy, Piola-Kirchhoff stress, and temperature of the form



$$\varepsilon = \bar{\varepsilon}(\mathbf{F}, \eta), \quad \mathbf{S} = \bar{\mathbf{S}}(\mathbf{F}, \eta), \quad \theta = \bar{\theta}(\mathbf{F}, \eta),$$

where  $\mathbf{F}$  is the deformation gradient and  $\eta$  specific entropy. The paper makes a distinction between local states, referring to a material point in a body, and global states, referring to the body as a whole.

For the local states the authors propose the constitutive inequality

$$\bar{\varepsilon}(\mathbf{F}^*, \eta^*) > \bar{\varepsilon}(\mathbf{F}, \eta) + \bar{\mathbf{S}}(\mathbf{F}, \eta) \cdot (\mathbf{F}^* - \mathbf{F}) + \bar{\theta}(\mathbf{F}, \eta)(\eta^* - \eta) \quad (12)$$

for all pairs  $(\mathbf{F}^*, \eta^*) \neq (\mathbf{F}, \eta)$  such that

$$\mathbf{F}^* = \mathbf{G}\mathbf{F}$$

where  $\mathbf{G}$  is a symmetric positive definite tensor. They show that this implies the thermodynamic relations

$$\mathbf{S} = \partial_{\mathbf{F}} \bar{\varepsilon}, \quad \bar{\theta} = \partial_{\eta} \bar{\varepsilon} \quad (13)$$

plus some additional restrictions on  $\bar{\varepsilon}$ . For isotropic elastic materials Postulate (12) implies that the internal energy is a (jointly) convex function of the principal stretches  $v_1, v_2, v_3$  and  $\eta$ , i.e., if we write

$$\bar{\varepsilon}(\mathbf{F}, \eta) = \Phi(v_1, v_2, v_3, \eta)$$

then  $\Phi$  is convex. For elastic fluids the internal energy can be expressed as a function of the specific volume  $v = \det \mathbf{F}$  and  $\eta$ ,

$$\bar{\varepsilon}(\mathbf{F}, \eta) = \Phi(v, \eta).$$

It turns out that Postulate (12) is equivalent to the joint convexity of  $\Phi$  in  $\sqrt[3]{v}$  (!) and  $\eta$ .

A subsequent discussion showed that these two consequences of (12) are too restrictive. A number of objections have been given, of which perhaps the most important is the one (apparently due to R. S. Rivlin) which points out that the convexity in  $v_1, v_2, v_3$  cannot hold for an almost incompressible material, due to the non-convexity of the surface  $v_1 v_2 v_3 = 1$ . This finally showed the untenability of Inequality (12). After a debate that lasted more than two decades, the final solution of the *Hauptproblem* came in 1977 with the work J. M. Ball. He showed that the triplet of weakened convexity conditions, viz., *polyconvexity*, *Morrey's quasiconvexity*, and the *rank 1 convexity* (essentially the nonstrict version of the strong ellipticity) is exactly what is missing. The quasiconvexity and its consequence rank 1 convexity are *necessary conditions* for the existence of a minimizer of the potential energy and for the lower semicontinuity of the total energy. Furthermore, for isotropic solids the quasiconvexity implies the Baker-Ericksen inequalities expressing the condition that principal stresses are always ordered in the same way as principal stretches. For fluids the quasiconvexity reduces to the convexity of internal energy on the specific volume and entropy, which is well founded. On the other hand, the *sufficient condition* for the existence of minima under the condition on the density of the stored energy

$$\bar{\psi}(\mathbf{F}) \rightarrow \infty \quad \text{as} \quad \det \mathbf{F} \rightarrow 0$$

require the polyconvexity, a condition stronger than quasiconvexity.

Of course, further investigations of J. M. Ball and R. James showed that even the weakened convexity conditions are not satisfied always, which leads to formation

of microstructure... Nevertheless, the weakened convexity conditions form definite reference points: their satisfaction as well as their violation provide important basic information about the body.

The second part of the paper *On the Thermostatics of Continuous Media* deals with the stability of global states. In global states the local quantities such as the deformation gradient, specific volume, temperature, etc., vary from point to point. If  $\mathcal{B}$  is the reference configuration of the body, a global state is a pair  $(\boldsymbol{\phi}, \eta)$  consisting of the deformation  $\boldsymbol{\phi} : \mathcal{B} \rightarrow \mathbb{R}^3$  and of the field  $\eta : \mathcal{B} \rightarrow \mathbb{R}$  of specific entropy. Associated with  $(\boldsymbol{\phi}, \eta)$  are the total energy, entropy, and volume, given by

$$\mathbf{E}(\boldsymbol{\phi}, \eta) = \int_{\mathcal{B}} \bar{\varepsilon}(\mathbf{F}, \eta) d\mathcal{m}, \quad \mathbf{H}(\boldsymbol{\phi}, \eta) = \int_{\mathcal{B}} \eta d\mathcal{m}, \quad \mathbf{V}(\boldsymbol{\phi}, \eta) = \int_{\mathcal{B}} \det \mathbf{F} d\mathcal{m},$$

