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On Polyekthetic Processes

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Abstract
This Preprint introduces *polyekthetic* processes, a generalization of polytropic processes. The etymology of the new term is given, and the concept is explained theoretically. A useful associated definition for constant-property processes, for arbitrary properties and expressions thereof, is given, and associated polyekthetic exponents $k_{ij\ell}$ are defined and a general solution is obtained. Examples on van-der-Waals, general, and ideal gas substances are provided with discussions.

Keywords
Thermodynamics — Polyekthetic Processes — Polyekthetic Exponent — Bridgman's Relations — Polytropic Processes

Highlights
Proposes 'polyekthetic' process: a generalization of polytropic processes — Proposes constant-arbitrary property process polyekthetic exponents $k_{ij\ell}$ — Gives general solution for $k_{ij\ell}$ — Provides examples and discussions.

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1. Introduction

Polytropic processes—*poly*: many, *tropic*: forms, ways [8]—are a versatile class of equilibrium thermodynamics processes with many applications in engineering thermodynamics [7, 11, 4, 3], given by the following relationship

$$Pv^n = \mathsf{c} = \text{const.}, \tag{1}$$

where P is the system pressure, v the system specific volume, and n is the polytropic exponent.

Polytropic processes are said to find support in measurements [11, 7, 10]; however, theory [2, 8] predicts a fairly restrictive set of conditions—on the process boundary and internal conditions and on the underlying substance model—are required for a process to follow Eq. (1) *exactly*—see, for instance, Theorem 3 of reference [8].

Thus, in non-ideal settings, polytropic processes either (i) hold approximately in a *local* neighborhood of a given state, for constant-n, or (ii) the polytropic exponent must be generalized into a function of a state property, such as temperature, or even further generalized.

Reference [8] brings useful definitions for discussions like this, such as that of a *logical process*, and also those of *exact* and of *local* polytropic processes.

In *exact polytropic process*, Eq. (1) holds exactly with a constant, unique polytropic exponent, for the entire duration of the *logical process*. They are shown to be able to represent any straight line segment process in $\log P \times \log v$ coordinates [8].

Moreover, process whose representations in $\log P \times \log v$ coordinates are curved, are shown to be able to be approximated by a finite number of *local polytropic processes* within finite error intervals [8]. Observations like these attest the flexibility of processes based on the polytropic relationship, thus justifying the flexibility encoded in their name.

Despite their enormous flexibility, the defining concept of polytropic processes can be further generalized as to allow for increased flexibility, so that some processes families with curved representation in $\log P \times \log v$ coordinates might have an exact representation in such further generalized process relation concept. The introduction of such generalizations can be of theoretical and of applied interest.

Therefore, this work proposes one such generalization, named *polyekthetic processes*, that form a *larger process set* of which the polytropic process set is a proper subset, so that any polytropic process is a particular case of a polyekthetic process, but not necessarily the opposite.

The origin (etymology) for the proposed 'polyekthetic' term is also given, and an application yielding exact polyekthetic processes (but not exactly polytropic ones) is provided.

2. Polyekthetic Processes

2.1 Literature Generalizations of Polytropic Processes

Concerning isentropic processes written in the form of Eq. (1), Bejan [1] derives a definition for the *isentropic expansion exponent*, k, by differentiating an $s : s(P, v)$ function and describing the isentropic process as:

$$ds = \left(\frac{\partial s}{\partial P}\right)_v dP + \left(\frac{\partial s}{\partial v}\right)_P dv = 0. \tag{2}$$

It is worth noting that Eq. (2) is valid in general, and not only to a particular substance equation of state. By a suitable manipulation of the $(\partial s/\partial P)_v$ and $(\partial s/\partial v)_P$ coefficients, Eq. (2) can be recast into:

$$\frac{dP}{P} = -k\frac{dv}{v}, \tag{3}$$

with

$$k \equiv \frac{-v}{P}\left(\frac{\partial P}{\partial v}\right)_s. \tag{4}$$

As $k : k(P, v)$ in general, let k be taken as a *constant* in the *local* vicinity of a state of interest; therefore, the *local* solution of Eq. (3) is the local polytropic process $Pv^k =$ const.

