THE THERMOELASTIC SQUARE

A mnemonic for remembering thermodynamic identities

The state of a material is the collection of variables such as stress, strain, temperature, entropy. A variable is a state variable if its integral over any closed path in the other state variables is zero. Clearly, this definition is circular unless we assume there exists a minimal set *postulated* state variables. For example, the zeroth law of thermodynamics postulates the existence of a temperature. The pressure is usually postulated to be a state variable. For typical applications involving inviscid fluids, only these two state variables — temperature and pressure — are needed in order to determine the other state variables. For solids, more state variables are needed. The state postulate of thermodynamics says that the minimum number of state variables needed to determine all other state variables is equal to one plus the number of quasistatic work modes. For a gas, there is only one work mode, namely pdV where pressure p works to produce a volume change dV. For a more general material, there are a total of six work modes, corresponding to the six independent components of stress causing changes in the six components of strain. In addition to the six state variables that characterize stress or strain, the state postulate says there must be one more variable such as temperature or entropy that characterizes the thermal state of the material. Suppose we take strain and entropy to be our primitive state variables. Such a material is said to be thermoelastic, and the first law of thermodynamics implies that the *specific* stress tensor (i.e., stress divided by density) is given by a derivative of the internal energy function with respect to strain, while the temperature is the derivative of energy with respect to entropy. The relationship between stress and strain does not have to be linear — the principal characteristic of thermoelasticity is that stress must be expressible as a true function of strain and entropy. In what follows, we speak of the stress tensor as a *single* entity rather than a collection of six individual components (just as, say, velocity is regarded as a *single* vector rather than a collection of three components). Likewise, the strain tensor is a single entity. Thus, the state postulate says, given a tensor variable (stress or strain) and a thermal variable (temperature or entropy), then there exist equations of state such that all of the other state variables may be computed from these two primitive independent state variables. Thermodynamical identities such as the Legendre transformations and the Maxwell and Gibbsian relations have nothing to do with thermodynamics — they are simply relationships that hold whenever you work with *any* function of two variables. When one of these variables is a tensor, some identities take slightly modified forms involving the tensor inner product instead of ordinary scalar multiplication.

Notation and basic thermodynamical concepts. To emphasize the connection with ordinary PdV identities, the *specific* stress tensor (i.e., stress divided by density) is denoted $\underset{\approx}{\mathbf{P}}$ and the strain tensor is denoted $\underset{\approx}{\mathbf{v}}$. The numerical plus/minus signs in our identities may differ from what you are accustomed to because *our stress and our strain are both positive in tension.*

For inviscid fluids, the increment in mechanical work per unit mass is given by Pdv, where P is the pressure and v is the specific volume (i.e., volume per unit mass, which is simply the inverse of the density ρ). The most useful measure of volumetric strain is $\varepsilon_v = \ln(v/v_o)$, for which the material time rate is $\dot{\varepsilon}_v = \dot{v}/v$. With this logarithmic strain measure, derivatives of the form $v[d(\ )/dv]$ become simply $d(\ )/d\varepsilon_v$ and the specific work increment becomes

$$Pdv = vPd\varepsilon_v = \left(\frac{P}{\rho}\right)d\varepsilon_v$$

Note that the specific work increment is a *specific* stress (i.e., pressure divided by density) times a strain increment. When generalizing to solids and viscous fluids which have nonzero shear stresses, the increment in work is given by $\underset{\approx}{\mathbf{P}}:d\underset{\approx}{\mathbf{v}}$, where $\underset{\approx}{\mathbf{P}}$ is the second Piola Kirchhoff (PK2) stress divided by reference density ρ_o, and $\underset{\approx}{\mathbf{v}}$ is Lagrange strain. The double dot is the tensor inner product defined between any two tensors, $\underset{\approx}{\mathbf{A}}$ and $\underset{\approx}{\mathbf{B}}$, as $\underset{\approx}{\mathbf{A}}:\underset{\approx}{\mathbf{B}} = A_{ij}B_{ij}$. Incidentally, *a <u>different</u> scalar product defined by* $A_{ij}B_{ji}$ *should be avoided because it is not an <u>inner</u> product* (it fails the positivity axiom).

