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A unifying framework for watershed thermodynamics: constitutive relationships

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Abstract

The balance equations for mass and momentum, averaged over the scale of a watershed entity, need to be supplemented with constitutive equations relating flow velocities, pressure potential differences, as well as mass and force exchanges within and across the boundaries of a watershed. In this paper, the procedure for the derivation of such constitutive relationships is described in detail. This procedure is based on the method pioneered by Coleman and Noll through exploitation of the second law of thermodynamics acting as a constraint-type relationship. The method is illustrated by its application to some common situations occurring in real world watersheds. Thermodynamically admissible and physically consistent constitutive relationships for mass exchange terms among the subregions constituting the watershed (subsurface zones, overland flow regions, channel) are proposed. These constitutive equations are subsequently combined with equations of mass balance for the subregions. In addition, constitutive relationships for forces exchanged amongst the subregions are also derived within the same thermodynamic framework. It is shown that, after linearisation of the latter constitutive relations in terms of the velocity, a watershed-scale Darcy's law governing flow in the unsaturated and saturated zones can be obtained. For the overland flow, a second order constitutive relationship with respect to velocity is proposed for the momentum exchange terms, leading to a watershed-scale Chezy formula. For the channel network REW-scale Saint–Venant equations are derived. Thus, within the framework of this approach new relationships governing exchange terms for mass and momentum are obtained and, moreover, some well-known experimental results are derived in a rigorous manner.

Keywords: Watersheds; Hydrologic theory; Second law of thermodynamics; Mass and force balances; Constitutive relationships; Coleman and Noll procedure

1. Introduction

This work represents the sequel to a previous paper (Reggiani et al. [33]) concerned with the derivation of watershed-scale conservation equations for mass, momentum, energy and entropy. These equations have been derived by averaging the corresponding point scale balance equations over a well defined averaging region called the Representative Elementary Watershed (REW). The REW is a fundamental building block for hydrological analysis, with the watershed being discretised into an interconnected set of REWs, where the stream channel network acts as a skeleton or organising structure. The stream network associated with a watershed is a bifurcating, tree-like structure consisting of nodes inter-connected by channel reaches or links. Associated with each reach or link, there is a well-defined area of the land surface capturing the atmospheric precipitation and delivering it towards the channel reach. These areas uniquely identify the sub-watersheds which we define as REWs. As a result, the agglomeration of the REWs forming the entire watershed resembles the tree-like structure of the channel network on which the discretisation is based, as shown schematically in Fig. 1.

The volume making up a REW is delimited externally by a prismatic mantle, defined by the shape of the ridges circumscribing the sub-watershed. On top, the REW is delimited by the atmosphere, and at the bottom by either an impermeable substratum or an assumed limit depth. The stream reach associated with a given REW can be either a source stream, classified as a *first order*

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Nomenclature

Latin symbols

A	mantle surface with horizontal normal delimiting the REW externally
$\mathscr{A}$	linearisation coefficent for the mass exchange terms, $[T/L]$
$\mathbf{A}$	areal vector defined through Eq. (2.4)
b	external supply of entropy, $[L^2/T^3\ {}^{\circ}]$
$\mathscr{B}$	linearisation coefficent for the mass exchange terms, $[M/L^3]$
e	mass exchange per unit surface area, $[M/TL^2]$
$\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z$:	unit vectors pointing along the x, y and z axes, respectively
E	internal energy per unit mass, $[L^2/T^2]$
$\mathscr{E}$	extensive internal energy, $[ML^2/T^2]$
f	external supply term for ψ
F	entropy exchange per unit surface area projection, $[M/T^3\ {}^{\circ}]$
$\mathbf{g}$	the gravity vector, $[L/T^2]$
G	production term in the generic balance equation
h	external energy supply, $[L^2/T^3]$
$\mathbf{i}$	general flux vector of ψ
$\mathbf{j}$	microscopic non-convective entropy flux, $[M/T^3\ {}^{\circ}]$
J	rate of rainfall input or evaporation, $[M/L^2T]$
L	rate of net production of entropy per unit area, $[M/T^3\ {}^{\circ}L^2]$
m^{r}	volume per unit channel length, equivalent to the average cross sectional area, $[L^3/L]$
M	number of REWs making up the entire watershed
$\mathbf{n}^{ij}$	unit normal vector to the boundary between subregion i and subregion j
$\mathbf{n}^i_n$	unit normal vector to i-subregion average flow plane
$\mathbf{n}^i_t$	unit tangent vector to i-subregion average flow plane
O	the global reference system
p	pressure, $[F/L^2]$
$\mathbf{q}$	heat vector, $[M/T^3]$
Q	energy exchange per unit surface area projection, $[M/T^3]$
$\mathbf{R}$	first order friction term, $[FT/L^3]$
$\mathbf{U}$	second order friction term, $[FT^2/L^4]$
s	the saturation function, $[-]$
$\mathbf{t}$	microscopic stress tensor, $[M/T^2L]$
$\mathbf{T}$	momentum exchange per unit surface area projection, $[M/T^2L]$
$\mathbf{v}$	velocity vector of the bulk phases, $[L/T]$
V	volume, $[L^3]$
$\mathbf{w}$	velocity vector for phase and subregion boundaries, $[L/T]$
y^i	average vertical thickness of the i-subregion along the vertical, $[L]$
w^{r}	average channel top width, $[L]$

Greek symbols

γ^i	slope angle of the i-subregion flow plane with respect to the horizontal plane
Δ	indicates a time increment
ϵ	porosity, $[-]$
ϵ^i_α	i-subregion α-phase volume fraction, $[-]$
η	the entropy per unit mass, $[L^2/T^2\ {}^{\circ}]$
θ	the temperature
Λ^{co}	contour curve separating the two overland flow regions from each other
Λ^{or}	contour curve forming the edge of the channel
ξ^{r}	the length of the main channel reach C^{r} per unit surface area projection Σ, $[1/L]$
ρ	mass density, $[M/L^3]$
Σ	projection of the total REW surface area S onto the horizontal plane, $[L^2]$
$\bar{\boldsymbol{\tau}}$	the non-equilibrium part of the momentum exchange terms
ϕ	the gravitational potential
ω^i	The time-averaged surface area fraction occupied by the j-subregion, $[-]$

Subscripts and superscripts

i, j	superscripts which indicate the various phases or subregions within a REW
k	subscript which indicates the various REWs within the watershed
top	superscript for the atmosphere, delimiting the domain of interest at the top
bot	superscript for the the region delimiting the domain of interest at the bottom
α, β	indices which designate different phases
m, w, g	designate the solid matrix, the water and the gaseous phase, respectively

stream by Horton and Strahler [26,38], or can interconnect two internal nodes of the network, in which case it is classified as a *higher order stream*.

The size of the REWs used for the discretisation of the watershed is determined by the spatial and temporal resolutions, which are sought for the representation of the watershed and its response, as well as by the resolution of available data sets. Change of resolution is equivalent to a change of stream network density, while still maintaining the bifurcating tree-like structure.

