ON THE SYSTEMATICS OF ENERGETIC TERMS IN CONTINUUM MECHANICS, AND A NOTE ON GIBBS (1877)

FALK H. KOENEMANN
Im Johannistal 19
D-52064 Aachen, Germany
peregrine@t-online.de

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The systematics of energetic terms as they are taught in continuum mechanics deviate seriously from the standard doctrine in physics, resulting in a profound misconception. It is demonstrated that the First Law of Thermodynamics has been routinely re-interpreted in a sense that would make it subordinate to Bernoulli's energy conservation law. Proof is given to the effect that the Cauchy stress tensor does not exist. Furthermore, it is shown that the attempt by Gibbs to find a thermodynamic understanding for elastic deformation does not sufficiently account for all the energetic properties of such a process.

Keywords: elasticity, thermodynamics, deformation theory

1. Introduction

Late in his life, Kestin[1] observed, "The subject of 'conventional' thermodynamics, as it is taught more or less correctly, ... and the subject of solid mechanics, often taught as strength of materials, have developed largely independently of each other. Although both, ultimately, allow engineers to use them for design and testing with rather satisfactory results, they are not consistent with each other. They certainly failed to converge to this day. In a situation like this it is quite natural to think that, perhaps, the foundations of both disciplines are at fault." It is strange to see that some people have indeed noticed the profound chasm between continuum mechanics and thermodynamics, and still they were clueless as to how this contrast came about, or how it could be closed.

By its mathematical structure and physical outline the thermodynamic theory is in line with potential theory: it considers changes of the energetic state, hence during a thermodynamic process there are energetic fluxes between system and surrounding, thus an approach must start mathematically with a Poisson equation, $\nabla^2 U = \varphi$, as Born[2] requested for all of continuum physics. There is only one exception. Continuum mechanics was founded long before the necessity to distinguish system and surrounding was recognized, before it was realized that Newtonian work and *PdV*-work are very different things, and even before energy and force were clearly separated as different entities. Hence, the mathematical structure of continuum mechanics is conservative; in effect, the quaint concept of a *force conservation law* has survived until today from an era when it was not known yet that the energy of a system can be a variable. For Euler in the late 18th century it made perfect sense to postulate that $tr\,\sigma = 0$ (σ = stress tensor); today the condition is recognized as one form of the Laplace condition which characterizes the process as conservative, which is against the nature of an elastic deformation.

The assumptions made in the derivation of the Cauchy stress tensor have been shown to be incompatible with potential theory.[3] The continuum mechanics theory has been critically reviewed, and the first steps towards a new approach have been outlined.[4] It is this author's firm opinion that continuum mechanics should have been founded again 150 years ago, right after the discovery of the First Law of Thermodynamics when the systematics of energetic terms became completely known; unfortunately this has not been done. Instead, the difference between conservative and non-conservative physics, the most profound and fundamental difference among the classes of physical processes, was so thoroughly blurred in material science that up to this day people have serious difficulties to recognize it – because they have been trained not to see it. Plainly, an equation of motion is only and exclusively the proper first step into a theory if the process under discussion is conservative, involving the mechanics of *n* discrete bodies in free space, which does not change the total energy of the system of *n* bodies; whereas a nonconservative process, by definition a change of state, must be approached by an equation of state. By nature, all of continuum physics falls into the latter category, including elasticity. The rather profound physical differences between conservative Newtonian mechanics and thermodynamics are listed in Table 1.

In the first part of this communication I give an example to demonstrate that the systematics of energetic terms in continuum mechanics is at variance with modern physics. In the second part I wish to demonstrate that even a man who is rightfully counted among the founding fathers of modern thermodynamics, had a hard time to free himself completely from the spell cast over the 19th century by Euler and his conservative concepts.