The work increment is $dW = \underset{\approx}{\mathbf{P}}:d\underset{\approx}{\mathbf{v}}$. Here, the symbol d is an *inexact* differential, indicating that the integral of work over a closed path in state space is not necessarily zero. Thus work W is not a state variable. If dQ denotes the heating increment, then first law of thermodynamics states that the *sum* of the work and heat *inexact* differentials is itself an *exact* differential. Hence there must exist a state variable — the internal energy u — such that

$$du = dW + dQ$$

The entropy s is defined such that $Tds = dQ + dD$, where T is temperature and dD is the increment in dissipation. A reversible process has zero dissipation, so the first law becomes

$$du = \underset{\approx}{\mathbf{P}}:d\underset{\approx}{\mathbf{v}} + Tds$$

The form of this equation *suggests* (but does not *require*) that the internal energy u may be regarded as a function of strain $\underset{\approx}{\mathbf{v}}$ and entropy s. If this *thermoelastic assumption* is adopted, then it follows that

$$\mathbf{\underset{\approx}{P}} = \left(\frac{\partial u}{\partial \mathbf{\underset{\approx}{v}}}\right)_s \quad and \quad T = \left(\frac{\partial u}{\partial s}\right)_{\mathbf{\underset{\approx}{v}}}$$

Subscripts indicate which variable is being held constant in the partial derivative. The indicial form of the first equation is $P_{ij} = (\partial u / \partial v_{ij})_s$. Material properties are frequently defined in terms of second derivatives of the energy function. For example, the (specific) fourth-order isentropic elastic stiffness tensor is the derivative of (specific) stress $\mathbf{\underset{\approx}{P}}$ with respect to strain $\mathbf{\underset{\approx}{v}}$ holding entropy constant, so it has components $(\partial P_{ij} / \partial v_{kl})_s = (\partial^2 u / \partial v_{ij} \partial v_{kl})_s$, which we write in symbolic notation as $\left(\dfrac{\partial \mathbf{\underset{\approx}{P}}}{\partial \mathbf{\underset{\approx}{v}}}\right)_s = \left(\dfrac{\partial^2 u}{\partial \mathbf{\underset{\approx}{v}}^2}\right)_s$. The (specific) *isothermal* elastic stiffness is the derivative of $\mathbf{\underset{\approx}{P}}$ with respect to $\mathbf{\underset{\approx}{v}}$ holding *temperature* constant. Its relationship to the isentropic stiffness may be determined through application of the chain rule:

$$\left(\frac{\partial \mathbf{\underset{\approx}{P}}}{\partial \mathbf{\underset{\approx}{v}}}\right)_T = \left(\frac{\partial \mathbf{\underset{\approx}{P}}}{\partial \mathbf{\underset{\approx}{v}}}\right)_s + \left(\frac{\partial \mathbf{\underset{\approx}{P}}}{\partial s}\right)_{\mathbf{\underset{\approx}{v}}}\left(\frac{\partial s}{\partial \mathbf{\underset{\approx}{v}}}\right)_T$$

By using combinations of Maxwell and Gibbsian relations, the last term may be expressed in terms of the Gruneisen or thermal expansion tensor and the constant strain specific heat, both of which are regarded as measurable properties. Thus knowledge of the Maxwell and Gibbsian relations is essential whenever one wishes to find connections between one material property and another. The thermoelastic square helps you remember these relationships.