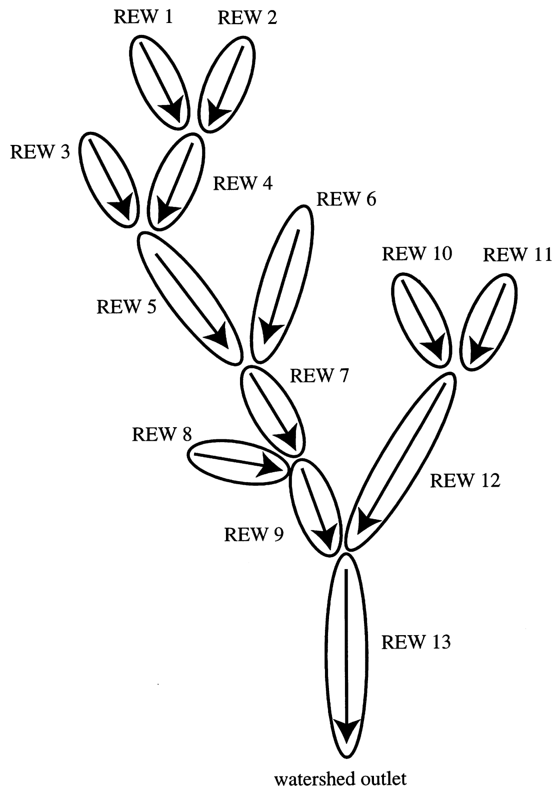

Fig. 1. Hierarchical arrangement of 13 REWs forming a watershed.

Consequently, the way we have defined the REWs with respect to the stream network assures the invariance of the concept of REW with change of spatial scale.

The ensemble of REWs constituting the watershed communicate with each other by way of exchanges of mass, momentum and energy through the inlet and outlet sections of the associated channel reaches. In addition, they can also communicate laterally through exchanges of these thermodynamic properties across the mantle separating them (through the soils). The REW-scale conservation equations are formulated by averaging the balance laws over five subregions forming the REW, as depicted in Fig. 2. These subregions have been chosen on the strength of previous field evidence about different processes which operate within catchments, their flow geometries and time scales. The five subregions chosen in this work are denoted as follows: Unsaturated zone, Saturated zone, Concentrated overland flow, saturated Overland flow and main channel Reach. The unsaturated and saturated zones form the subsurface regions of the REW where the soil matrix coexists with water (and the gas phase in the case of the unsaturated zone). The concentrated overland flow subregion includes surface flow within rills, gullies and small channels, and the regions affected by Hortonian overland flow. It covers the unsaturated portion of the land surface within the REW. The saturated overland flow subregion comprises the seepage faces, where the water table intersects the land surface and make up the saturated portion of the REW land surface. For more in-depth explanations about the concept of REW the reader is referred to Reggiani et al. [33].

The REW-scale balance equations obtained by the averaging procedure represent the various REWs as spatially lumped units. Hence these equations form a set of coupled non-linear ordinary differential equations (ODE), in time only; the only spatial variability allowed is between REWs. Any spatial variability at the

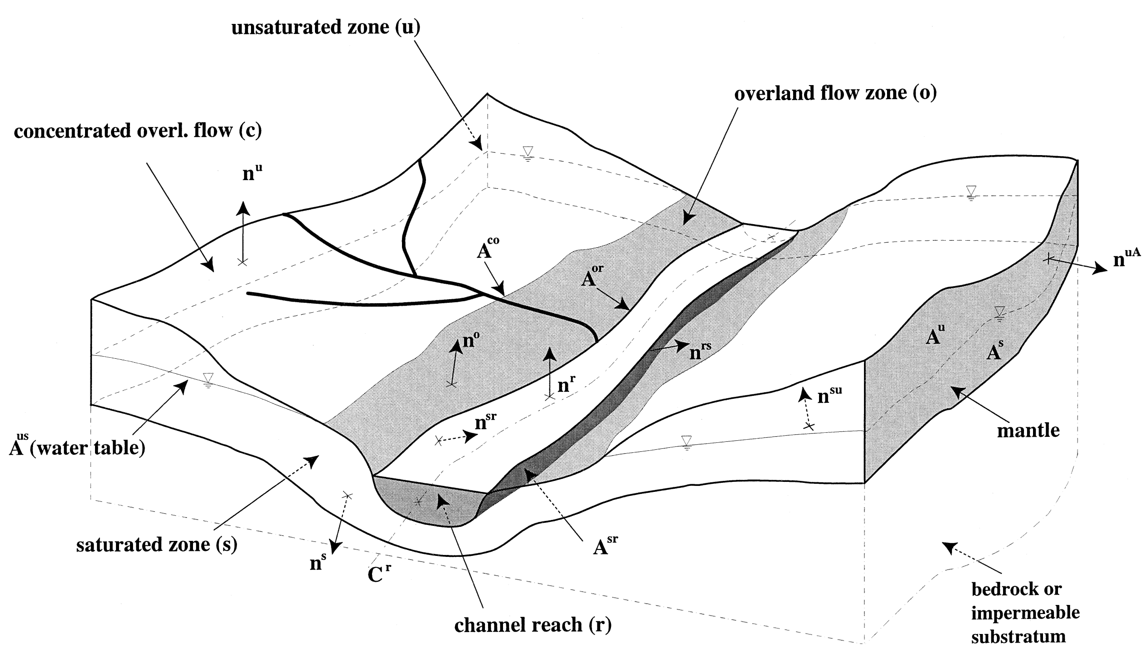

Fig. 2. Detailed view of the five subregions forming a REW.

sub-REW-scale is averaged over the REW and can be represented in terms of *effective* parameterisations in the constitutive equations to be derived in this paper.

In the course of the averaging procedure a series of exchange terms for mass, momentum, energy and entropy among phases, subregions and REWs have been defined. These terms are the unknowns of the problem. A major difficulty is that the total number of unknowns exceeds the number of available equations. The deficit of equations with respect to unknowns requires that an appropriate *closure scheme* has to be proposed, which will lead to the derivation of constitutive relationships for the unknown exchange terms. In this paper we resolve the closure problem by exploiting the second law of thermodynamics (i.e., entropy inequality) as a constraint-type relationship. This allows us to obtain *thermodynamically* admissible and *physically* consistent constitutive equations for the exchange terms within the framework of a single procedure, applied uniformly and consistently across the REWs. This approach for the derivation of constitutive relationships is known in the literature as *Coleman and Noll* [5] method.

The second law of thermodynamics constitutes an inequality representing the total entropy production of a system. The inequality can be expressed in terms of the variables and exchange terms for mass, momentum and energy of the system and is subject to the condition of non-negativity. Furthermore, the entropy inequality is subject to a minimum principle, as explained, for example, by Prigogine [32]. An absolute minimum of entropy production is always seen to hold under *thermodynamic equilibrium* conditions. Consequently, under these circumstances, the entropy production is zero. In non-equilibrium situations the entropy inequality has to assume always positive values, because the second law of thermodynamics dictates that the entropy production of the system is never negative. This imposes precise constraints on the functional form of the constitutive parameterisations and reduces the degree of arbitrariness in their choice.

The Coleman and Noll method has been successfully applied by Hassanizadeh and Gray for deriving constitutive relationships in the area of multiphase flow [22,18], for flow in geothermal reservoirs [17], for the theoretical derivation of the Fickian dispersion equation for multi-component saturated flow [21] and for flows in unsaturated porous media [23,19].

Next to the thermodynamic admissibility, a further guideline for the constitutive parameterisations is the necessity of capturing the observed physical behaviour of the system, including field evidence. For example, it has been shown that overland and channel flows obey Chezy-type relationships, where the momentum exchange between water and soil is given by a second order function of the flow velocity. Similarly, according to Darcy's law, the flow resistivities for slow subsurface flow can be expressed as linear functions of the velocity. We will show that the proposed constitutive parameterisations will lead, under steady state conditions, to a REW-scale Darcy's law for the unsaturated and the saturated zones, and to a REW-scale Chezy formula for the overland flow. In the case of flow in the channel network an equivalent of the *Saint–Venant* equations for a bifurcating structure of reaches will be obtained.