Table 1

	Newtonian Mechanics	**Thermodynamics**
governing equation	equation of motion $\mathbf{f} = m\mathbf{a}$	equation of state $PV = nRT$
condition of equilibrium	Newton's Third Law: equilibrium of two two colliding bodies: $\mathbf{f}_1 + \mathbf{f}_2 = 0$	equilibrium of system and sur-rounding: $P_{syst} + P_{surr} = 0$
definition of work	$w = \mathbf{f} \cdot \mathbf{d}$ always linear	$\int dw = \int PdV$ always spatial
energy conservation law	Bernoulli: $E_{kin} + E_{pot} = const$	First Law: $dU = dw + dq$
purpose of theory	understanding of work done *within* a system against inertia, acceleration work	understanding of energetic changes of state, work done *upon* a system against its internal energy
path independence of work	in Euclidean space	in *PV*-space
reference potential	velocity potential	thermodynamic-electromagnetic potentials
time as a parameter	indispensable	time-independent
application	physics of discrete bodies in free space	physics of continuously distributed mass

Is it at all possible to understand elastic behavior as a linear physical process? The idea comes from Hooke[5] and his experiments. In modern light the range of his data is so small that not much can be concluded from them, except that the work function is continuous. In the technical application the law is long known to be insufficient. Also, a proper discussion of the boundary conditions is usually missing in the statement of the law. It does matter, however, if the displacement type is that of plane pure shear, plane simple shear, or axial shortening; whether the reference mass is part of a larger continuum of solid, or whether free surfaces are nearby, such as for a bar; and even its shape is important. Furthermore, whether a pattern of data points follows a straight line, a circle, a sine function or a power law cannot in general be decided from the phenomenology of the graph – consider the shape of the Earth at small scale – but only and exclusively from the theoretical context. Elastic deformation is a change of state; all thermodynamic work functions are logarithmic, hence elasticity must be logarithmic. The difference between a linear law and a logarithmic law may not matter phenomenologically, especially within the very short range that is available to reversible elastic behavior before failure. However, it has the most profound consequences for the mathematical structure of the theory which, after all, serves as the guide in uncharted theoretical terrane. If it is wrong, it leads astray.

2. Systematics of Energetic Terms in Physics

From the systematics of energetic terms as they are understood today (Fig.1), the sum of the kinetic energy and the potential energy of *n* discrete bodies give the *entire mechanical energy* of a kinetic system,

$$E_{\text{kin}} + E_{\text{pot}} = H = const; \tag{1}$$

this sum is known as Bernoulli's law, the energy conservation law of conservative physics. E_{pot} represents all potentials that may be observed, e.g. gravity; in the context here the emphasis is on the electromagnetic potentials of the atoms, since the bonds in a solid are electromagnetic in nature. Whereas the transfer of kinetic energy from one body to another requires bodily contact, electromagnetic forces act over a distance. A force in the sense of the equation of motion $\mathbf{f} = m\mathbf{a}$ is only one single vector whereas electromagnetic forces are always field forces; thus the two types of forces differ profoundly in their physical, and mathematical properties.

By convention, the notation *H* is used in mechanics if processes are considered where eqn.1 is observed, i.e. $H = const$. If the RHS is a variable, however, the common notation differs since

$$H = U \tag{2}$$

is the *internal energy* of thermodynamics in the standard state. Any change of the state U_0 requires energetic fluxes between system and surrounding, either in form of work *dw* or in form of heat *dq*; hence the *change of state* is given by

$$dU = dw + dq, \tag{3}$$

which is the First Law of Thermodynamics, the energy conservation law for nonconservative processes. The changed state is thus given by $U_0 + dU = U_0 + dw + dq$.
It is not possible to understand the mechanical behavior of solids in terms of $\mathbf{f} = m\mathbf{a}$. Clausius[6] and Grüneisen[7] identified the forces effective within and without a solid

$$\frac{1}{3}\left(\sum m\overline{\mathbf{v}^2} + \sum rf(r)\right) = PV \tag{4a}$$

where the first term LHS contains the kinetic energies of the oscillating atoms (m = atomic mass, $\mathbf{v}$ = velocity); the second term contains the product of the distance r between two atoms and the forces f acting between them; V is the molar volume and P the pressure to which the solid is subjected. Eqn.4a is identical to eqn.1. Clausius[6] equated the first term LHS (kinetic energy) with heat; for adiabatic mechanical loading it is without consequences in solids at temperatures below the diffusion limit, and subsequently ignored. Grüneisen[7] expanded the second term LHS into the potential due to the attracting forces f_1 and the potential due to the repulsive forces f_2 in a solid. In the unloaded state the RHS is zero, and since a solid in a vacuum is in equilibrium with itself, eqn.4a reduces to

$$\left(\sum rf_1 + \sum rf_2\right) = 0 \qquad (4b)$$

where both f_1 and f_2 are electromagnetic in nature, and r is the zero potential distance. These are the forces with which forces f_{surr} due to external loading (eqn.4a when RHS $\neq 0$) must interact.