Irreversible processes. Recall that the first law may be written in the form $du = \underset{\approx}{\mathbf{P}}:d\underset{\approx}{\mathbf{v}} + T ds$ only for *reversible* processes. Many authors claim that this equation holds even in the presence of dissipation. In this case, the stress and strain are *not* the real stress $\underset{\approx}{\mathbf{P}}^{\text{real}}$ and real strain $\underset{\approx}{\mathbf{v}}^{\text{real}}$. Instead so-called thermodynamic stress and strain must be defined so that $\underset{\approx}{\mathbf{P}}:d\underset{\approx}{\mathbf{v}} = \underset{\approx}{\mathbf{P}}^{\text{real}}:d\underset{\approx}{\mathbf{v}}^{\text{real}} - dD$. Consider, for example, plastic flow. The thermodynamic stress is *chosen* to equal the real stress: $\underset{\approx}{\mathbf{P}} = \underset{\approx}{\mathbf{P}}^{\text{real}}$. The strain increment is broken into elastic plus plastic parts: $d\underset{\approx}{\mathbf{v}}^{\text{real}} = d\underset{\approx}{\mathbf{v}}^{\text{e}} + d\underset{\approx}{\mathbf{v}}^{\text{p}}$. For plasticity, the dissipation is $dD = \underset{\approx}{\mathbf{P}}:d\underset{\approx}{\mathbf{v}}^{\text{p}}$. Consequently, the thermodynamic strain increment must be defined such that $\underset{\approx}{\mathbf{P}}:d\underset{\approx}{\mathbf{v}} = \underset{\approx}{\mathbf{P}}:d\underset{\approx}{\mathbf{v}}^{\text{e}}$. Thus, for plastic deformations, the equations contained in the thermoelastic square are valid so long as the strain $\underset{\approx}{\mathbf{v}}$ is regarded as the *elastic* strain, not the total strain! This makes sense intuitively since the mechanical part of internal energy corresponds to the stretching of the elastic lattice (which is characterized by $\underset{\approx}{\mathbf{v}}^{\text{e}}$). The thermal part of the internal energy comes from ordinary external heating and from dissipation associated with irreversible plastic flow (characterized by $d\underset{\approx}{\mathbf{v}}^{\text{p}}$) of material "through" the lattice.

Other energy measures. If we define a new variable $h \equiv u - \underset{\approx}{\mathbf{P}}:\underset{\approx}{\mathbf{v}}$, called *enthalpy*, then the first law ($du = \underset{\approx}{\mathbf{P}}:d\underset{\approx}{\mathbf{v}} + T ds$) may be alternatively written as $dh = -\underset{\approx}{\mathbf{v}}:d\underset{\approx}{\mathbf{P}} + T ds$. By using enthalpy, we have transformed the first law into a form where specific stress $\underset{\approx}{\mathbf{P}}$ and entropy s appear to be the natural independent variables, which might be more convenient for certain applications such as stress-controlled loading. Other energy measures such as Gibbs energy and Helmholtz free energy are more helpful in other situations. The thermodynamic square provides a means of (1) remembering how these alternative energy measures are related to each other and (2) recalling the natural independent variables associated with the energies, and (3) recalling how derivatives of the energy measures are related to other state variables or to other derivatives.

How to use the thermoelastic square.

The thermoelastic square (shown on the next page) contains key thermoelastic relationships in recognizable patterns. The easiest way to learn the square is to deduce for yourself how the identities all obey consistent geometrical patterns in the square. The numerical plus/minus signs are always related in some manner to the arrows on the thermoelastic square. The paragraphs below provide further details in case the patterns are not evident to you.

The edges of the thermoelastic square tell you the four energies and their natural independent variables. For example, internal energy u is naturally a function of entropy s and strain $\underset{\approx}{\mathbf{V}}$. Enthalpy h is naturally a function of entropy, s, and specific stress, $\underset{\approx}{\mathbf{P}}$. The contact (Legendre) transformations that relate one energy to another run parallel to the arrows in the thermoelastic square. (For example, u–a is parallel to the arrow connecting T and s, so $u - s = Ts$).

To find the derivative of an energy with respect to one of its natural variables (holding the other one constant), simply travel from the differentiation variable (which always lies at a corner near the energy) to the diagonally opposite point across the square. The plus/minus is assigned according to whether you move *with* (+) or *against* (–) the arrows.

For example, note that T is opposite s and the arrow points from s to T. Therefore we have

$$\left(\frac{\partial h}{\partial s}\right)_{\underset{\approx}{\mathbf{P}}} = + T, \left(\frac{\partial u}{\partial s}\right)_{\underset{\approx}{\mathbf{V}}} = + T \text{ and } \left(\frac{\partial g}{\partial T}\right)_{\underset{\approx}{\mathbf{P}}} = -s. \text{ Similarly, } \left(\frac{\partial h}{\partial \underset{\approx}{\mathbf{P}}}\right)_{s} = -\underset{\approx}{\mathbf{V}} \text{ and } \left(\frac{\partial a}{\partial T}\right)_{\underset{\approx}{\mathbf{V}}} = -s.$$