Bejan [1] also derives an *isothermal-expansion exponent*, k_T, so that $Pv^{k_T} =$ const., for isothermal processes in a similar fashion as Eqs. (2)–(4).

In this type of generalization, one *defines new polytropic exponents*, so that the resulting process, *written as a polytropic relationship*, has a predetermined *behavior* in terms of a third thermodynamic property.

In this "Bejan" generalization of polytropic process, one has

$$Pv^{k_\alpha} = \mathsf{c} = \text{const.}, \tag{5}$$

for const-α processes.

Moreover, Nederstigt [9] generalizes isentropic exponents γ_{Pv}, γ_{Tv}, and γ_{PT}, so that isentropic processes can be described as either $Pv^{\gamma_{Pv}} =$ const, or $Tv^{\gamma_{Tv}} =$ const, or $PT^{\gamma_{PT}} =$ const.

In this "Nederstigt" generalization of isentropic processes, exponents $k_{\alpha\beta}$ are such that

$$\alpha\beta^{k_{\alpha\beta}} = \mathsf{c} = \text{const.}, \tag{6}$$

for const-s processes.

2.2 Polyekthetic Processes Definition

The generalization of these ideas follows:

Definition 1. *Let property indices i, and j be any intensive system properties or algebraic expressions thereof, then any process relation in the form*

$$ij^n = \mathsf{c} = \textit{const.}, \tag{7}$$

*for constant or variable n, is a **polyekthetic process**.*

Therefore, polyekthetic processes allow any property pair—and not just Pv—to be the "base," for its power relationship with exponent n of Eq. (7). Moreover, since polytropic processes are recovered by setting $i \equiv P$, $j \equiv v$, and letting the exponent n have any real value, clearly the polytropic process set is a proper subset of the polyekthetic process set.

A useful application is to find suitable exponents $k_{ij\ell}$, so that polyekthetic processes in base ij with exponent $k_{ij\ell}$ describe const-ℓ processes; hence the following:

Definition 2. *Let **constant-property process polyekthetic exponents** $k_{ij\ell}$—or just polyekthetic exponents $k_{ij\ell}$, for short—be such that the polyekthetic process relation*

$$ij^{k_{ij\ell}} = \mathsf{c} = \textit{const.}, \tag{8}$$

holds, at least locally, for an iso-ℓ process, in which ℓ is any intensive system property or algebraic expressions thereof.

Thus, the following are all (simple) examples of polyekthetic process descriptions:

$$T v^{k_{Tvs}} = \mathsf{c}_1 = \text{const.}, \tag{9}$$

$$s P^{k_{sPT}} = \mathsf{c}_2 = \text{const.}, \tag{10}$$

$$s v^0 = \mathsf{c}_3 = \text{const.}, \tag{11}$$

$$\lim_{n\to+\infty} h v^n = \mathsf{c}_4 = \text{const.}, \tag{12}$$

in which Eq. (9) describes an isentropic process in a Tv base; Eq. (10) describes an isothermal process in an sP base; Eq. (11) describes an isentropic process in an sv base, and Eq. (12) an isenthalpic process in an hv base.

Theorem 1. *Any constant-property process is a polyekthetic process.*

Proof. Let ℓ be the property held constant for a constant-property process of Theorem 1. Then, by Definition 2, the polyekthetic process of Eq. (8) is a const-ℓ process. ☐

2.3 Polyekthetic Processes Etymology

Following the etymology of polytropic processes [8], and given that this generalization engenders many (πολύ) exponents (εκϑέτης) [5], the set of processes described by the relation of Eq. (7) are named “polyekthetic”, i.e., a *multiple exponent* process set.

3. General Solution

Owing to Definition 1 being very broad, the focus now shifts towards the more applicable Definition 2, i.e., in finding expressions for constant-property polyekthetic exponents $k_{ij\ell}$.