An elastic vibration requires an elastically loaded state $U_1 = U_0 + \Delta U$ as starting condition. During a vibration there is a continuous transformation of ΔU into kinetic energy E_{vib} and back, but this is not the kinetic energy E_{kin} of conservative physics in eqn.1; the transformation of E_{pot} into E_{kin} and back requires Newtonian work to be done while the state H is invariant, whereas a vibration causes alternating states with the extremes U_0 and U_1 or, in the case of a volume vibration, $U_0 \pm \Delta U$. The motion of a body in free space is a free motion with free velocity (within the limits given by H) whereas a vibration is not a free motion, and its 'velocity' is a material property. The energy conservation laws $E_{kin} + E_{pot} = const$ and $\Delta U + E_{vib} = const$ look similar, but they should not be mixed up.

If the surface A of a system is understood to contain n discrete bodies in free space, we can consider either the transformation of their E_{pot} into E_{kin} and vice versa according to eqn.1, or we can consider energetic exchanges between the system as a whole and a surrounding according to eqn.3 to the effect that the dimensions of the system and/or the velocities $\mathbf{v}$ of the n bodies change; in the latter case H changes and thus the internal energy U of the entire system, but the interior of the n bodies themselves is not accessible to consideration in either case, especially not their internal energetic state. If the system is understood to coincide with the dimensions of a discrete body or to form a subregion within it, only the interaction of system and surrounding can be considered, but any kinetic energy associated with this body in some external free space is irrelevant. That is, E_{kin} is by nature a subset of U; neither in the first nor in the second case can an internal energy U and an external kinetic energy E_{kin} be logically summed.

The contrast between eqn.1 and eqn.3 is expressed in concise form by the tools of potential theory. The divergence of a force field div $\mathbf{f}$ is interpreted as „a measure of the work done upon/by a system" (Ref.8:79-81). The Laplace condition $\nabla^2 U = \text{div}\,\mathbf{f} = 0$ (U = some potential) characterizes conservative physical problems, indicating that work was done only *within* the system, and no change of state has occurred. However, if a change of state is observed, the Poisson condition div $\mathbf{f} = \varphi$ indicates that there were non-zero energetic exchanges between system and surrounding, and the process is non-conservative, i.e. work has been done *upon* the system. The divergence φ is a measure of thermodynamic work per unit mass, it is also called the source density or charge density. (The condition $tr\,\sigma = 0$ above is a form of the Laplace condition, implying that no work was done during elastic loading.)

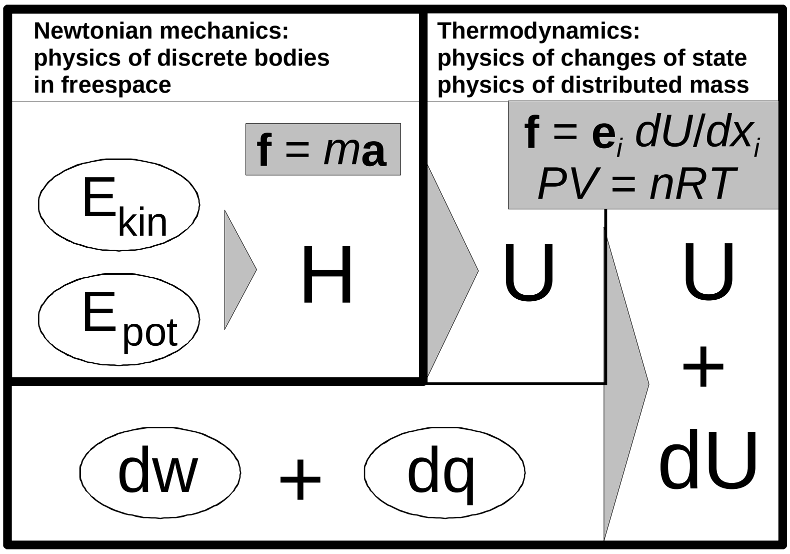

Fig.1 Systematics of energetic terms in physics. For explanation see text.