Maxwell relations involve derivatives of a variable at a *corner* of the square with respect to an adjacent corner variable. On the thermoelastic square, the derivative of one corner variable with respect to another is equal to plus or minus the derivative of the *mirror images* of these two variables. The mirror image of $\underset{\approx}{\mathbf{V}}$ *across the horizontal* is T whereas the mirror image of $\underset{\approx}{\mathbf{V}}$ *across the vertical* is s. The numerical sign used in the Maxwell relation is positive if the two arrows on the thermoelastic square are symmetric in the same mirror image direction. The variable held constant in the derivative is found by continuing the sequence to the next corner. For example, $(\partial \underset{\approx}{\mathbf{V}} / \partial s)_{\underset{\approx}{\mathbf{P}}}$ involves variables $\underset{\approx}{\mathbf{V}}$ and s on the far left edge, so the constant $\underset{\approx}{\mathbf{P}}$ is then next corner after travelling from $\underset{\approx}{\mathbf{V}}$ to s. The mirror image derivative $(\partial T / \partial \underset{\approx}{\mathbf{P}})_{s}$ involves variables on the far right edge. The two arrows on the thermoelastic square are *not* symmetric across this *horizontal* mirror direction, so the sign must be negative. That is, $(\partial \underset{\approx}{\mathbf{V}} / \partial s)_{\underset{\approx}{\mathbf{P}}} = -(\partial T / \partial \underset{\approx}{\mathbf{P}})_{s}$.

The formulas for the second derivatives obey somewhat more complicated patterns, as you can deduce yourself. With a little bit of practice, you will find the thermoelastic square to be an extremely valuable memory aid. We hope you find it helpful!

Thermoelastic square

Energies	isotropic state	tensor state
$u(\underset{\approx}{\mathbf{v}}, s)$, internal	v, specific volume $= \dfrac{1}{\rho}$	$\underset{\approx}{\mathbf{v}}$, strain tensor*
$a(\underset{\approx}{\mathbf{v}}, T)$, Helmholtz	p, *tensile* pressure	$\underset{\approx}{\mathbf{P}}$, specific stress*
$g(\underset{\approx}{\mathbf{P}}, T)$, Gibbs	T, temperature	T, temperature
$h(\underset{\approx}{\mathbf{P}}, s)$, enthalpy	s, entropy	s, entropy
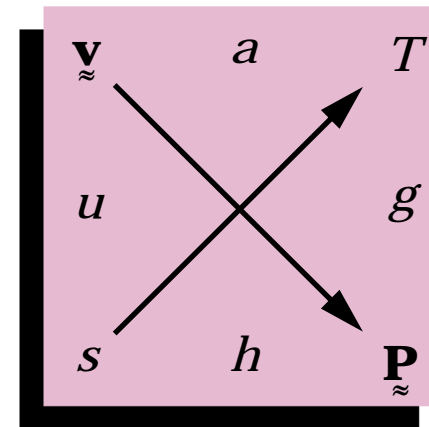
*For isotropic, $\underset{\approx}{\mathbf{v}} = \frac{1}{3}\ln(v/v_o)\underset{\approx}{\mathbf{I}}$ and $\underset{\approx}{\mathbf{P}} = pv\underset{\approx}{\mathbf{I}}$, positive in *tension*.
Otherwise, $\underset{\approx}{\mathbf{v}}$ is Lagrange strain and $\underset{\approx}{\mathbf{P}}$ is PK2 stress divided by ρ_o.

contact (Legendre) transformations

$$u - a = Ts = h - g$$
$$u - h = \underset{\approx}{\mathbf{v}}:\underset{\approx}{\mathbf{P}} = a - g$$

Conjugate relations   Gibbsian relations

$$\left(\frac{\partial u}{\partial \underset{\approx}{\mathbf{v}}}\right)_s = \underset{\approx}{\mathbf{P}} \quad \text{and} \quad \left(\frac{\partial u}{\partial s}\right)_{\underset{\approx}{\mathbf{v}}} = T \;\Rightarrow\; \dot{u} = \underset{\approx}{\mathbf{P}}:\dot{\underset{\approx}{\mathbf{v}}} + T\dot{s}$$

$$\left(\frac{\partial a}{\partial \underset{\approx}{\mathbf{v}}}\right)_T = \underset{\approx}{\mathbf{P}} \quad \text{and} \quad \left(\frac{\partial a}{\partial T}\right)_{\underset{\approx}{\mathbf{v}}} = -s \;\Rightarrow\; \dot{a} = \underset{\approx}{\mathbf{P}}:\dot{\underset{\approx}{\mathbf{v}}} - s\dot{T}$$