The final outcome of this paper is a system of 19 nonlinear coupled ordinary differential equations in as many unknowns for every REW. This set of equations needs to be solved simultaneously with the equation systems governing the flow in all the remaining REWs forming the watershed. A coupled (simultaneous) solution of the equation systems is necessary, since the flow field in one REW can influence the flow field in neighbouring REWs through up- and downstream backwater effects along the channel network, and through the regional groundwater flow crossing the REW boundaries. In developing the constitutive theory presented in this paper, we will make a number of simplifying assumptions to keep the problem manageable. Especially, the theory focusses on runoff processes at the expense of evapotranspiration, and hence the treatment of the latter is less than complete. Thermal effects, effects of vapour diffusion, vegetation effects and interactions with the atmospheric boundary layer will be neglected. These will be left for further research.

2. Balance laws, second law of thermodynamics and conditions of continuity

2.1. REW-scale balance laws

REW-scale conservation laws for mass, momentum, energy and entropy for the five subregions occupying the REW have been derived rigorously by Reggiani et al. [33] for a generic thermodynamic property ψ. In addition, the balance laws have been averaged in time, to accommodate different time scales associated with the various flow processes occurring within the watershed. The generic conservation law for the α-phase (water, soil, gas) within the i-subregion of an REW can be formulated as follows:

$$\frac{1}{2\Delta t}\frac{\mathrm{d}}{\mathrm{d}t}\int_{t-\Delta t}^{t+\Delta t}\int_{V_\alpha^i}\rho\psi\,\mathrm{d}V + \sum_{j\neq i}\frac{1}{2\Delta t}\int_{t-\Delta t}^{t+\Delta t}\int_{A_\alpha^{ij}}\mathbf{n}^{ij}\cdot[\rho\psi(\mathbf{v}-\mathbf{w}^{ij})-\mathbf{i}]\,\mathrm{d}A = \frac{1}{2\Delta t}\int_{t-\Delta t}^{t+\Delta t}\int_{V_\alpha^i}\rho f\,\mathrm{d}V + \frac{1}{2\Delta t}\int_{t-\Delta t}^{t+\Delta t}\int_{V_\alpha^i}\rho G\,\mathrm{d}V \qquad (2.1)$$

where f is the external supply of ψ, G is its rate of production per unit mass, ρ is the mass density, $\mathbf{v}$ is the velocity of the phase, $\mathbf{w}^{ij}$ is the velocity of the boundary, and Δt is an appropriate time averaging interval. The volume $V_\alpha^i, [L]$ indicates the volume filled by the i-subregion α-phase, normalised with respect to the horizontal surface area projection of the REW, Σ. The surface A_α^{ij} is the portion of boundary, delimiting the i-subregion α-phase towards the phase or subregion j. A_α^{ij} can assume the symbol A^{us} for the water table, A^{uc} for the unsaturated land surface, A^{os} for the seepage face, A^{sr} for the surface formed by the channel bed, A^{oc} or A^{or} to indicate the flow cross sections forming the boundaries between the saturated and the concentrated overland flow or the saturated overland flow and the channel, respectively. We note that the order of the superscripts can be interchanged arbitrarily. The surfaces delimiting the concentrated overland flow, saturated overland flow or the channel towards the atmosphere, are indicated with $A^{o\ top}$, $A^{c\ top}$ and $A^{r\ top}$, respectively. The portion of mantle surface delimiting the unsaturated and the saturated zones laterally, are indicated with A^{uA} and A^{sA}. Finally, phase interfaces, such as the water–gas, water–soil and soil–gas interfaces are indicated with the symbols S^{wg}, S^{ws} and S^{sg}. All these surfaces are summarised in Table 1.

We further observe that, in the case of the unsaturated zone, there are three phases present: the soil matrix indicated with m, the water phase w and the air–vapour mixture g. The saturated zone contains two phases, the water and the soil matrix. The overland flow zones and the channel reach comprise only the water phase. The various volumina V_α^i, expressed on a per-unit-area basis Σ, can be expressed as products of respective geometric variables. In the case of the unsaturated and saturated zones, V_α^i is the product of the area fractions $\omega^i, [-]$, occupied by the i-subregion, the average vertical thickness of the respective subregion, $y^i, [L]$, and the α-phase volume fraction, ϵ_α^i. For the saturated and the concentrated overland flow regions, the volume V^i of the only phase present (water), is the product of the horizontal area fraction ω^i and the average vertical thickness of the flow sheet, y^i. Finally, in the case of the channel, V^r is the product of the length of the channel reach per unit area, $\xi^r, [L^{-1}]$, and the average channel cross sectional area, $m^r, [L^2]$. The notations for these quantities are summarised in Table 1.

To obtain specific balance equations for mass, momentum, energy and entropy, the corresponding microscopic quantities indicated in Table 2 need to be substituted into Eq. (2.1). We note that, according to which type of balance equation we wish to obtain, the thermodynamic property, ψ, can be either equal to 1, or can assume the symbol of the velocity, $\mathbf{v}$, the sum of the internal and kinetic energy, $E + v^2/2$, or the entropy, η. The non-convective flux, $\mathbf{i}$, can be set equal to the zero vector, the stress tensor, $\mathbf{t}$, the sum of the product $\mathbf{t} \cdot \mathbf{v}$ plus the heat flux, $\mathbf{q}$, or the entropy flux, $\mathbf{j}$. The external supply term of ψ, f, can be set equal to zero, to the gravity vector, $\mathbf{g}$, the product $\mathbf{g} \cdot \mathbf{v}$ plus the energy supply, h, or the external entropy supply, b. We observe that the gravity can be alternatively expressed as the gradient of the gravitational potential, $\phi - \phi_0 = g(z - z_0)$, defined with respect to a datum. This form of f will be needed for the derivation of constitutive relationships. Finally, the internal production of ψ, G, is non-zero only for the balance of entropy and is set equal to L.

In addition, watershed-scale exchange for mass, forces, heat and entropy are introduced, which account for the transfer of these quantities among phases, subregions and REWs. These have been accurately defined on a case-by-case basis by Reggiani et al. [33]. Furthermore, these exchange terms constitute unknown quantities of the problem, for which constitutive relationships need to be sought. The following paragraphs present the resulting expressions for the balance

Table 1
Summary of the properties in the conservation equations

Subregion	Index i	Index α	Boundaries A^{ij}	Volume V_α^i
Unsaturated zone	u	w,m,g	$A_\alpha^{us}, A_\alpha^{uc}, A_\alpha^{uA}, S^{wm}, S^{wg}, S^{gm}$	$\epsilon_\alpha^u y^u \omega^u$
Saturated zone	s	w,m	$A_\alpha^{us}, A_\alpha^{so}, A_\alpha^{sA}, S^{wm}$	$\epsilon_\alpha^s y^s \omega^s$
Saturated overland flow	o	None	$A^{oc}, A^{so}, A^{or}, A^{o\ top}$	$y^o \omega^o$
Concentrated overland flow	c	None	$A^{oc}, A^{uc}, A^{c\ top}$	$y^c \omega^c$
Channel reach	r	None	$A^{rA}, A^{rs}, A^{ro}, A^{r\ top}$	$m^r \xi^r$

Table 2
Summary of the properties in the conservation equations

Balance equation	ψ	$\mathbf{i}$	f	G
Mass	1	0	0	0
Linear Momentum	$\mathbf{v}$	$\mathbf{t}$	$\mathbf{g}$ *or* $-\nabla(\phi - \phi_0)$	0
Energy	$E + \frac{1}{2}v^2$	$\mathbf{t} \cdot \mathbf{v} + \mathbf{q}$	$\mathbf{g} \cdot \mathbf{v} + h$ *or* $-\nabla(\phi - \phi_0) \cdot \mathbf{v} + h$	0
Entropy	η	$\mathbf{j}$	b	L

equations for mass, momentum, energy and entropy for the α-phase contained within the *i*-subregion. The balance equations are all expressed on a per-unit-area basis through division by the surface area projection Σ of the REW.