Whereas a real gas may be understood simplistically as a kinetic system of *n* bodies which interact only and exclusively through collisional contact, that is certainly not possible for solids. Solids and fluids consist of condensed matter, they are internally bonded. They have a considerable internal pressure (ca.0,5kbar for solid K, 2,5kbar for solid Li) which is a concept of use entirely in a thermodynamic context. The internal pressure is defined as the pressure a mol of substance would have if it were an unbonded ideal gas that is compressed to the molar volume of the same substance in solid form. That pressure is internally balanced by the bonds (eqn.4b), such that solids have a finite volume in equilibrium with a vacuum, and any external load interacts with that internal pressure. This concept has no place within the framework of Newtonian mechanics. Characteristically, bonds in solids are never mentioned in all textbooks on continuum mechanics known to this author. Consequently, the discussion of forces effective in the deformation of continua has in fact never been complete.

3. Textbook Examples

The following examples are taken from textbooks which are often cited as reference authorities, their authors are deceased. There is no dearth of evidence to demonstrate that elastic deformation is understood as an energetically conservative process up to this day.

1. Love (Ref.9:94) gives the First Law of Thermodynamics as

$$\iiint (\delta T_1 + \delta U)\,dxdydz = \delta W_1 + \delta Q \qquad (5a)$$

where δT is the kinetic energy, δU the intrinsic (internal) energy, δW is the work, and δQ the supplied heat.

2. Fung (Ref.10:346) gives the First Law of Thermodynamics in the form

$$\dot{K} + \dot{E} = \dot{Q} + P \tag{5b}$$

where the dot denotes the material derivative D/Dt. K is the kinetic energy, E the internal energy per unit mass, and Q the heat input. P is the sum of the work done by the body force per unit volume and the surface traction. The time derivative is implied because the acting force is understood as moment per unit time, i.e. it is a direct reference to Newton's Second Law.

3. Budó (Ref.11:356) gives the First Law of Thermodynamics in the form

$$dQ + dA_a = dE_k + dU \tag{5c}$$

where Q is the supplied heat, A_a is the work done by the external forces, E_k is the kinetic energy, and U the internal energy, all per unit volume.

This is not the First Law of Thermodynamics. These formulations are in fact an attempt to reinterpret the energy conservation law for changes of state (eqn.3) as conservative in the sense of Bernoulli (eqn.1), and in fact to turn the First Law upside down. The kinetic energy E_{kin} is a subset of the internal energy U (eqn.2, eqn.4a, Fig.1). They cannot be treated as independent terms, therefore they cannot be summed.[12] It is this conservative structure in the theory of elasticity – which is due to Euler – that results invariably in the conclusion that a volume-neutral deformation does not require work (see below).

The expression of the First Law as a time derivative (eqn.5b) must be startling to any thermodynamicist. After all, changes of state are time-independent. The reason is simple: because continuum mechanics is an adaptation of Newton's theory, continuum mechanics does not know any other definition of a force than $\mathbf{f} = m\, d\mathbf{p}/dt = m\mathbf{a}$, the rate of momenta $\mathbf{p}$ per unit time. But this definition is a very special one, it applies only and exclusively to the acceleration $\mathbf{a}$ of a discrete body with inertial mass m in free space, but not to continuum physics. The far more general definition $\mathbf{f} = \mathbf{e}_i \partial U/\partial x_i$ where U may be any potential, including thermodynamic (electromagnetic) potentials, defines a force field, and it is time-independent. However, it has never been used in continuum mechanics. Continuum mechanics in its present form is not a field theory in the sense this term is commonly understood because force fields must be derived from a potential.

Newton's mechanics starts with an equation of motion because the state of the kinetic system is invariant, and Newtonian work is work done *within* the system; it is acceleration work, leading to a transformation of E_{kin} into E_{pot} and vice versa, with the energy function, the Hamiltonian H remaining constant (eqn.1). Such processes describe a path in the Hamiltonian position-velocity space. Instead, the approach to a change of state starts with an equation of state because the state of the system U is a variable, and PdV-work is work done *upon* a system; it describes a path in PV-space.