3.1 In Partial Differential Notation

Let property $\ell : \ell(i, j)$; then, the total differential of ℓ is, for a const-ℓ process:

$$d\ell = \left(\frac{\partial \ell}{\partial i}\right)_j di + \left(\frac{\partial \ell}{\partial j}\right)_i dj = 0 \tag{13}$$

which must be recast into an ODE whose solution, *at least locally*, is Eq. (8). Isolating di:

$$di = -\left(\frac{\partial \ell}{\partial j}\right)_i \left(\frac{\partial i}{\partial \ell}\right)_j dj, \tag{14}$$

which can be arranged as:

$$\frac{di}{i} = \frac{-j}{i}\left(\frac{\partial \ell}{\partial j}\right)_i \left(\frac{\partial i}{\partial \ell}\right)_j \frac{dj}{j}. \tag{15}$$

The polyekthetic exponent, $k_{ij\ell}$, is therefore:

$$k_{ij\ell} = \frac{j}{i}\left(\frac{\partial \ell}{\partial j}\right)_i \left(\frac{\partial i}{\partial \ell}\right)_j. \tag{16}$$

Using the cyclic relationship:

$$-1 = \left(\frac{\partial j}{\partial i}\right)_\ell \left(\frac{\partial \ell}{\partial j}\right)_i \left(\frac{\partial i}{\partial \ell}\right)_j, \tag{17}$$

the polyekthetic exponent can be rewritten as:

$$k_{ij\ell} = \frac{-j}{i}\left(\frac{\partial i}{\partial j}\right)_\ell. \tag{18}$$

Eq. (18) is thus the general solution for $k_{ij\ell}$.

3.2 In Terms of Bridgman’s Relations

Perhaps the easiest way of expressing any polyekthetic exponent $k_{ij\ell}$ (for simple properties ℓ) in terms of quantities measurable in laboratory is by rewriting it in terms of Bridgman’s relations [1], which are expressed in terms of a peculiar notation.

$$\frac{(\partial i)_\ell}{(\partial j)_\ell} \equiv \left(\frac{\partial i}{\partial j}\right)_\ell. \tag{19}$$

Please note that the $\equiv$ sign on Eq. (19) indicates the definition of the *ratio* between shown Bridgman’s primitives $(\partial i)_\ell$ and $(\partial j)_\ell$ in terms of $(\partial i/\partial j)_\ell$, rather than the other way around.

Bridgman’s relations are tabulated, and can be found on reference [1].

The general expression for $k_{ij\ell}$, using Bridgman’s relations notation, is therefore:

$$k_{ij\ell} = \frac{-j}{i}\frac{(\partial i)_\ell}{(\partial j)_\ell}. \tag{20}$$

3.3 Properties of Polyekthetic Exponents

Theorem 2. *if $k_{ij\ell}$ is a constant-property process polyekthetic exponent, then the constant-property process polyekthetic exponent*

$$k_{ji\ell} = \frac{1}{k_{ij\ell}}. \tag{21}$$

Proof. Let $k_{ij\ell}$ be a constant-property process polyekthetic exponent, then, Eq. (18) holds.

Applying Eq. (18) for a $k_{ji\ell}$, i.e., with swapped i and j property indices, gives :

$$k_{ji\ell} = \frac{-i}{j}\left(\frac{\partial j}{\partial i}\right)_{\ell} \qquad \rightharpoondown \tag{22}$$

$$k_{ji\ell} = \left[\frac{-j}{i}\left(\frac{\partial i}{\partial j}\right)_{\ell}\right]^{-1} \qquad \rightharpoondown \tag{23}$$

$$k_{ji\ell} = \left(k_{ij\ell}\right)^{-1} = \frac{1}{k_{ij\ell}}, \tag{24}$$

thus proving the theorem. ☐

Theorem 3. *All constant-property process polyekthetic exponents* $k_{iji} = 0$.

Proof. Let $k_{ij\ell}$ be a constant-property process polyekthetic exponent, then, Eq. (18) holds.

Applying Eq. (18) for a k_{iji}, i.e., obtaining a const-i polyekthetic exponent, gives

$$k_{iji} = \frac{-j}{i}\left(\frac{\partial i}{\partial j}\right)_{i} \qquad \rightharpoondown \tag{25}$$

$$k_{iji} = 0, \tag{26}$$

by properties of partial derivatives, thus proving the theorem. ☐

Theorem 4. *All constant-property process polyekthetic exponents* $k_{ijj} \to \pm\infty$.