Conservation of mass. The conservation of mass for the *i*-subregion α-phase is stated as:

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho^i_\alpha V^i_\alpha) = \sum_{j\neq i} e^{ij}_\alpha \tag{2.2}$$

where the exchange terms e^{ij}_α express the mass source terms of *i*-subregion α-phase from the *j*-subregion. The mass exchange terms are normalised with respect to Σ and incorporate averaging in time. Their definition is:

$$e^{ij}_\alpha = \frac{1}{2\Delta t \Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{ij}_\alpha} \mathbf{n}^{ij}\cdot[\rho(\mathbf{w}^{ij}-\mathbf{v})]\,\mathrm{d}A\,\mathrm{d}\tau \tag{2.3}$$

Conservation of momentum. The appropriate microscopic quantities for the thermodynamic property ψ, the non-convective interaction **i**, the external supply of ψ, f, and the internal production, G, which need to be substituted into the generic balance Eq. (2.1), can be found in Table 2. First we employ $f = \nabla(\phi - \phi_0)$. For reasons of convenience we also introduce a specific areal vector $\mathbf{A}^{ij}_\alpha$:

Definition: We define $\mathbf{A}^{ij}_\alpha$ as a time-averaged vector, representing the fluid exchange surface and normalised with respect to the REW's surface area projection Σ:

$$\mathbf{A}^{ij}_\alpha = \frac{1}{2\Delta t \Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{ij}_\alpha} \mathbf{n}^{ij}\,\mathrm{d}A\,\mathrm{d}\tau. \tag{2.4}$$

Scalar multiplication of $\mathbf{A}^{ij}_\alpha$ with the unit vectors pointing, for example, along the axes of a Cartesian reference system, yield respective projections of area A^{ij}_α onto the *yz*, *xz* and *xy* planes, respectively:

$$A^{ij}_{\alpha,\lambda} = \mathbf{A}^{ij}_\alpha \cdot \mathbf{e}_\lambda, \quad \lambda = x, y, z. \tag{2.5}$$

After introducing appropriate symbols for the momentum exchange terms, and employing the definition Eq. (2.4), we obtain for constant mass densities:

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho^i_\alpha \mathbf{v}^i_\alpha V^i_\alpha) = \sum_{j\neq i}\left[e^{ij}_\alpha \mathbf{v}^i_\alpha + \mathbf{T}^{ij}_\alpha - \frac{1}{2\Delta}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{ij}_\alpha}(\phi-\phi_0)\mathbf{n}^{ij}\,\mathrm{d}A\,\mathrm{d}\tau\right]. \tag{2.6}$$

The integral in the last term can be replaced by introducing the average gravitational potential of the α-phase with respect to a datum, calculated over A^{ij}_α:

$$(\phi^{ij}_\alpha - \phi^i_0)\int_{t-\Delta t}^{t+\Delta t}\int_{A^{ij}_\alpha}\mathrm{d}A\,\mathrm{d}\tau = \int_{t-\Delta t}^{t+\Delta t}\int_{A^{ij}_\alpha}(\phi-\phi_0)\,\mathrm{d}A\,\mathrm{d}\tau \tag{2.7}$$

with ϕ^i_0 a common reference potential for all phases of the *i*-subregion. The operation yields the momentum balance in the form:

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho^i_\alpha \mathbf{v}^i_\alpha V^i_\alpha) = \sum_{j\neq i}\left[e^{ij}_\alpha \mathbf{v}^i_\alpha + \mathbf{T}^{ij}_\alpha - \rho^i_\alpha(\phi^{ij}_\alpha - \phi^i_0)\mathbf{A}^{ij}_\alpha\right]. \tag{2.8}$$

The REW-scale momentum exchange terms $\mathbf{T}^{ij}_\alpha$ are given by the expression:

$$\mathbf{T}^{ij}_\alpha = \frac{1}{2\Delta t \Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{ij}_\alpha} \mathbf{n}^{ij}\cdot[\mathbf{t} - \rho(\mathbf{v}-\mathbf{w}^{ij})\tilde{\mathbf{v}}]\,\mathrm{d}A\,\mathrm{d}\tau, \tag{2.9}$$

where the microscopic stress effects, attributable to the deviations $\tilde{\mathbf{v}}$ of the REW-scale velocity from its spatial and temporal average, have been incorporated into the momentum exchange terms. Alternatively we can employ the gravity vector as external supply of momentum, $f = \mathbf{g}$, instead of the gravitational potential. Consequently we obtain an expression for the momentum balance equivalent to Eq. (2.8):

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho^i_\alpha \mathbf{v}^i_\alpha V^i_\alpha) = \rho^i_\alpha \mathbf{g}^i_\alpha V^i_\alpha + \sum_{j\neq i}\left[e^{ij}_\alpha \mathbf{v}^i_\alpha + \mathbf{T}^{ij}_\alpha\right]. \tag{2.10}$$

We emphasise that, while the use of Eq. (2.8) is necessary for the development of the constitutive relationship, Eq. (2.10) is employed as a governing equation, because the explicit consideration of the gravity vector will prove more useful, when projection of the equations along the axes of a reference system is required, as will be shown in Section 6.

Conservation of energy. The balance equation for total energy includes the sum of kinetic, internal and potential energies. The appropriate microscopic quantities ψ, **i**, f and G, which need to be substituted into Eq. (2.1), are reported in Table 2. For constant density systems we obtain:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left[\left[E^i_\alpha + \frac{1}{2}(v^i_\alpha)^2\right]\rho^i_\alpha V^i_\alpha\right] = \sum_{j\neq i} e^{ij}_\alpha\left[E^i_\alpha + \frac{1}{2}(v^i_\alpha)^2\right] + \sum_{j\neq i}\left[\mathbf{T}^{ij}_\alpha - \rho^i_\alpha(\phi^{ij}_\alpha - \phi^i_0)\mathbf{A}^{ij}_\alpha\right]\cdot\mathbf{v}^i_\alpha + \sum_{j\neq i} Q^{ij}_\alpha + \rho^i_\alpha h^i_\alpha V^i_\alpha \tag{2.11}$$

The REW-scale heat exchange terms Q^{ij}_α are defined as:

$$Q^{ij}_\alpha = \frac{1}{2\Delta t \Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{ij}_\alpha} \mathbf{n}^{ij}\cdot[\mathbf{q} + \mathbf{t} + \rho(\phi-\phi_0)\mathbf{I}]\cdot\tilde{\mathbf{v}} - \rho(\mathbf{v}-\mathbf{w}^{ij}) \times [\tilde{E}^i_\alpha + (\tilde{v}^i_\alpha)^2/2]\,\mathrm{d}A\,\mathrm{d}\tau. \tag{2.12}$$

We observe, that the surface integrals of the velocity, internal and kinetic energy fluctuations $\tilde{\mathbf{v}}$, $\tilde{E}^i_\alpha$, and $(\tilde{v}^i_\alpha)^2/2$, can be envisaged as contributing to watershed-scale heat exchanges. Therefore, these quantities have been incorporated into the heat exchange term Q^{ij}_α.