4. Love (Ref.9:166) treats deformation as a variation, starting with Hamilton's principle

$$\int \delta(T - V)\, dt + \int \delta W dt = 0 \tag{6}$$

where T and V are the kinetic and potential energy. The same is done by Sneddon & Berry (Ref.13:15, 2nd eqn.) and Green & Zerna (Ref.14:73, eqn.2.7.6).

A variation is a conservative concept in strict observation of Bernoulli's law, i.e. any changes of state are *by definition* excluded from consideration. (One must consider that the theory of variations was invented by Euler who died 60 years before the First Law, and thus nonconservative physics, was discovered. The only energy conservation law known to Euler was Bernoulli's law, eqn.1. It is also worth knowing that Euler did not consider elastic deformation of solids, but the flow of water which he visualized as a friction-free Newtonian fluid, i.e. a perfectly unbonded substance.) The difference (T - V) is known as the *kinetic potential*, hence δW is interpreted as Newtonian work, i.e. acceleration work, i.e. within the constraints of Bernoulli's law, but not as PdV-work; the sum ($T + V$) is, after all, invariant (eqn.1).

5. Revealing is the remark by Green & Zerna (Ref.14:73f, nearly literally repeated by Sneddon & Berry, Ref.13:15): „If the strained body is in equilibrium then $\mathbf{f} = \mathbf{0}$ and the virtual work (A in Ref.14 = W in Ref.9) of the external forces acting on the body becomes $\delta^*A = \delta U$; […] this states that the variation of the total potential energy (U in Ref.14 = V in Ref.9) has a stationary value."

That equilibrium condition is the external one, Newton's Third Law, the sum of all external forces. It is not the thermodynamic equilibrium condition $\mathbf{f}_{int} + \mathbf{f}_{surr} = 0$, it has in fact not been considered. The expression 'virtual work' is fitting – in the light of the condition $H = const$ (eqn.1).

It has escaped the mechanics of solids community that William Hamilton was an astronomer who pondered *celestial* mechanics, i.e. the physics of discrete bodies in freespace. His theory could be adapted to the mechanics of solids only by ignoring the properties of solids altogether. Elastic deformation work is not at all virtual, but very real indeed, it is akin to PdV-work; elastic deformation is a change of state, to be approached only and exclusively by means of an equation of state such as $PV = nRT$ (for a solid a more general form must be sought), and not a variation.

4. Consequences

The consequence of the attempt to interpret elastic deformation as a conservative process in the sense of eqn.1 is that it is not possible to derive a non-zero work term for a volume-constant elastic deformation. This shall be demonstrated in three different ways.

1. Euler's continuity condition is

$$\frac{\partial \rho}{\partial t} + \rho \frac{\partial v_i}{\partial x_i} = 0 \qquad (7)$$

where ρ is the density of the inertial mass, and **v** is the velocity. If volume and thus density are invariant, the first term is zero. The second term indicates that all paths cancel for a volume-constant deformation, that stretch displacements and contraction displacements sum to zero. If so, the work done must cancel as well since stretch work and contraction work have opposite sign. Hence the total work is zero.

2. The First Law of Thermodynamics is

$$dU = - PdV + TdS \qquad (8a)$$

in expanded form

$$dU = - PdV - \sigma_{ij}d\varepsilon_{ij} + TdS \tag{8b}$$

where the first term RHS is isotropic, and the second term contains only the isochoric deformation work (σ = stress tensor, ε = strain tensor). Thus for a volume-neutral deformation $PdV = 0$, the condition of reversibility is $TdS = 0$, and we are left with $dU = - \sigma_{ij}d\varepsilon_{ij}$. Although tensor products do not communicate (**AB** ≠ **BA**) in general, the trace of a tensor is an invariant, and the trace of the tensor product does communicate (tr **AB** = tr **BA**, tr **A** tr **B** = tr **B** tr **A**). But the condition of volume invariance is both $\sigma_{ii} = 0$ and $d\varepsilon_{ii} = 0$. It follows that for a volume-neutral deformation dU = 0, and no work is done. – Batchelor (Ref.15:141-147) uses a different terminology, but he is perfectly clear in his discussion of the deviatoric stress tensor that it does not contribute energetically to the deformation.