where  $\mathbf{F} = \nabla \boldsymbol{\phi}$  is the deformation gradient and  $d\mathcal{m}$  the element of mass, i.e., the multiple of the element of volume  $d\mathcal{v}$  by the density  $\rho_{\mathbf{R}}$  of the body in the reference configuration. In the treatment below we put, as we may,  $\rho_{\mathbf{R}} = 1$  to simplify the formulas. Furthermore, one defines the potential energy of the body in the given loads. In the case of dead loadings we assume that the body is subjected to a the prescribed body force  $\mathbf{b}$ , prescribed surface traction  $\mathbf{s}$  on the free part  $\mathcal{S} \subset \partial\mathcal{B}$  of the boundary, while its complement  $\mathcal{D}$  is held fixed. Then

$$\mathbf{W}(\boldsymbol{\phi}) = - \int_{\mathcal{B}} \mathbf{b} \cdot \boldsymbol{\phi} d\mathcal{m} - \int_{\mathcal{S}} \mathbf{s} \cdot \boldsymbol{\phi} d\mathcal{s} \quad (14)$$

for each deformation  $\boldsymbol{\phi}$  satisfying

$$\boldsymbol{\phi} = \boldsymbol{\phi}_0 \quad \text{on } \mathcal{D},$$

where  $\boldsymbol{\phi}_0$  is a prescribed function, and where in (14)  $d\mathcal{s}$  is the element of area of  $\partial\mathcal{B}$ . The total energy of the global state  $(\boldsymbol{\phi}, \eta)$  is

$$\mathbf{U}(\boldsymbol{\phi}, \eta) = \mathbf{E}(\boldsymbol{\phi}, \eta) + \mathbf{W}(\boldsymbol{\phi}).$$

This framework allows an unambiguous formulation of the extremum principles of thermodynamics, formulated by the authors as definitions of stability. Thus, for example, a global state  $(\boldsymbol{\phi}, \eta)$  is said to be adiabatically stable if

$$\mathbf{U}(\boldsymbol{\phi}^*, \eta^*) > \mathbf{U}(\boldsymbol{\phi}, \eta)$$

for all states  $(\boldsymbol{\phi}^*, \eta^*) \neq (\boldsymbol{\phi}, \eta)$ , perhaps from some neighborhood of  $(\boldsymbol{\phi}, \eta)$ , that satisfy the constraints

$$\mathbf{H}(\boldsymbol{\phi}^*, \eta^*) = \mathbf{H}(\boldsymbol{\phi}, \eta) \quad \text{and} \quad \boldsymbol{\phi}^* = \boldsymbol{\phi}_0 \quad \text{on } \mathcal{D}.$$

One can formulate a similar notion of isothermal stability using the minimum of the (canonical) free energy  $\mathbf{F}(\boldsymbol{\phi}, \eta) = \mathbf{U}(\boldsymbol{\phi}, \eta) - \theta^\circ \mathbf{H}(\boldsymbol{\phi}, \eta)$  where  $\theta^\circ$  is a number representing the ambient temperature of the body. For fluids one can consider a gibbsian style thermostatics with several seemingly different minima and maxima principles, such as minimum energy under fixed entropy, maximum entropy under fixed energy, etc. This part of *On the Thermostatics of Continuous Media* returns to the stability definitions considered by Gibbs and J. Hadamard. In summary, the paper *On the Thermostatics of Continuous Media* showed that for varying fields of local quantities the inequalities of thermostatics get concrete meaning, in contrast to the case of homogeneous states, where they reduce to equalities. The subsequent paper by Coleman

*Mechanical and Thermodynamical Admissibility of Stress-Strain Functions* gives a reformulation of the inequality (12) in which the energy does not enter, but rather arises as a consequence.

**Coleman-Noll procedure** The paper by Coleman & Noll of 1963, *The thermodynamics of elastic materials with heat conduction and viscosity*, provides the basis for the well-known “Coleman-Noll procedure.” It was featured as a “citation classic” in a 1990 issue of *Current Contents*; it is certainly one of the most popular ones from the workshop of Coleman’s & Noll. The “procedure” is mathematical and systematic, and has widespread ramifications in the constitutive modeling of solids, fluids and “everything else in-between.” Every serious book on nonlinear continuum written since the late 1960’s—including modern texts on plasticity, viscoelasticity and non-Newtonian fluids—covers this topic.