Balance of entropy. Finally, we obtain the balance equations of entropy. After substituting the necessary microscopic values, by observing that the internal generation of entropy, G, is non-zero, and introducing REW-scale exchange terms of entropy, we obtain:

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho^i_\alpha \eta^i_\alpha V^i_\alpha) = \sum_{j \neq i}\left[e^{ij}_\alpha \eta^i_\alpha + F^{ij}_\alpha\right] + \rho^i_\alpha b^i_\alpha V^i_\alpha + \rho^i_\alpha L^i_\alpha V^i_\alpha, \tag{2.13}$$

where F^{ij}_α is given in analogy to previous definitions for the exchange terms:

$$F^{ij}_\alpha = \frac{1}{2\Delta t \Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{ij}_\alpha} \mathbf{n}^{ij}\cdot[\mathbf{j} - \rho(\mathbf{v} - \mathbf{w}^{ij})\tilde{\eta}]\,\mathrm{d}A\,\mathrm{d}\tau \tag{2.14}$$

where $\tilde{\eta}$ are the fluctuations of the entropy from its space-time average over the i-subregion α-phase.

2.2. The second law of thermodynamics

The second law of thermodynamics states that the total production of entropy within a physical system has to be always non-negative. In the present case, the system under consideration is taken to be the entire watershed, which has been discretised into an ensemble of M REWs. The decision to take the entire watershed as the physical system, instead of a single REW or subregion, is dictated by the fact that the sign of the inter-REW and inter-subregion entropy exchange terms are not known. According to the second law of thermodynamics, the total entropy production on a per-unit-area basis, L, for the entire watershed composed of M REWs, obeys the following inequality:

$$L = \sum_{k=1}^{M}\left[\sum_i \sum_\alpha \rho^i_\alpha L^i_\alpha V^i_\alpha\right]_k \geqslant 0. \tag{2.15}$$

The inequality (2.15) can be expressed in terms of the balance equation of entropy Eq. (2.13) for the individual phases and subregions by applying the chain rule of differentiation to the left-hand side term and making use of the conservation equation of mass Eq. (2.2):

$$L = \sum_{k=1}^{M}\left[\sum_i \sum_\alpha \rho^i_\alpha V^i_\alpha \frac{\mathrm{d}\eta^i_\alpha}{\mathrm{d}t}\right]_k - \sum_{k=1}^{M}\left[\sum_i \sum_\alpha \sum_{j\neq i} F^{ij}_\alpha\right]_k - \sum_{k=1}^{M}\left[\sum_i \sum_\alpha \rho^i_\alpha b^i_\alpha V^i_\alpha\right]_k \geqslant 0. \tag{2.16}$$

2.3. Conditions of continuity (jump conditions)

In addition to the above balance laws, there are restrictions imposed on the properties' exchange terms at the boundaries, where different phases, subregions or REWs come together. These restrictions simply express the fact that the net transfer of a property between phases across an inter-phase boundary (e.g. water-gas interface) needs to be zero. A similar restriction applies to the net transfer of properties between subregions (e.g. across the water table, the channel bed or the saturated land surface). This is equivalent to the assumption that the boundary surfaces are neither able to store mass, energy or entropy, nor to sustain stress. The total net exchange of a property across a boundary is zero. These restrictions are commonly known as *jump conditions* and are, as such, derived in the standard literature of continuum mechanics (see e.g. Ref. [16]). The specific jump conditions which supplement the balance equations for mass, momentum, energy and entropy are stated specifically in the next paragraphs.

Continuity of mass exchange. The jump condition for mass expresses the fact that the net transfer of material from the i and the j subregions towards the interface A^{ij}_α must equal zero:

$$e^{ij}_\alpha + e^{ji}_\alpha = 0. \tag{2.17}$$

Continuity of momentum exchange. The sum of forces exchanged across the interface need to satisfy conditions of continuity. These include apparent forces attributable to the mass exchange and the total stress force attributable to viscous and pressure forces:

$$\begin{aligned} &e^{ij}_\alpha(\mathbf{v}^i_\alpha - \mathbf{v}^j_\alpha) + \mathbf{T}^{ij}_\alpha + \mathbf{T}^{ji}_\alpha - \left[\rho^i_\alpha(\phi^{ij}_\alpha - \phi^i_0)\right. \\ &\quad \left. - \rho^j_\alpha(\phi^{ji}_\alpha - \phi^j_0)\right]\mathbf{A}^{ij}_\alpha = 0, \end{aligned} \tag{2.18}$$

where we have exploited the fact that $\mathbf{A}^{ij}_\alpha = -\mathbf{A}^{ji}_\alpha$. We also note that in the case of interfaces within the same fluid, the densities are equal and, therefore:

$$\left[\phi^{ij}_\alpha - \phi^i_0\right] - \left[\phi^{ji}_\alpha - \phi^j_0\right] = 0 \tag{2.19}$$

yielding the jump conditions in the form derived in Reggiani et al. [33]. For reasons of convenience in the manipulations of the entropy inequality in Section 4, the gravitational potentials are retained in the jump conditions.

Continuity of energy exchange. The continuity of exchange of energy across the A^{ij}_α interface requires that the transfer of internal and kinetic energies due to mass exchange, and the work of the REW-scale viscous and pressure forces, obeys the following expression:

$$\begin{aligned} &e^{ij}_\alpha\left[E^i_\alpha - E^j_\alpha + \frac{1}{2}\left[(v^i_\alpha)^2 - (v^j_\alpha)^2\right]\right] + \mathbf{T}^{ij}_\alpha\cdot\mathbf{v}^i_\alpha + \mathbf{T}^{ji}_\alpha\cdot\mathbf{v}^j_\alpha \\ &\quad -\left[\rho^i_\alpha(\phi^{ij}_\alpha - \phi^i_0)\mathbf{v}^i_\alpha - \rho^j_\alpha(\phi^{ji}_\alpha - \phi^j_0)\mathbf{v}^j_\alpha\right]\cdot\mathbf{A}^{ij}_\alpha + Q^{ij}_\alpha + Q^{ji}_\alpha = 0. \end{aligned} \tag{2.20}$$

Continuity of entropy exchange. The continuity of exchange of entropy across the interface requires satisfaction of the condition:

$$e^{ij}_\alpha(\eta^i_\alpha - \eta^j_\alpha) + F^{ij}_\alpha + F^{ji}_\alpha \geqslant 0, \tag{2.21}$$

where the inequality sign accommodates the possibility of entropy production of the interface.

3. The global reference system

The conservation equation of momentum for the various subregions constitute vectorial equations, defined in terms of components with respect to an appropriate reference system. In order to be able to employ the equation for the evaluation of the velocity, we have to introduce a global reference system and effective directions of flow, along which the vectorial equations can be projected.

Saturated zone: In Ref. [33] we have assumed that the regional groundwater flow can be exchanged between neighbouring REWs. A global reference system O needs to be introduced for the entire watershed, with respect to which the whole ensemble of REWs can be positioned. The origin of the reference system can be placed for example at the watershed outlet. We observe that other locations for the origin O can also be chosen, as long as the reference elevation is positioned properly for the ensemble of REWs. The global reference system O has two mutually perpendicular coordinates x and y lying in the horizontal plane and a coordinate z directed vertically upwards. We introduce three unit vectors, $\mathbf{e}_x$, $\mathbf{e}_y$, $\mathbf{e}_z$, pointing along the three directions, respectively. The forces acting on the water within the saturated zone will be projected along the three directions by taking the scalar product between the conservation equation of momentum and the respective unit vector. The gravity vector has its only non-zero component along the vertical direction in the reference system O:

$$\mathbf{g} = -g\mathbf{e}_z. \tag{3.1}$$

Fig. 3 shows the global reference system O positioned at the outlet of a watershed which has been discretised into 13 REWs.