3. In Landau & Lifschitz (Ref.16:7-9) the equilibrium condition is

$$\frac{\partial \sigma_{ij}}{\partial x_j} = 0 , \tag{9}$$

and the work of the internal tensions per unit volume is

$$\delta R = -\sigma_{ij}\delta u_{ij} \tag{10}$$

where u is the displacement, such that

$$\int dR\, dV = \int \frac{\partial \sigma_{ij}}{\partial x_j} du_i\ dV \tag{11}$$

(eqn.3,1 in the source text). But according to eqn.9 the integrand on the RHS is zero such that the total work is zero. Additionally, the volume-constant condition is $\partial u_i/\partial x_i = 0$, hence $\int dR\ dV$ has no choice but to be zero, and no work is done in an elastic deformation.

A subtle inconsistency in the three arguments concerns the mass term. Eqn.7 uses the inertial mass [kg], whereas in the following arguments the thermodynamic mass is implied which is dimensionless and measured in mol. In other words, Newtonian and thermodynamic concepts are implicitly taken to be equivalent. However, this is incorrect. If Newtonian terms are used, the work done in the process under discussion concerns the acceleration or displacement of inertial mass in freespace *within* a kinetic system, under the constraint that the energy of the isolated system is invariant, $E_{\text{kin}} + E_{\text{pot}} = const.$ If thermodynamic terms are used, the energy conservation law is necessarily the First Law (eqn.3), and the work is done *upon* a system: the system interacts with a surrounding, its energy U is a variable. Mixing these concepts produces impressive equations, but not useful physics.

Another inconsistency exists in the contrast of the understanding of the stress tensor by Love[9], Fung[10], Budó[11], Sneddon & Berry[13], and Green & Zerna[14] on one hand, here called the Euler-Cauchy-stress, and Landau & Lifschitz[16] on the other. The Euler-Cauchy-stress tensor is solidly based on the entire Newtonian framework for the mechanics of discrete bodies in freespace. The Euler-Cauchy-theory of deformation and flow was concluded in 1821 by Cauchy. Necessarily, physical concepts based on the First Law (eqn.3) cannot have been considered since the latter was discovered only in 1842. It is not possible to transform it into a proper differential approach; none of the quoted sources make an attempt to do so, nor any other sources known to me. Yet Landau's tensor is embedded in a differential approach. Apparently Landau saw the necessity to postulate his tensor in order to develop a differential approach because that is the standard path into modern physics. Landau's tensor is postulated and without conceptual root. Thus, the Euler-Cauchy-stress tensor and Landau's tensor are not identical, and in fact incompatible with one another; they are two independent propositions.

5. Refutation of Cauchy Stress

Above (eqn.9-11) it is shown that Landau's tensor is insufficient. The refutation of Cauchy's tensor is repeated here from Ref.3. Consider a system of distributed mass within a larger volume of distributed mass. For simplicity, the system is assumed to be spherical, and the distributed mass may be bonded as in a solid, or unbonded as in a gas. Its pressure is given by $P = \Delta U/\Delta V$ which is an explicit statement of the proportionality of mass and energy in some given state. Both the externally applied forces and the forces exerted by the system upon the surrounding form radial force fields, one directed inward, one outward, such that at every point on the system surface A the equilibrium condition is $\mathbf{f}_{syst} + \mathbf{f}_{surr} = 0$, which translates into the thermodynamic equilibrium $P_{syst} + P_{surr} = 0$. Since the system contains mass, and since it interacts with the surrounding through exchange of work, it acts as a source of forces. An existence theorem in potential theory requires that if there is a function f of a point Q such that

$$\int f(Q) dV = \kappa\,, \tag{12}$$

both sides must vanish simultaneously with the maxium chord of V if $V \to 0$ (Ref.8:45). The relation can thus be represented by the Gauss divergence theorem,

$$\int \mathbf{f}\cdot\mathbf{n}\, dA = \int \nabla\cdot\mathbf{f}\; dV = \kappa \tag{13}$$