The paper showed how to use the entropy inequality as a means of deriving constitutive restrictions on the response functions of general materials. The appropriate continuum version of the second law of thermodynamics is the Clausius-Duhem inequality formulated by C. Truesdell & R. A. Toupin in the article *Classical field theories of mechanics* in Flügges’ *Encyclopedia of Physics*. Its form combines the Clausius inequality for the rate of change of entropy  $\dot{H}(\mathcal{P}, t)$  of the part  $\mathcal{P}$  of the body  $\mathcal{B}$

$$\dot{H}(\mathcal{P}, t) \geq \int_{\mathcal{P}} \frac{r}{\theta} dm \quad (15)$$

with the surface term appropriate to continuous bodies which was introduced by P. Duhem

$$\dot{H}(\mathcal{P}, t) \geq - \int_{\partial\mathcal{P}} \frac{\mathbf{q} \cdot \mathbf{n}}{\theta} d\mathcal{A}, \quad (16)$$

to obtain the general form

$$\dot{H}(\mathcal{P}, t) \geq - \int_{\partial\mathcal{P}} \frac{\mathbf{q} \cdot \mathbf{n}}{\theta} d\mathcal{A} + \int_{\mathcal{P}} \frac{r}{\theta} dm. \quad (17)$$

Here  $r$  is the supply of energy (e.g., due to radiation),  $\theta$  the absolute temperature,  $\partial\mathcal{P}$  the boundary of  $\mathcal{P}$  and  $\mathbf{n}$  the unit outer normal to it, and  $\mathbf{q}$  the heat flux vector. Coleman and Noll postulate that (17) must be satisfied by every part, at any time, and in any process compatible with the constitutive equations and balance equations. The balance equations consist of the balance equations of linear momentum and energy. The essential feature of the postulate is that the body force  $\mathbf{b}$  and the supply of energy  $r$  occurring in these balances may be varied arbitrarily. Interpreted in this way, for materials with heat conduction and viscosity the Clausius-Duhem inequality leads to the thermostatic relations (13) and the residual dissipation inequality

$$\mathbf{T}_v \cdot \dot{\mathbf{F}} - \frac{\mathbf{q} \cdot \nabla \theta}{\theta} \geq 0$$

in which  $\mathbf{T}_v$  is the viscous part of the Piola-Kirchhoff stress,  $\dot{\mathbf{F}}$  the material time derivative of deformation gradient and  $\nabla \theta$  the referential gradient of temperature. The subsequent paper by Coleman & Mizel, *Thermodynamics and departures from Fourier’s law of heat conduction* presents the matter more systematically and for the

first time the rule of equipresence was applied effectively to eliminate superfluous variables. The works of Coleman & Noll from the period 1959–1963 substantially contributed to a clear separation of the issues of dissipation from those of stability.

In 1964 Coleman published two major studies *Thermodynamics of Materials with Memory* and *On Thermodynamics, Strain Impulses, and Viscoelasticity*. These show him as the principal architect of rational thermodynamics. They treat materials governed by the constitutive equations

$$\left. \begin{aligned} \eta(t) &= \mathfrak{h}(\mathbf{F}(t), \theta(t), \mathbf{F}_r^t, \theta_r^t, \mathbf{g}(t)), \\ \psi(t) &= \mathfrak{p}(\mathbf{F}(t), \theta(t), \mathbf{F}_r^t, \theta_r^t, \mathbf{g}(t)), \\ \mathbf{S}(t) &= \mathfrak{S}(\mathbf{F}(t), \theta(t), \mathbf{F}_r^t, \theta_r^t, \mathbf{g}(t)), \\ \mathbf{q}(t) &= \mathfrak{q}(\mathbf{F}(t), \theta(t), \mathbf{F}_r^t, \theta_r^t, \mathbf{g}(t)). \end{aligned} \right\} (18)$$

Here  $\eta(t)$  is the specific entropy,  $\psi(t)$  the specific free energy,  $\mathbf{S}(t)$  the Piola-Kirchhoff stress and  $\mathbf{q}(t)$  the heat flux vector at time  $t$  and at the given point of the body (not indicated explicitly), and  $\mathbf{F}(t)$ ,  $\theta(t)$  and  $\mathbf{g}(t)$  are the present values of the deformation gradient, temperature and the referential gradient of temperature and  $\mathbf{F}_r^t$  and  $\theta_r^t$  are the *past* histories of the deformation gradient and temperature prior to time  $t$ , given by

$$\mathbf{F}_r^t(s) = \mathbf{F}(t-s), \quad \theta_r^t(s) = \theta(t-s), \quad s > 0.$$