$$\left(\frac{\partial g}{\partial \underset{\approx}{\mathbf{P}}}\right)_T = -\underset{\approx}{\mathbf{v}} \quad \text{and} \quad \left(\frac{\partial g}{\partial T}\right)_{\underset{\approx}{\mathbf{P}}} = -s \;\Rightarrow\; \dot{g} = -\underset{\approx}{\mathbf{v}}:\dot{\underset{\approx}{\mathbf{P}}} - s\dot{T}$$

$$\left(\frac{\partial h}{\partial \underset{\approx}{\mathbf{P}}}\right)_s = -\underset{\approx}{\mathbf{v}} \quad \text{and} \quad \left(\frac{\partial h}{\partial s}\right)_{\underset{\approx}{\mathbf{P}}} = T \;\Rightarrow\; \dot{h} = -\underset{\approx}{\mathbf{v}}:\dot{\underset{\approx}{\mathbf{P}}} + T\dot{s}$$

Maxwell's relations

$$+\left(\frac{\partial T}{\partial \underset{\approx}{\mathbf{v}}}\right)_s = \frac{\partial^2 u}{\partial \underset{\approx}{\mathbf{v}}\,\partial s} = +\left(\frac{\partial \underset{\approx}{\mathbf{P}}}{\partial s}\right)_{\underset{\approx}{\mathbf{v}}}$$

$$-\left(\frac{\partial s}{\partial \underset{\approx}{\mathbf{v}}}\right)_T = \frac{\partial^2 a}{\partial \underset{\approx}{\mathbf{v}}\,\partial T} = +\left(\frac{\partial \underset{\approx}{\mathbf{P}}}{\partial T}\right)_{\underset{\approx}{\mathbf{v}}}$$

$$-\left(\frac{\partial s}{\partial \underset{\approx}{\mathbf{P}}}\right)_T = \frac{\partial^2 g}{\partial \underset{\approx}{\mathbf{P}}\,\partial T} = -\left(\frac{\partial \underset{\approx}{\mathbf{v}}}{\partial T}\right)_{\underset{\approx}{\mathbf{P}}}$$

$$+\left(\frac{\partial T}{\partial \underset{\approx}{\mathbf{P}}}\right)_s = \frac{\partial^2 h}{\partial \underset{\approx}{\mathbf{P}}\,\partial s} = -\left(\frac{\partial \underset{\approx}{\mathbf{v}}}{\partial s}\right)_{\underset{\approx}{\mathbf{P}}}$$

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$$\left(\frac{\partial^2 u}{\partial \underset{\approx}{\mathbf{v}}^2}\right)_s = \left(\frac{\partial \underset{\approx}{\mathbf{P}}}{\partial \underset{\approx}{\mathbf{v}}}\right)_s = \underset{\approx}{\mathbf{E}}_s \qquad \text{and} \qquad \left(\frac{\partial h}{\partial \underset{\approx}{\mathbf{v}}}\right)_s = -\underset{\approx}{\mathbf{v}}:\left(\frac{\partial \underset{\approx}{\mathbf{P}}}{\partial \underset{\approx}{\mathbf{v}}}\right)_s$$

$$\left(\frac{\partial^2 a}{\partial \underset{\approx}{\mathbf{v}}^2}\right)_s = \left(\frac{\partial \underset{\approx}{\mathbf{P}}}{\partial \underset{\approx}{\mathbf{v}}}\right)_T = \underset{\approx}{\mathbf{E}}_T \qquad \text{and} \qquad \left(\frac{\partial g}{\partial \underset{\approx}{\mathbf{v}}}\right)_T = -\underset{\approx}{\mathbf{v}}:\left(\frac{\partial \underset{\approx}{\mathbf{P}}}{\partial \underset{\approx}{\mathbf{v}}}\right)_T$$

$$\left(\frac{\partial^2 g}{\partial \underset{\approx}{\mathbf{P}}^2}\right)_T = -\left(\frac{\partial \underset{\approx}{\mathbf{v}}}{\partial \underset{\approx}{\mathbf{P}}}\right)_T = -\underset{\approx}{\mathbf{E}}_T^{-1} \qquad \text{and} \qquad \left(\frac{\partial a}{\partial \underset{\approx}{\mathbf{P}}}\right)_T = +\underset{\approx}{\mathbf{P}}:\left(\frac{\partial \underset{\approx}{\mathbf{v}}}{\partial \underset{\approx}{\mathbf{P}}}\right)_T$$