where $\mathbf{f}$ is either one of the forces mentioned above, $\nabla\cdot\mathbf{f} = \varphi$ is the source density or charge density which is a constant that characterizes the state in which the system is, and $\kappa = \varphi V$ is the charge which is known to be proportional to mass in a given state. Thus in eqn.13, LHS $\propto \kappa \propto V$. Since $V \propto r^3$ where $r = |\mathbf{r}|$ is the radius of the system, but $A \propto r^2$, for LHS $\propto V$ to hold it follows that

$$\frac{|\mathbf{f}|}{|\mathbf{r}|} = const \tag{14}$$

This result is known since Poisson derived it in 1813 (Ref.8:156). Thus if $V \to 0$, both f and r vanish such that eqn.12 is observed. However, as $V \to 0$, $\Delta U/\Delta V \to const$, but

$$|\mathbf{f}|/A \to \infty. \tag{15}$$

The limit does not exist. The argument is necessary and sufficient proof that the Cauchy stress tensor does not exist.

Thus, the two definitions of pressure known to us, Newton's $P = |\mathbf{f}|/A$ and the thermodynamic $P = \Delta U/\Delta V$, are not equivalent, and only the latter can be used here. The continuity approach in Cauchy's theory of stress is based on the assumption that $|\mathbf{f}|/A \to const$ as $V \to 0$. This is not the case. Newton's definition only applies to free surfaces A, or to sections of closed surfaces at constant V, but not if A is closed and V is a variable. When Cauchy[17] worked out his theory, potential theory was still in its infancy, and the importance to distinguish system and surrounding was not understood yet (it is in fact missing entirely from continuum mechanics literature up to this day, cf. Ref.4). Thus he used Newton's Third Law as equilibrium condition – as did Euler – whereas the correct equilibrium condition is that of thermodynamics, of system vs. surrounding. Cauchy believed that in his continuity approach, P is independent of $|\mathbf{r}|$. He did not consider that $|\mathbf{r}|$ is a measure of the scale of the system, and mathematically related to mass, which is a variable in his limit operation. Today **r** must be equated with the zero potential distance [Ref.8:63] which may be infinite or finite, but it cannot be zero. In thermodynamics, **r** is the radius of the thermodynamic system, and thus finite, like n and V in $PV = nRT$. Cauchy's continuity approach is understood to be the proof of existence of the stress tensor. His reasoning violates the condition in eqn.12. (Batchelor [Ref.15:9f] noted the difference in behavior of volume terms and surface terms as $V \to 0$, but took the scale-independence of $|\mathbf{f}|/A$ for granted.)

6. Comment on Gibbs (1877)

The first sentence in Gibbs (Ref.18:343) is: „In treating of the physical properties of a solid, it is necessary to consider its *state of strain*."
It is therefore postulated *a priori* that strain is a state function. Here Gibbs follows Lagrange, who in turn follows Euler. The natural alternative would have been displacement. If strain *were* a state function, all identical states of strain should cost the same amount of work. It is known experimentally that the energetics of deformation differ for pure shear and simple shear for identical measures of strain, both in the elastic and the plastic field (and in an inverse manner[4]). Hence the state of *strain* is of limited physical interest, it bears insufficient information – energetic and geometric. Strain cannot be a thermodynamic state function; it can at best be understood as a geometric configuration state, but not as an energetic state.

On p.345 Gibbs derives an expression where ε_V is the energy per unit volume, the dx' etc. are the coordinates of the reference (unloaded) state, the dx etc. are the coordinates of the deformed state, and the X etc. are the axes of an external coordinate set in which the x' and the x are related to one another. The expression is

$$\delta\,\varepsilon_{V'}\,dx'\,dy'\,dz' = X_{X'}\,\delta\frac{dx}{dx'}\,dx'\,dy'\,dz'\,. \qquad (16)$$

"Now the first member of this equation evidently represents the work done upon the element by the surrounding elements; the second member must therefore have the same value. Since we must regard the forces acting on opposite faces of the elementary parallelepiped as equal and opposite, the whole work done will be zero except for the face which moves parallel to X."