The constitutive functionals  $\mathfrak{h}$ ,  $\mathfrak{p}$ ,  $\mathfrak{S}$  and  $\mathfrak{q}$  are assumed to obey the principle of fading memory. In the present case this means the continuity of  $\mathfrak{h}$ ,  $\mathfrak{S}$  and  $\mathfrak{q}$  and continuous Fréchet differentiability of  $\mathfrak{p}$  in the space of the quintuples  $(\mathbf{F}(t), \theta(t), \mathbf{F}_r^t, \theta_r^t, \mathbf{g}(t))$  with finite norm analogous to that in (9). Thus each of the arguments  $\mathbf{F}$ ,  $\theta$ ,  $\mathbf{g}$ ,  $\mathbf{F}_r$ ,  $\theta_r$  can be varied independently of the others and the functional  $\mathfrak{p}$  has well defined partial Fréchet derivatives with respect to each of the variables  $\mathbf{F}$ ,  $\theta$ ,  $\mathbf{g}$ ,  $\mathbf{F}_r$ ,  $\theta_r$ , which we denote by  $\mathbf{D}_{\mathbf{F}} \mathfrak{p}$ ,  $\mathbf{D}_{\theta} \mathfrak{p}$ ,  $\mathbf{D}_{\mathbf{g}} \mathfrak{p}$ ,  $\delta_{\mathbf{F}} \mathfrak{p}$ , and  $\delta_{\theta} \mathfrak{p}$ , respectively. The application of the Coleman-Noll procedure results in the following restrictions on the constitutive functionals, the main result of the *Thermodynamics of Materials with Memory*:

- (i) the functionals  $\mathfrak{p}$ ,  $\mathfrak{h}$ , and  $\mathfrak{S}$  are independent of  $\mathbf{g}$ , i.e., they depend only on  $(\mathbf{F}, \theta, \mathbf{F}_r, \theta_r)$ ;
- (ii) the thermodynamic relations

$$\mathfrak{S} = \mathbf{D}_{\mathbf{F}} \mathfrak{p}, \quad \mathfrak{h} = -\mathbf{D}_{\theta} \mathfrak{p}$$

hold for all collections  $(\mathbf{F}, \theta, \mathbf{F}_r, \theta_r)$ ;

- (iii) the residual dissipation inequality

$$\delta_{\mathbf{F}} \mathfrak{p}(\Lambda | \dot{\mathbf{F}}_r) + \delta_{\theta} \mathfrak{p}(\Lambda | \dot{\theta}_r) - \frac{\mathfrak{q}(\Lambda, \mathbf{g}) \cdot \mathbf{g}}{\theta} \geq 0$$

holds for all vectors  $\mathbf{g}$  and all  $\Lambda = (\mathbf{F}, \theta, \mathbf{g}, \mathbf{F}_r, \theta_r)$ .

In (iii),  $\dot{\mathbf{F}}_r$  and  $\dot{\theta}_r$  are the derivatives of the past histories with respect to the elapsed times  $s > 0$ . Furthermore, the partial derivatives  $\delta_{\mathbf{F}} \mathfrak{p}(\Lambda | \cdot)$  and  $\delta_{\theta} \mathfrak{p}(\Lambda | \cdot)$  with respect to past histories are, by definition, linear functionals on the spaces of all tensor-valued functions  $\mathbf{G} = \mathbf{G}(s)$  and scalar-valued functions  $\phi = \phi(s)$ ,  $s > 0$ , respectively, of finite norms analogous to that in (9). The symbols  $\delta_{\mathbf{F}} \mathfrak{p}(\Lambda | \dot{\mathbf{F}}_r)$  and

$\delta_\theta \mathfrak{p}(\Lambda | \dot{\theta}_r)$  denote the values of these functionals at the arguments  $\mathbf{G} = \dot{\mathbf{F}}_r$  and  $\phi = \dot{\theta}_r$ , respectively.

Coleman then goes on to discuss a number of additional important topics like the behavior of the material in slow processes, relaxation, equilibrium thermostatic relations, integrated dissipation inequalities, decrease of the free energy during the approach to equilibrium etc.

Subsequent papers of 1966–1968 by B. D. Coleman & V. J. Mizel, much appreciated by connoisseurs, are devoted to fine mathematical tuning of the theory of fading memory. Thus *Norms and Semi-Groups in the Theory of Fading Memory* is based on an observation that not every function  $h$  in the expression for the norm of the type (9) can qualify as a reasonable influence function. Any reasonable influence function has to guarantee three natural postulates, viz., that any constant history belongs to the class of histories  $\mathcal{K}$  defined by (9), and that with any  $\mathbf{H} \in \mathcal{K}$  all time shifts of  $\mathbf{H}$  by amount  $\sigma > 0$  to the future belong to  $\mathcal{K}$  and all time shifts of  $\mathbf{H}$  by amount  $\sigma > 0$  to the past belong to  $\mathcal{K}$  also. The paper derives explicit restrictions on  $h$  placed by these requirements. The papers *A General Theory of Dissipation in Materials with Memory* and *On the General Theory of Fading Memory* go even farther and deal with spaces of histories equipped with an abstract norm  $\nu \equiv \|\cdot\|$  which need not have the integral representations like that in (9), and formulates elementary requirements on  $\|\cdot\|$  instead, like the compatibility with the ordering of histories by pointwise norms of  $\mathbf{H}(s)$ , sequential Fatou property, etc., studied in the theories of abstract Banach function spaces. The theory of fading memory and the thermodynamic restrictions within this general framework is developed in *A General Theory of Dissipation in Materials with Memory* and *On the General Theory of Fading Memory*.