Fig. 3. A real world watershed subdivided into 13 REWs and the global reference system (Sabino Canyon, Santa Catalina Mountains, SE-Arizona, Reproduced from K. Beven and M.J. Kirkby, Channel Network Hydrology, Wiley.

Unsaturated zone: The flow in the unsaturated zone can be considered as directed mainly along the vertical direction from the soil surface downwards into the saturated zone or rising vertically upwards from the water table due to capillary forces. The possibility of horizontal motion within the unsaturated zone is also considered. We can project the balance equation for momentum in the unsaturated zone along the axes of the global reference system by taking the scalar product with $\mathbf{e}_x$, $\mathbf{e}_y$ and $\mathbf{e}_z$.

Saturated and concentrated overland: The flow in the overland flow zones is occurring on a complex, curvilinear surface, for which only the direction of the *effective normal* to the surface with respect to the vertical or the horizontal plane can be determined uniquely. There are infinite possible directions for the choice of *effective tangents* to the flow surface. Fortunately, we know that, in the absence of micro-topographic effects on the land surface, the flow on the land surface crosses the contour lines perpendicularly, along the direction of steepest descent. As a consequence the flow can be assumed to be effectively one-dimensional and to occur on a plane with an average inclination as depicted in Fig. 4. Effects of any departures from this assumption can be incorporated into the constitutive parameterisation, but is left for future research.

The average angle of inclination γ of the line of steepest descent with respect to the vertical direction or the horizontal plane can be determined from topographic data (e.g. digital elevation maps). In order to account for two separate *effective slopes* for the concentrated and the saturated overland flow zones we introduce the following two formulas:

$$\gamma^{\mathrm{o}} = cos^{-1}(\Sigma^{\mathrm{o}}/S^{\mathrm{o}}) \tag{3.2}$$

and

$$\gamma^{\mathrm{c}} = cos^{-1}(\Sigma^{\mathrm{c}}/S^{\mathrm{c}}). \tag{3.3}$$

The quantities S^{o} and S^{c} are the surface areas covered by the saturated and the concentrated overland flow subregions, while Σ^{o} and Σ^{c} are their respective projections onto the horizontal plane. Even though the direction of flow with respect to the global reference system cannot be determined for overland flow, we introduce fictitious unit vectors which are tangent and normal to the inclined flow plane and labelled with $\mathbf{n}^{\mathrm{o}}_t$ and $\mathbf{n}^{\mathrm{o}}_n$ in the case of the saturated overland flow, as can be seen from Fig. 4. For the concentrated overland flow the unit vectors $\mathbf{n}^{\mathrm{c}}_t$ and $\mathbf{n}^{\mathrm{c}}_n$ are introduced.

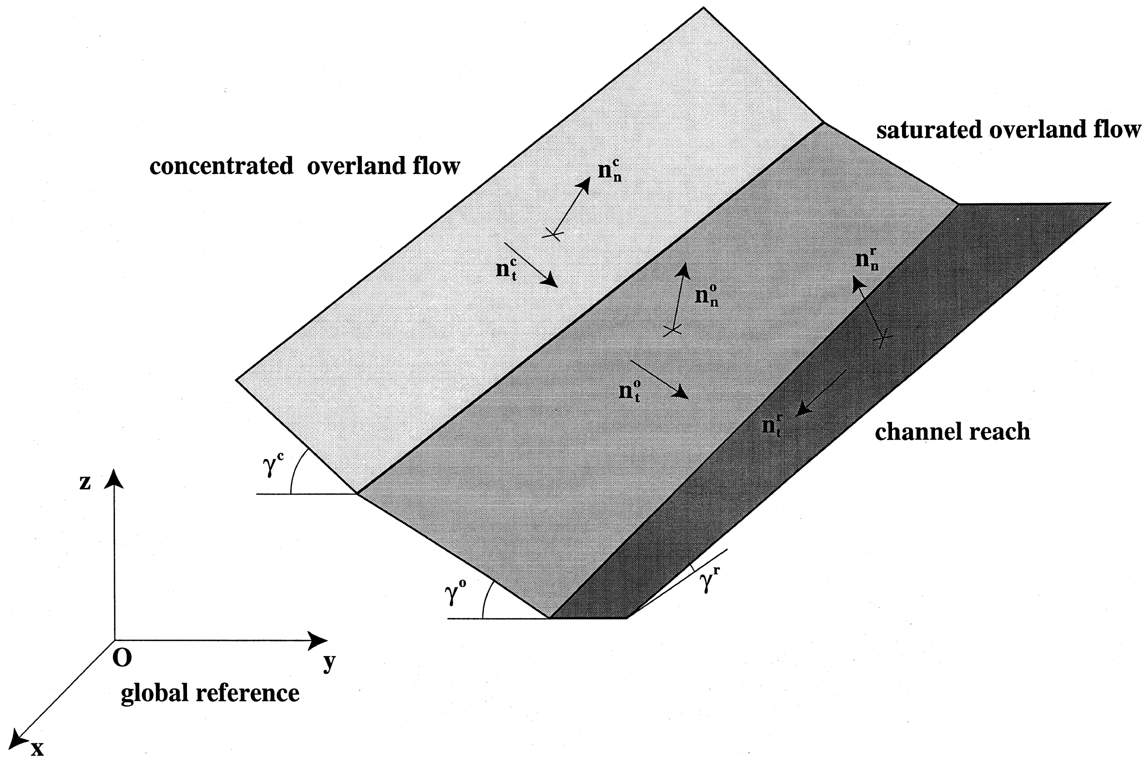

Fig. 4. Effective directions of flow and slope angles for the overland regions and the channel reach.

Channel reach: Channel flow occurs along a tortuous path from the highest point at the REW inlet to the lowest point at the outlet. Effects of the curvatures or meandering of stream channels can sometimes have a significant impact on the momentum exchanges and energy dissipation, and would need to be factored in the constitutive relations. For the present, however, we will assume that the channel flow is directed along a straight line, whose angle with respect to the horizontal surface can be determined from topographic data by using the following formula:

$$\gamma^{\mathrm{r}} = \sin^{-1}(\Delta H / C^{\mathrm{r}}), \tag{3.4}$$

where ΔH is the elevation drop of the channel bed between inlet and outlet and C^{r} is the length of the curve forming the channel axis. Also in this case we introduce unit vectors tangent and normal to the effective direction of flow, labelled with $\mathbf{n}_t^{\mathrm{r}}$ and $\mathbf{n}_n^{\mathrm{r}}$, respectively, as shown in Fig. 4.

4. Constitutive theory

The system of equations in Section 2, derived for the description of thermodynamic processes in a REW, comprises in total 24 balance equations for the water, solid and gaseous phases in the unsaturated zone, the water and the solid phases in the saturated zone and the water phase in the two overland flow zones and in the channel. The total number of available equations is given by 8 mass balance equations, 8 (vectorial) momentum balance equations and 8 energy balance equations, respectively. In order to keep the theory development manageable, we adopt a number of simplifying assumptions which seem reasonable when studying runoff processes:

Assumption I. We consider the soil matrix as a rigid medium. The respective velocities can, therefore, be set equal to zero:

$$\mathbf{v}_m^{\mathrm{u}} = \mathbf{v}_m^{\mathrm{s}} = 0. \tag{4.1}$$

In addition, the effects of dynamics of the gas phase on the system are assumed to be negligible:

$$\mathbf{v}_g^{\mathrm{u}} = 0. \tag{4.2}$$

Assumption II. The system is unithermal, i.e., the temperatures of all phases and subregions of the M REWs forming the watershed are equal to a common reference temperature denoted by θ. This assumption is valid in the absence of (geo) thermal activities and limited temperature excursions of the land surface. The assumption is justified whenever the focus of hydrology is restricted to runoff processes, which is the case in this study. It is clearly not justified, if the focus is on evapotranspiration processes where thermal effects and water vapour transport are critical. The unithermal assumption subsequently allows us to eliminate those terms in the entropy inequality which account for the production of entropy due to heat exchanges among subregions and REWs.