$$\left(\frac{\partial^2 h}{\partial \underset{\approx}{\mathbf{P}}^2}\right)_s = -\left(\frac{\partial \underset{\approx}{\mathbf{v}}}{\partial \underset{\approx}{\mathbf{P}}}\right)_s = -\underset{\approx}{\mathbf{E}}_s^{-1} \qquad \text{and} \qquad \left(\frac{\partial u}{\partial \underset{\approx}{\mathbf{P}}}\right)_s = +\underset{\approx}{\mathbf{P}}:\left(\frac{\partial \underset{\approx}{\mathbf{v}}}{\partial \underset{\approx}{\mathbf{P}}}\right)_s$$

Contact (Legendre) transformations

$$u - a = Ts = h - g$$

$$u - h = \underset{\approx}{\mathbf{v}}:\underset{\approx}{\mathbf{P}} = a - g$$

Don't forget: $\underset{\approx}{\mathbf{P}}$ is *specific* stress (i.e., stress divided by density) and it is positive in *tension*. Thus, the stiffness (below) is conventional stiffness divided by density.

The "double dot" is the tensor inner product (i.e., $\underset{\approx}{\mathbf{A}}:\underset{\approx}{\mathbf{B}} = A_{ij}B_{ij}$).

$$\left(\frac{\partial^2 u}{\partial s^2}\right)_{\underset{\approx}{\mathbf{v}}} = +\left(\frac{\partial T}{\partial s}\right)_{\underset{\approx}{\mathbf{v}}} = -\frac{1}{s}\left(\frac{\partial a}{\partial s}\right)_{\underset{\approx}{\mathbf{v}}}$$

$$\left(\frac{\partial^2 a}{\partial T^2}\right)_{\underset{\approx}{\mathbf{v}}} = -\left(\frac{\partial s}{\partial T}\right)_{\underset{\approx}{\mathbf{v}}} = -\frac{1}{T}\left(\frac{\partial u}{\partial T}\right)_{\underset{\approx}{\mathbf{v}}} = -\frac{c_v}{T}$$

$$\left(\frac{\partial^2 g}{\partial T^2}\right)_{\underset{\approx}{\mathbf{P}}} = -\left(\frac{\partial s}{\partial T}\right)_{\underset{\approx}{\mathbf{P}}} = -\frac{1}{T}\left(\frac{\partial h}{\partial T}\right)_{\underset{\approx}{\mathbf{P}}} = -\frac{c_p}{T}$$

$$\left(\frac{\partial^2 h}{\partial s^2}\right)_{\underset{\approx}{\mathbf{P}}} = +\left(\frac{\partial T}{\partial s}\right)_{\underset{\approx}{\mathbf{P}}} = -\frac{1}{s}\left(\frac{\partial g}{\partial s}\right)_{\underset{\approx}{\mathbf{P}}}$$

Thermal expansion tensor: $\underset{\approx}{\boldsymbol{\beta}} = \left(\frac{\partial \underset{\approx}{\mathbf{v}}}{\partial T}\right)_{\underset{\approx}{\mathbf{P}}}$

spec. thermal stiffness: $\underset{\approx}{\mathbf{B}} = \left(\frac{\partial \underset{\approx}{\mathbf{P}}}{\partial T}\right)_{\underset{\approx}{\mathbf{v}}} = \underset{\approx}{\mathbf{E}}_T:\underset{\approx}{\boldsymbol{\beta}}$

Grüneisen tensor: $\underset{\approx}{\boldsymbol{\gamma}} = -\frac{1}{T}\frac{\partial^2 u}{\partial \underset{\approx}{\mathbf{v}}\partial s} = \frac{\underset{\approx}{\mathbf{B}}}{c_v}$

Specific stiffness: $\underset{\approx}{\mathbf{E}}_s = \underset{\approx}{\mathbf{E}}_T + Tc_v\underset{\approx}{\boldsymbol{\gamma}}\underset{\approx}{\boldsymbol{\gamma}}$.

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