**Stability** Another part of Coleman's work are his researches on the thermodynamic basis for the *dynamical* stability of homogeneous equilibrium states of fluids. Maybe they are not so well-known as the other parts of Coleman's work, but equally important and, in addition, of great aesthetic appeal. They were conducted partly in collaboration with J. M. Greenberg, E. H. Dill, and V. J. Mizel.

The approach in the paper *On the Stability of Equilibrium States of General Fluids* is based on a rigorous development of the classical Gibbsian thermostatics of fluids. It extends and deepens the corresponding treatment in the essay with W. Noll *On the Thermostatics of Continuous Media* discussed above. Consider a fluid with the reference configuration  $\mathcal{B}$  and the equilibrium response functions for the internal energy, temperature and pressure  $\bar{\varepsilon}$ ,  $\bar{\theta}$ , and  $\bar{p}$ , expressed as functions of the specific volume  $v$  and the specific entropy  $\eta$ . If we identify nonhomogeneous equilibrium states with pairs  $(v, \eta)$  of real-valued functions on  $\mathcal{B}$  giving the fields of the specific volume and the specific entropy, we can define the total energy, entropy, and volume of  $(v, \eta)$  by

$$\mathbf{E}(v, \eta) = \int_{\mathcal{B}} \bar{\varepsilon}(v, \eta) d\mathcal{M}, \quad \mathbf{V}(v, \eta) = \int_{\mathcal{B}} v d\mathcal{M}, \quad \mathbf{H}(v, \eta) = \int_{\mathcal{B}} \eta d\mathcal{M}.$$

Suppose that a given homogeneous equilibrium state of uniform specific volume  $v^\circ$  and uniform specific entropy  $\eta^\circ$  satisfies the principle of minimum energy at constant volume and entropy, i.e., that

$$\mathbf{E}(v, \eta) > \mathbf{E}(v^\circ, \eta^\circ)$$

whenever the state  $(v, \eta)$  satisfies

$$\mathbf{V}(v, \eta) = \mathbf{V}(v^\circ, \eta^\circ), \quad \mathbf{H}(v, \eta) = \mathbf{H}(v^\circ, \eta^\circ).$$

This turns out to hold if and only if  $(v^\circ, \eta^\circ)$  is a point of strict convexity of the function  $\bar{\varepsilon}$ , i.e.,

$$\bar{\varepsilon}(v, \eta) > \bar{\varepsilon}(v^\circ, \eta^\circ) - p^\circ(v - v^\circ) + \theta^\circ(\eta - \eta) \quad (19)$$

for all pairs  $(v, \eta) \neq (v^\circ, \eta^\circ)$ , where  $p^\circ = \bar{p}(v^\circ, \eta^\circ)$ ,  $\theta^\circ = \bar{\theta}(v^\circ, \eta^\circ)$ . Suppose that  $\bar{\varepsilon}$  is strictly convex at some point  $(v^\circ, \eta^\circ)$  in the domain  $\mathcal{D}$  of  $\bar{\varepsilon}$  in the sense of (19) and that all pairs  $(v, \eta)$  from  $\mathcal{D}$  are points of (possibly) nonstrict convexity except for pairs from some compact subset of  $\mathcal{D}$ . Coleman proves that then any global state  $(v, \eta)$  whose total energy is sufficiently close to the total energy of  $(v^\circ, \eta^\circ)$  is itself close to  $(v^\circ, \eta^\circ)$  in the sense that the integrals

$$\|v - v^\circ\| := \int_{\mathcal{B}} |v - v^\circ| d\mathcal{M} \quad \text{and} \quad \|\eta - \eta^\circ\| := \int_{\mathcal{B}} |\eta - \eta^\circ| d\mathcal{M}$$

are small. Formally, for each  $\varepsilon > 0$  there exists a  $\mathcal{d} > 0$  such that any global state  $(v, \eta)$  such that

$$\mathbf{E}(v, \eta) - \mathbf{E}(v^\circ, \eta^\circ) < \mathcal{d}$$

satisfies

$$\|v - v^\circ\| < \varepsilon \quad \text{and} \quad \|\eta - \eta^\circ\| < \varepsilon.$$