Assumption III. We assume that we are dealing with a *simple thermodynamic system*. For such systems it is generally assumed that the external energy supply terms, b, are related only to external energy sources, h:

$$b^i_\alpha = \frac{h^i_\alpha}{\theta}. \tag{4.3}$$

We realise that the assumption of zero velocity of the gaseous phase is very restrictive and cannot be sustained when studying evaporation. For the purposes pursued within the framework of this paper, where the main focus is oriented towards the study of the water phase motion, Assumption I allows significant notational simplifications and simplifies the derivation considerably. Inclusion of the motion of the gaseous phase will be pursued in the future.

Assumption II can and should be relaxed if one is interested in thermal processes and modelling of land-atmosphere interactions involving energy transfer. Assumption III is generally accepted in continuum mechanics and is reported in the standard literature (see e.g. Ref. [16]).

We recall that there are still unknown quantities, represented by the exchange terms for mass, e, and momentum, $\mathbf{T}$, as well as the entropies η. The external supply term h in the balance equations for energy and the gravity $\mathbf{g}$ are known functions.

Assumptions I and II allow us to eliminate the balance equations for thermal energy and the balance equations for mass and momentum for the gaseous and the solid phases. The system is thus reduced to 5 mass and 5 (vectorial) momentum balance equations (one for each subregion). It is evident, that the unknown variables and exchange terms involved in the equations exceed by far the number of available equations, leading to an indeterminate system. The deficit will have to be provided for by *constitutive relationships*. For this purpose, a set of *independent variables* needs to be selected. The remaining unknowns are successively expressed as functions of the independent variables and are, therefore, labelled as *dependent variables*.

For the system under study we expect, for example, the velocities of the fluid phases $\mathbf{v}$, the saturation function s^u for the unsaturated zone, the volumina $y^u\omega^u$, $y^s\omega^s$, $y^c\omega^c$, $y^o\omega^o$ and $m^r\xi^r$ of the various subregions to be important descriptors of the system. We have chosen the products of two quantities as independent variables because they always appear together in the equations. Finally, the mass densities of water also have to be included in the list of independent variables. The resulting complete list of these unknowns for all subregions is summarised in Table 3. We are thus confronted with a system of 10 equations in 16 unknowns. To overcome the deficit of equations we will have to introduce constitutive relationships. The development of the constitutive equations will be pursued in a systematic fashion, in order to reduce arbitrariness in the possible choices for the parameterisations. For this purpose we will make use of the method of Coleman and Noll [5], based on the exploitation of the entropy inequality. This analysis will be presented in the following sections.

4.1. Constitutive assumptions for the internal energies

The Coleman and Noll method involves postulation of the functional dependencies of the phase internal energies. We adopt the fundamental approach pioneered by Callen [4] as a guideline for this development. According to Callen, the extensive internal energies $\mathscr{E}$ for the five subregions and respective phases are dependent on their extensive entropy $\mathscr{S}$, volume $\mathscr{V}$ and total mass $\mathscr{M}$:

$$\mathscr{E} = \mathscr{E}(\mathscr{S}, \mathscr{V}, \mathscr{M}). \tag{4.4}$$

The *Euler forms* of the internal energies (see Ref. [4]) are obtained by taking a first order Taylor series expansion of Eq. (4.4):

$$\mathscr{E} = \theta\mathscr{S} - p\mathscr{V} + \mu\mathscr{M}, \tag{4.5}$$

where θ is the temperature, p is the pressure of the phase and μ is the chemical potential. The extensive internal energy needs to be converted into a corresponding specific internal energy, such as energy per unit mass or volume. We select energy per unit volume as the variable of choice. The expression (4.5) is subsequently divided by the volume:

$$\hat{E} = \theta\hat{\eta} - p + \mu\rho, \tag{4.6}$$

where $\hat{E}$ and $\hat{\eta}$ are the internal energy and the entropy per unit volume. With particular reference to the i-subregion α-phase, we specifically obtain:

Table 3
List of independent variables

Variable	Nomenclature	Number of unknowns
Water saturation	s^u	1
Volumina	$y^u\omega^u, y^s\omega^s, y^c\omega^c, y^o\omega^o, m^r\xi^r$	1, 1, 1, 1, 1
Water phase densities	$\rho^u, \rho^s, \rho^c, \rho^o, \rho^r$	1, 1, 1, 1, 1
Water phase velocity (vectorial)	$\mathbf{v}^u, \mathbf{v}^s, \mathbf{v}^c, \mathbf{v}^o, \mathbf{v}^r$	1, 1, 1, 1, 1
Total		16

$$\hat{E}^i_\alpha = \theta\hat{\eta}^i_\alpha - p^i_\alpha + \mu^i_\alpha\rho^i_\alpha. \tag{4.7}$$

Subsequently, we differentiate the internal energy Eq. (4.7) with respect to time and rearrange:

$$\frac{\mathrm{d}\hat{\eta}^i_\alpha}{\mathrm{d}t} = \frac{1}{\theta}\frac{\mathrm{d}\hat{E}^i_\alpha}{\mathrm{d}t} - \frac{\hat{\eta}^i_\alpha}{\theta}\frac{\mathrm{d}\theta}{\mathrm{d}t} + \frac{1}{\theta}\frac{\mathrm{d}p^i_\alpha}{\mathrm{d}t} - \frac{\mu^i_\alpha}{\theta}\frac{\mathrm{d}\rho^i_\alpha}{\mathrm{d}t} - \frac{\rho^i_\alpha}{\theta}\frac{\mathrm{d}\mu^i_\alpha}{\mathrm{d}t}. \tag{4.8}$$

The Gibbs–Duhem equality, derived from the first law of thermodynamics [4], provides the information that:

$$\hat{\eta}^i_\alpha \mathrm{d}\theta - \mathrm{d}p^i_\alpha + \rho\,\mathrm{d}\mu^i_\alpha = 0 \tag{4.9}$$

so that Eq. (4.8), after multiplication by the volume V^i_α, assumes the form:

$$V^i_\alpha \frac{\mathrm{d}\hat{\eta}^i_\alpha}{\mathrm{d}t} = \frac{V^i_\alpha}{\theta}\frac{\mathrm{d}\hat{E}^i_\alpha}{\mathrm{d}t} - \frac{V^i_\alpha\mu^i_\alpha}{\theta}\frac{\mathrm{d}\rho^i_\alpha}{\mathrm{d}t}. \tag{4.10}$$

Substitution of Eq. (4.10) into equation Eq. (2.16), where the entropy has been previously converted on a per-unit-volume basis, yields:

$$L = \sum_{k=1}^{M}\left[\sum_i\sum_\alpha V^i_\alpha\left(\frac{1}{\theta}\frac{\mathrm{d}\hat{E}^i_\alpha}{\mathrm{d}t} - \frac{\mu^i_\alpha}{\theta}\frac{\mathrm{d}\rho^i_\alpha}{\mathrm{d}t}\right)\right]_k + \hat{\eta}^i_\alpha\frac{\mathrm{d}V^i_\alpha}{\mathrm{d}t} - \sum_{k=1}^{M}\left[\sum_i\sum_\alpha\sum_{j\neq i}F^{ij}_\alpha\right]_k - \sum_{k=1}^{M}\left[\sum_i\sum_\alpha \rho^i_\alpha b^i_\alpha V^i_\alpha\right]_k \geqslant 0. \tag{4.11}$$

We employ the conservation equation of energy Eq. (2.11), together with the balance equation of mass Eq. (2.2) and the jump conditions for mass, momentum energy and entropy Eqs. (2.17)–(2.21) to eliminate the rate of change of internal energy and the exchange term for entropy. This process is significantly simplified by making the following assumption.