Proof. From Theorem 2, one has

$$k_{ijj} = 1/k_{jij}, \tag{27}$$

which, from Theorem 3 which establishes $k_{jij} = 0$, leads to

$$k_{ijj} = 1/0 \to \pm\infty, \tag{28}$$

thus proving the theorem. ☐

Moreover, from Theorems 3 and 4, whenever property indices are repeated, the corresponding polyekthetic exponent k is a trivial one.

If properties i, j, and ℓ, $i \neq j \neq \ell \neq i$, are chosen from the "usual" $\{P, T, v, u, h, s, a, g\}$ engineering thermodynamics intensive property set, there will be $8!/5! = 336$ combinations of non-trivial $k_{ij\ell}$. However, due to the reciprocity property of Theorem 2, there will be 168 non-trivial, non-reciprocal $k_{ij\ell}$ required to easily deduce the remaining ones.

4. Example Applications

4.1 Iso-s Process in const-c_v, van-der-Waals Substance

Consider a substance whose Helmholtz characteristic function [3] in reduced coordinates is given by:

$$a_r = \frac{8T_r}{3}\left[\phi\left(1 - \log T_r\right) - \log(3v_r - 1)\right] - \frac{3}{v_r}, \tag{29}$$

where $a_r \equiv a/(P_{cr}v_{cr})$ is the reduced specific Helmholtz energy, $T_r \equiv T/T_{cr}$ is the reduced temperature, $\phi \equiv \bar{c}_v/\bar{R}$ is a constant dimensionless isochoric specific heat, $v_r \equiv v/v_{cr}$ is the reduced specific volume, P_{cr} is the substance critical pressure, T_{cr} is the substance critical temperature, and $v_{cr} = Z_{cr}(RT_{cr}/P_{cr})$ is the substance model critical specific volume, with $Z_{cr} = 3/8$.

The Equation of State, EoS, of this substance is obtained by differentiating Eq. (29) partially with respect to v_r [3]:

$$P_r = \left(\frac{\partial a_r}{\partial v_r}\right)_{T_r} \qquad \rightharpoondown \tag{30}$$

$$P_r = \frac{8T_r}{3v_r - 1} - \frac{3}{v_r^2}, \tag{31}$$

where $P_r \equiv P/P_{cr}$ is the reduced pressure, and P the (dimensional) pressure. Eq. (31) is known as the universal [6] van-der-Waals [1, 11, 3] equation of state in reduced coordinates.

The entropy of this substance is obtained by differentiating Eq. (29) partially with respect to T_r [3]:

$$s_r = -\left(\frac{\partial a_r}{\partial T_r}\right)_{v_r} \qquad \rightharpoondown \tag{32}$$

$$s_r = \frac{8}{3}\left[\phi \log T_r + \log(3v_r - 1)\right], \tag{33}$$

where $s_r \equiv s(T_{cr}/P_{cr}v_{cr})$, is the reduced specific entropy of the substance and s is the (dimensional) specific entropy.

Let

$$\omega_r \equiv v_r - \frac{1}{3}, \tag{34}$$

be the reduced specific voids volume—since the minimum van-der-Waals substance specific reduced volume, $v_{r,min} = 1/3$, for which $\omega_{r,min} = 0$.

Therefore, *isentropic processes* in this const-c_v, van-der-Waals substance, between states (T_{r1}, ω_{r1}) and (T_{r2}, ω_{r2}) are given by:

$$s_{r2} - s_{r1} = 0 \qquad \rightharpoondown \tag{35}$$

$$\phi \log T_{r2} + \log \omega_{r2} = \phi \log T_{r1} + \log \omega_{r1}, \tag{36}$$

which, exponentiated and rearranged, leads to

$$\omega_{r2}T_{r2}^{\phi} = \omega_{r1}T_{r1}^{\phi}, \tag{37}$$

which is a polyekthetic process of constant ij^n with $i \equiv \omega_r$, $j \equiv T_r$, and $n \equiv \phi$.

Since the process is also isentropic, one has the following constant-property process polyekthetic exponent

$$k_{\omega_r T_r s} = \phi \equiv \frac{\bar{c}_v}{\bar{R}}, \tag{38}$$

for this constant-c_v, van-der-Waals substance.