(The converse, of course, is trivial.) Coleman then defines thermodynamic processes of “regular fluids,” a class of fluids which includes fluids that exhibit linear and non-linear viscosity, heat conduction, and stress relaxation in a long-range memory as well as the perfect fluids of classical hydrodynamics. He also gives a precise meaning to the physical concept of a body immersed in an environment at fixed pressure  $p^\circ$  and temperature  $\theta^\circ$  and introduces the canonical free energy of the body in the environment  $p^\circ, \theta^\circ$  by

$$\mathbf{P}(t) = \mathbf{E}(t) + \mathbf{K}(t) + p^\circ \mathbf{V}(t) - \theta^\circ \mathbf{H}(t)$$

where  $\mathbf{V}(t)$  is the total volume of the fluid,  $\mathbf{K}(t)$  the kinetic energy,  $\mathbf{H}(t)$  the total non-equilibrium entropy and  $\mathbf{E}(t)$  the total internal energy. Extending an earlier argument of P. Duhem, he proves that  $\mathbf{P}$  is monotone decreasing with time in every process compatible with the environment. The main result of the paper *On the Stability of Equilibrium States of General Fluids* gives a dynamical significance to the stability criterion (19) in terms of Liapunov stability: Under the above assumptions on the convexity of  $\bar{\varepsilon}$ , for each  $\varepsilon > 0$  there exists a  $\mathcal{d} > 0$  such that for any process compatible with the environment that satisfies

$$\mathbf{P}(t) - \mathbf{P}(v^\circ, \eta^\circ) < \mathcal{d}$$

at some time  $t$ , satisfies

$$\mathbf{K}(t') < \varepsilon, \quad \|v(\cdot, t') - v^\circ\| < \varepsilon \quad \text{and} \quad \|\eta(\cdot, t') - \eta^\circ\| < \varepsilon$$

for all times  $t' \geq t$ . Here  $v(\cdot, t')$  and  $\eta(\cdot, t')$  denote the fields of the specific volume and specific nonequilibrium entropy at time  $t'$  in the process.

**Foundations of thermodynamics** A substantial part of Coleman's efforts in the seventies and early eighties was devoted to the foundations of thermodynamics. His work here goes against the arrow of time: his 1963 paper on thermodynamics with W. Noll starts from the postulation of temperature and entropy satisfying the Clausius-Duhem inequality. His 1974 paper with D. Owen *A mathematical foundation for thermodynamics*, to be discussed below, constructs the nonequilibrium entropy provided the absolute temperature is available that satisfies the Clausius inequality for cyclic processes

$$-\int_{\partial\mathcal{P}} \frac{\mathbf{q} \cdot \mathbf{n}}{\theta} d\mathcal{S} + \int_{\mathcal{P}} \frac{r}{\theta} dm \leq 0,$$

often written in an abbreviated form

$$\int \frac{dQ}{\theta} \leq 0.$$

Finally, the paper by B. D. Coleman, D. R. Owen, and J. Serrin, *The second law of Thermodynamics for Systems with Approximate Cycles* derives the absolute temperature satisfying the Clausius inequality from the existence of the empirical temperature (J. Serrin's *hotness*) which enters into a precise "primitive" statement of the second law that formalizes the verbal maxims of S. Carnot, Lord Kelvin, and R. J. E. Clausius. The actual course of history was opposite to the sequence of Coleman's works. The analysis of the efficiency of heat engines resulted first in the notion of absolute temperature, then in the Clausius inequality for cyclic processes, and finally in the notion of entropy satisfying the entropy inequality in one form or another.

With the paper by B. D. Coleman & D. Owen, *A mathematical foundation for thermodynamics*, the notion of state has returned to rational thermodynamics. The abstract approach of Coleman & Owen introduces the collection  $\Sigma$  of states  $\sigma$  and the collection  $\Pi$  of processes  $P$  of a thermodynamical system. Both  $\Sigma$  and  $\Pi$  are treated as primitive concepts. A system is the pair  $(\Sigma, \Pi)$  such that  $\Sigma$  is a Hausdorff space and each element  $P$  of  $\Pi$  determines a continuous mapping  $\sigma \mapsto P\sigma$  of an open subset  $\mathcal{D}(P)$  of  $\Sigma$  into  $\Sigma$ , the "transformation induced by  $P$ ." The pair  $(\Sigma, \Pi)$  obeys two fundamental axioms: (I) for each  $\sigma$  in  $\Sigma$ , the set of states of the form  $P\sigma$  with  $P \in \Pi$  in (i.e., the set of states "accessible from  $\sigma$ ") is dense in  $\Sigma$ ; (II) if  $P'$  and  $P''$  are processes such that the range  $\mathcal{R}(P')$  of the transformation  $\sigma \mapsto P'\sigma$  induced by  $P'$  intersects the domain  $\mathcal{D}(P'')$  of the transformation  $\sigma \mapsto P''\sigma$  induced by  $P''$  then  $\Pi$  contains a process,  $P''P'$ , whose induced transformation is the composition of  $\sigma \mapsto P''\sigma$  and  $\sigma \mapsto P'\sigma$ .