If so, the work done must cancel for an isochoric deformation since stretch work and contraction work have opposite sign. Hence the total work is zero. Gibbs evidently assumed that no work is done in a direction in which nothing happens. This is a Newtonian thought, and it cannot possibly be correct; thermodynamic work is always done upon a *volume*. If we consider a volume of air in a tube that is closed by a piston, and we move the piston, the volume is changed. It is then found that a change of pressure has occurred on all air-container interfaces, not just the one that moved. If the substance were a solid (for the sake of the argument, the solid-tube interface is frictionless, and the solid is isotropic), the same result would be found.

The pressure in the Y and Z directions has increased *although* nothing has moved in these directions. This shows that the energetics of deformation can never be considered in one direction only. An example will demonstrate this in detail.

Step 1: if a gas is compressed in X, allowed to move in Z at constant external pressure, and Y is fixed, the gas will experience a change of shape – it is deformed – but not a change of state, $E_1 = E_0$ because $V_1 = V_0$. No work is done, no elastic potential has built up, $w_1 = 0$. If the same is done with a solid it will bulge in Z, but not freely because of the internal bonds, and an elastic-anisotropically loaded state is reached; the solid has undergone a change of state, $E_1 > E_0$, $w_1 > 0$. *Step 2*: if the dimensions X and Y are then kept fixed, and the walls in Z are moved back to their initial position, both gas and solid experience a change of state, $E_2 > E_1$ because $V_2 < V_0$, but whereas the gas is in an isotropically loaded state, the solid is still in an anisotropically loaded state. *Step 3*: to get the solid into an isotropically loaded state it is necessary to move all walls such that $\partial x/\partial x' = \partial y/\partial y' = \partial z/\partial z'$, resulting in a further volume change, and $E_3 > E_2$; ditto for the gas.

The total work done on the gas in E_3 is $w_2 + w_3$; the total work done on the solid is $w_1 + w_2 + w_3$. If the initial dimensions are changed from E_0 directly to E_2, the work done on the gas is thus w_2, for the solid it is $w_1 + w_2$. That is, the work component w_2 is due to the fact that the walls in Z do not move. This is counterintuitive at first, but this is the physical reality. It should also be clear that the state E_1 for the solid is not the lowest possible one for a given $\partial x_1/\partial x'$. Starting from E_1, if the wall in Y is allowed to move at constant $\partial x_1/\partial x'$, the solid would contract in Z, expand in Y until $\partial y/\partial y' = \partial z/\partial z'$, and the change of state would result in an energetic relaxation. If the same would be done with a gas it would not work; there would be no driving force for the expansion in Y, i.e. no potential that seeks to attain its lowest energetic state.

Thus a change of state, isotropic or anisotropic, is by nature a 3D-problem. Processes in one direction are never independent of the others. This also demonstrates that the equation of state $PV = nRT$ implies a particular set of boundary conditions – isotropic – which are always valid for slow flow of a gas because of the unbonded nature of gas, but not generally. All this was not considered by Gibbs, nor by anyone else.

It should be noted, too, that Gibbs' conclusion in the quote above is incompatible with standard continuum mechanics: Gibbs assumed that no work is done perpendicular to X if no change of length occurs in Y and Z. In conventional continuum mechanics the attenuation in Y and Z due to stretch in X is geometrically taken care of by Poisson's ratio, yet the work done is only considered to be due to stretch in X whereas work due to attenuation in Y and Z is never considered, and thus implicitly assumed to be zero. Neither can both assumption sets be valid simultaneously, nor is either one in line with reality in the present simplistic form. – It is curious that Gibbs[18] was not aware, or did not recognize the relevance of Clausius[6] and eqn.4 above.

7. Conclusion

The form of the First Law as in eqn.5a-c is invalid. Eqn.15 shows that the stress tensor does not exist. A detailed and exhaustive discussion of the Euler-Cauchy theory is given in Ref.4 where it is shown that the Euler-Cauchy theory, and thus the entire body of continuum mechanics, is profoundly incompatible with the theory of potentials;[8] in fact, the latter is entirely unknown in mechanics of solids although it is the theoretical framework of classical physics. The known theories of elastic deformation are therefore in need of revision. It must be realized that the simplest elastic law known to us is Boyle's law which so far only gives us what may be called an isotropic deformation, a volume change, for an ideal gas. A proper deformation theory must start with the First Law and the equation of state $PV = nRT$, and be fully compatible with general thermodynamics.[19]

8. References

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