The 'K-polytropic' theorem of reference [8, p. 8] states

> "Internally reversible processes in constant-specific-heat unreactive closed systems with negligible kinetic and potential energy changes and constant heat-to-work ratio interactions, K, are exact polytropic processes only if the substance is an ideal gas."

Isentropic compressions and expansions have constant heat-to-work ratio interactions of $K = 0$, since isentropic processes are also adiabatic. Therefore, the 'K-polytropic' theorem forbids non-ideal substances (such as van-der-Waals ones) to display exact polytropic processes under stated conditions.

Nonetheless, Eqs. (37) and (38) show that isentropic processes in constant-c_v, van-der-Waals substances *can* be written as exactly polyekthetic processes with constant polyekthetic exponents.

This one example illustrates how the polytropic process generalization proposed in this work achieved the desired outcome of exactly representing a process that could not be classified as an exact polytropic process [8].

4.2 General Const-Property Polytropic Processes

Since polytropic processes are also polyekthetic processes—by fixing the base as Pv—one can apply either Eq. (18) or (20) in deriving polytropic process exponents $k_{Pv\ell}$ for $\ell \in \{T, u, h, s, a, g\}$ for (i) generic substance models, and for (ii) particular cases, such as ideal gases. Table 1 brings such values *mostly* in terms of properties that are easily measurable in the laboratory, i.e., in terms of P, T, v, c_p, β, κ, and $\gamma \equiv c_p/c_v$, of which some definitions are given on Eq. (39), but also in terms of the specific entropy s:

$$\beta \equiv \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P, \qquad \kappa \equiv \frac{-1}{v}\left(\frac{\partial v}{\partial P}\right)_T. \tag{39}$$

Table 1. General values for $k_{Pv\ell}$ polyekthetic exponents, and for the ideal gas limit

Exponent	General Value	Ideal gas limit
k_{PvP}	0	0
k_{Pvv}	$\pm\infty$	$\pm\infty$
k_{PvT}	$\dfrac{1}{P\kappa}$	1
k_{Pvu}	$\dfrac{c_p - \beta P v}{P(\kappa c_p - T\beta^2 v)}$	1
k_{Pvh}	$\dfrac{c_p}{P[\kappa c_p + \beta v(1 - \beta T)]}$	1
k_{Pvs}	$\dfrac{c_p}{P(\kappa c_p - T\beta^2 v)}$	γ
k_{Pva}	$\dfrac{s + \beta P v}{P\kappa s}$	$1 + \dfrac{R}{s}$
k_{Pvg}	$\dfrac{s}{P(\kappa s - \beta v)}$	$\dfrac{s}{s - R}$

Results show an agreement between the polytropic and the corresponding Pv-based polyekthetic exponents. The polyekthetic exponent results also show that constant-a and constant-g process aren't exactly polytropic, even for constant-specific-heat ideal gases, given that such exponents are a function of the entropy.

5. Conclusions

In this work, a generalization of polytropic processes, inspired by their etymology (of many ways, many forms) and by the works of Bejan [1] and of Nederstigt [9], named 'polyekthetic' (multi-exponent) processes, is proposed.

It is shown that the polytropic process set is a proper subset of the polyekthetic one—meaning that every polytropic process is also a polyekthetic one but not necessarily the reverse.

Moreover, a useful kind (or subset) of polyekthetic processes consisting of constant arbitrary property, and their respective special-notation $k_{ij\ell}$ polyekthetic exponents were defined. Their basic properties were determined, and a general solution was found for them, stated either in terms of general partial derivatives, Eq. (18), or of Bridgman's primitives, Eq. (20).

An example of exact polyekthetic process that is not an exact polytropic process was given for a van-der-Waals substance. Moreover, generalized polytropic relationships for *any* substance model, and their corresponding ideal gas limit values were derived from Bridgman's relations and listed on Table 1. Results showed that constant-a and constant-g process aren't exactly polytropic, even for constant-specific-heat ideal gases, since the entropy explicitly appears in the polytropic exponent of such processes.

Conflict of Interest

The author declares that there is no conflict of interest in this work.

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