An action  $\alpha$  for a system assigns to a pair  $(P, \sigma)$  a number  $\alpha(P, \sigma)$ , referred to as the supply of  $\alpha$  on going from  $\sigma$  to  $P\sigma$  via the process  $P$ . The function  $(P, \sigma) \mapsto \alpha(P, \sigma)$  must be continuous in  $\sigma$  and additive on processes in the sense that

$$\alpha(P, \sigma) = \alpha(P'', P'\sigma) + \alpha(P', \sigma)$$

for each  $P', P''$  and  $\sigma$ . An action  $\alpha$  is said to have the Clausius property at a state  $\sigma$  if  $\alpha(P, \sigma)$  is approximately negative for every process  $P$  that is nearly cyclic at  $\sigma$ , i.e., if for each  $\varepsilon > 0$  there is a neighborhood  $\mathcal{O}$  of  $\sigma$  such that

$$\alpha(P, \sigma) < \varepsilon \tag{20}$$

whenever  $P$  is a process with  $P\sigma \in \mathcal{O}$ . In particular, if the process happens to be cyclic in the exact sense, i.e., if  $P\sigma = \sigma$ , then (20) implies

$$\alpha(P, \sigma) \leq 0. \quad (21)$$

Inequalities (20) and (21) are abstract counterparts of the Clausius inequality for cyclic processes. The need of the  $\varepsilon$ -version (20) arises because materials with fading memory have only few exact cycles while the supply of approximate cycles is large. A real-valued function  $A$  on a dense subset of  $\Sigma$  is called an upper potential for an action  $\alpha$  if for each pair  $(\sigma_1, \sigma_2)$  of states in the domain of  $A$  and for each  $\varepsilon > 0$ , there is a neighborhood  $\mathcal{O}$  of  $\sigma_2$  such that

$$A(\sigma_2) - A(\sigma_1) > \alpha(P, \sigma_1) - \varepsilon,$$

for every process  $P$  with  $P\sigma_1$  in  $\mathcal{O}$ . The main result of the paper *A mathematical foundation for thermodynamics* asserts that if there is a state  $\sigma \in \Sigma$  at which an action  $\alpha$  has the Clausius property, then  $\alpha$  has an upper semicontinuous upper potential, and conversely. The paper by Coleman & Owen deals with a number of topics such as the non-uniqueness of upper potentials, their extensions to larger domains, with stagnating families of processes, and relaxed states.

The paper then proceeds to apply the theory of actions on systems to concrete materials of continuum thermodynamics. The action  $\alpha$  is identified with the Clausius integral

$$- \int_{\partial \mathcal{P}} \frac{\mathbf{q} \cdot \mathbf{n}}{\theta} d\alpha + \int_{\mathcal{P}} \frac{r}{\theta} dm.$$

The postulation of the Clausius property for  $\alpha$  then amounts to the postulation of the Clausius inequality for cyclic process, and the resulting upper potential is the entropy. The paper then treats thermoelastic materials, materials with internal variables, materials with fading memory and viscous materials from the point of view of systems  $(\Sigma, \Pi)$  and shows that many results which have been obtained from the Clausius-Duhem inequality are consequences of a weaker form of the second law of thermodynamics.

The culmination of this line of thought is *The second law of thermodynamics for systems with approximate cycles*, co-authors Owen & Serrin, 1982. The paper formulates a precise statement of the second law which does not presuppose the existence of entropy or absolute temperature and employs only approximate cycles. Basic to the theory is the hotness manifold  $\mathcal{H}$ . This is a continuous, oriented, one-dimensional manifold whose points  $L$  are called levels of hotness. The orientation of  $\mathcal{H}$  induces a total strict order  $\prec$  on levels of hotness, with  $L_1 \prec L_2$  meaning that  $L_1$  is a lower level of hotness than  $L_2$ . The second ingredient is the concept of a thermodynamical system  $(\Sigma, \Pi, Q)$ . It consists of the state space  $\Sigma$ , class of processes  $\Pi$ , and the accumulation function  $Q$ . The pair  $(\Sigma, \Pi)$  is the system in the sense discussed above. The function  $Q$  which assigns to each triplet consisting of a process  $P \in \Pi$ , state  $\sigma \in \Sigma$ , and a hotness level  $L \in \mathcal{H}$  a number  $Q(P, \sigma, L)$ , the net heat transferred to the system at levels of hotness at or below  $L$  in the process  $P$  starting from the state  $\sigma$ . It is assumed that (I) for each  $L \in \mathcal{H}$  the real-valued function  $(P, \sigma) \mapsto Q(P, \sigma, L)$  is an action on  $(\Sigma, \Pi)$ , (II) for each pair  $(P, \sigma)$  the function  $L \mapsto Q(P, \sigma, \cdot)$  has at most a countable number of discontinuities and (III) there are hotness levels  $L^\ell$  and  $L''$  such that  $Q(P, \sigma, \cdot)$  vanishes for all  $L \prec L^\ell$  and is constant for all  $L$  such that  $L \succ L''$ . In other words, the system exchanges heat with its environment at hotness levels  $L$  satisfying  $L^\ell \leq L \leq L''$ . The process is then said to operate at or below  $L''$ .



The value  $\bar{Q}(P, \sigma) := Q(P, \sigma, L^\infty)$  is the total net heat transferred to the system in the process  $(P, \sigma)$ .

The main message of the second law is that a cycle that produces a positive work not only has to absorb heat but also emit at least small amount of heat. Accordingly, we say that a process  $(P, \sigma)$  is absorptive if for each level of hotness  $L$  there holds

$$Q(P, \sigma, L) \geq 0.$$

Noting that for cyclic processes the work done by a system is equal to the total net heat transferred to the system, we see that the second law says that every absorptive cyclic process satisfies

$$\bar{Q}(P, \sigma) = 0.$$

The second law for approximate cycles then requires that for each state  $\sigma \in \Sigma$ , for each  $\varepsilon > 0$ , and for each hotness level  $L \in \mathcal{H}$ , there is a neighborhood  $\mathcal{O}$  of  $\sigma$  such that

$$0 \leq \bar{Q}(P, \sigma) < \varepsilon$$

for every process  $P$  for which  $(P, \sigma)$  is absorptive, operates at or below  $L$ , and has its final state  $P\sigma$  in  $\mathcal{O}$ . Thus the overall net gain of heat cannot be significant in an absorptive approximate cycle which operates at or below a fixed level of hotness. The second law is assumed to hold for all members  $(\Sigma, \Pi, Q)$  of a thermodynamic universe  $\mathbb{U}$ , a collection of thermodynamical systems that is closed under the operation of union of thermodynamic systems and which contains at least one ideal system. We omit the natural definitions of the last two notions. The main result then says that the second law holds for all systems in  $\mathbb{U}$  if, and only if, there exists a monotone increasing function  $\varphi : \mathcal{H} \rightarrow (0, \infty)$  such that for each of these systems is such that the accumulation integral

$$e(P, \sigma) := \int_0^\infty \frac{Q(\sigma, P, \varphi^{-1}(\theta))}{\theta^2} d\theta \quad (22)$$

is “approximately negative” on “approximate cycles” operating at or below a fixed level of hotness. Formally, for each system  $(\Sigma, \Pi, Q)$  in  $\mathbb{U}$ , each state  $\sigma \in \Sigma$ , each level of hotness  $L \in \mathcal{H}$ , and each  $\varepsilon > 0$  there exists a neighborhood  $\mathcal{O}$  of  $\sigma$  such that

$$\int_0^\infty \frac{Q(\sigma, P, \varphi^{-1}(\theta))}{\theta^2} d\theta \leq \varepsilon \quad (23)$$

for each  $P \in \Pi$  satisfying  $P\sigma \in \mathcal{O}$ . If the accumulation function  $Q(P, \sigma, \cdot)$  is of bounded variation then an integration by parts yields

$$\int_0^\infty \frac{dQ(\sigma, P, \varphi^{-1}(\theta))}{\theta} \leq \varepsilon.$$

The absolute temperature scale  $\varphi$  is obtained from an analysis of an ideal system postulated to be contained in  $\mathbb{U}$ . By (23), the action  $e$  from (22) has the Clausius property. Consequently, it has an upper potential  $S$ , defined on a dense subset of  $\Sigma$ , such that for every  $\sigma_1$  in the domain of  $S$  every  $\sigma_2 \in \Sigma$  and every  $\varepsilon > 0$  there exists a neighborhood  $\mathcal{O}$  of  $\sigma_2$  such that

$$S(\sigma_2) - S(\sigma_1) > \int_0^\infty \frac{Q(\sigma, P, \varphi^{-1}(\theta))}{\theta^2} d\theta - \varepsilon,$$

for every process  $P$  with  $P\sigma_1$  in  $\mathcal{O}$ . This is the (abstract form) of the Clausius-Duhem inequality, the starting point of the 1963 paper on the Coleman-Noll procedure.

**DNA** Colemans most recent work is on the mechanics of DNA strands. Like everything other subject he touched, each important scientific aspect of the problem is considered – the chemistry, biology, mechanics and mathematical analysis. Perhaps his most compelling work in this area is that carried out with his former Ph.D. student David Swigon. Like many a biophysicist before them, they end up analyzing an elastic thin-rod model for the mechanical response of DNA – in an effort to understand things like supercoiling. In the age we now live in, experimental results for the twisting and bending of actual stands of DNA abound. In their paper “Theory of supercoiled elastic rings with self-contact and its application to DNA plasmids”, they were the first to account for and overcome the difficulty of global self-contact. That is, as the strand supercoils (say under imposed twist), it almost immediately makes contact with itself again and again, which Coleman and co-workers were able to capture in their analysis. In addition to providing an important and realistic application to the mechanical response of DNA—the first of its kind—their work provides the solution of an unsolved problem in the mechanics of rods.

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