Assumption IV. The phases are incompressible:

$\rho^i_\alpha = \text{constant}.$

We keep also in mind, that from Eq. (4.7) the pressure can be expressed in terms of the temperature and the chemical potential:

$$-p^i_\alpha(\theta, \mu^i_\alpha) = \hat{E}^i_\alpha - \theta\hat{\eta}^i_\alpha - \rho^i_\alpha\mu^i_\alpha. \tag{4.12}$$

The outlined manipulations yield, with the use of Assumptions I–IV, the final expression:

$$\begin{aligned} L = {} & \sum_{k=1}^{N}\left[\sum_i\sum_\alpha\sum_{j\neq i}\frac{1}{\theta}\left[\mu^{j,i}_\alpha + \phi^{j,i}_\alpha\right]e^{ij}_\alpha\right]_k \\ & + \sum_{k=1}^{N}\left[\sum_i\sum_\alpha\sum_{j\neq i}\frac{1}{\theta}\left[-\mathbf{T}^{ij}_\alpha + \rho^i_\alpha(\phi^{ij}_\alpha - \phi_0)\mathbf{A}^{ij}_\alpha - \frac{1}{2}e^{ij}_\alpha\mathbf{v}^i_\alpha\right]\cdot\mathbf{v}^i_\alpha\right]_k \\ & + \sum_{k=1}^{N}\left[\sum_i\sum_\alpha\frac{1}{\theta}\left[\rho^i_\alpha(\phi^i_\alpha - \phi_0) + p^i_\alpha\right]\dot{V}^i_\alpha\right]_k \geqslant 0, \end{aligned} \tag{4.13}$$

where ϕ_0 has been selected as the common reference potential for all phases, subregions and REWs constituting the watershed, and $\phi^i_\alpha - \phi_0$ is the gravitational potential for the i-subregion α-phase, calculated with respect to its centre of mass:

$$(\phi^i_\alpha - \phi_0)\rho^i_\alpha\int_{V^i_\alpha}\mathrm{d}V = \int_{V^i_\alpha}\rho(\phi - \phi_0)\,\mathrm{d}V. \tag{4.14}$$

We observe that, while the microscopic function $\phi - \phi_0$ is independent of time, $\phi^i_\alpha - \phi_0$ is a function of time.

4.2. The entropy inequality at equilibrium

According to the second law of thermodynamics, the entropy production of the entire system is always non-negative and will be zero only at thermodynamic equilibrium. To extract more information from the entropy inequality Eq. (4.13), the system will be analysed by imposing equilibrium. For the system of phases, subregions and REWs considered here, a situation of thermodynamic equilibrium can be defined as the configuration where there is absence of motion and the mass exchange terms between phases, subregions and REWs are zero. This can be expressed in quantitative terms by stating that the following set of variables in Eq. (4.13) are zero for the kth REW:

$$(z_\mu)_k = [\mathbf{v}^i_\alpha, \dot{V}^i_\alpha, e^{ij}_\alpha]_k = 0. \tag{4.15}$$

In addition, at equilibrium, all the temperatures of the different subregions and the surrounding environment (i.e. atmosphere, underlying strata) are at an equilibrium temperature θ, and none of the subregions is subject to expansion or contraction in terms of respective volumina occupied by the subregions and phases. Furthermore, the velocities of the water and the gaseous phases are zero. The above defined set $(z_\mu)_k$ identifies a variable space, wherein the entropy production L of the entire watershed is defined. The situation of thermodynamic equilibrium is equivalent to L being at its absolute minimum. At the origin of the variable space, where all $(z_\mu)_k$ are zero, we have that $L = 0$. The necessary and sufficient conditions to assure that L is at an absolute minimum are that:

$$\left[\frac{\partial L}{\partial (z_\lambda)_k}\right]_e = 0 \tag{4.16}$$

and that the functional is concave around the origin, which requires the second derivative

$$\left\|\left[\frac{\partial^2 L}{\partial (z_\mu)_k \partial (z_\lambda)_k}\right]_e\right\| \tag{4.17}$$

to be positive semi-definite. To further exploit the entropy inequality, an equilibrium situation needs to be defined for every subregion. These definitions are strongly dependent on the hydrologic situations under consideration and are presented in Section 5. Subsequently, the inequality (4.13) will be differentiated with respect to the set of variables Eq. (4.15) and condition

(4.16) needs to imposed. The result of this operation yields a series of equilibrium conditions. From the first line of Eq. (4.13) we obtain that

$$\mu^i_\alpha + \phi^i_\alpha = \mu^j_\alpha + \phi^j_\alpha, \tag{4.18}$$

while the differentiation of the second line with respect to $\mathbf{v}^i_\alpha$ yields:

$$-\mathbf{T}^{ij}_\alpha|_e + \rho^i_\alpha(\phi^{ij}_\alpha - \phi_0)\mathbf{A}^{ij}_\alpha = 0. \tag{4.19}$$

From the last term of Eq. (4.13) we obtain the equilibrium condition

$$p^i_\alpha + \rho^i_\alpha(\phi^i_\alpha - \phi_0) = 0. \tag{4.20}$$

Combination of Eqs. (4.19) and (4.20) finally leads to the equilibrium expression for the momentum exchange term:

$$\mathbf{T}^{ij}_\alpha|_e = [-p^i_\alpha + \rho^i_\alpha(\phi^{ij}_\alpha - \phi^i_\alpha)]\mathbf{A}^{ij}_\alpha. \tag{4.21}$$

Eq. (4.21) needs to be projected along the axes of the reference system O introduced in Section 3, to evaluate the pressure forces acting on the various phases. The expression can be used for two different purposes: first, if the pressure is known, Eq. (4.21) can be employed for the evaluation of $\mathbf{T}^{ij}_\alpha|_e$, second, if $\mathbf{T}^{ij}_\alpha|_e$ is known, Eq. (4.21) will prove useful for the evaluation of p^i_α.

4.3. Non-equilibrium parameterisation of the momentum exchange terms

Under non-equilibrium conditions, viscous forces appear next to the pressure forces due to the motion of the fluid and the resulting frictional resistance. Consequently, we propose to add a non-equilibrium component to the sum of all equilibrium forces acting on the phases, which becomes zero at equilibrium:

$$\sum_{j\neq i}\mathbf{T}^{ij}_\alpha = \sum_{j\neq i}\mathbf{T}^{ij}_\alpha|_e + \bar{\boldsymbol{\tau}}^i_\alpha, \tag{4.22}$$

where $\mathbf{T}^{ij}_\alpha|_e$ are given by Eq. (4.21) and $\bar{\boldsymbol{\tau}}^i_\alpha$ is the non-equilibrium component of the forces. The non-equilibrium part can be expanded as a first or second order function of the velocity, depending on which type of flow we are describing. This procedure is based on a Taylor series expansion. First-order approximations are suitable for conditions of slow flow, where second order terms can be considered unimportant. This is especially the case for the flow in the unsaturated and saturated zones. The linearised non-equilibrium term assumes the following form:

$$\bar{\boldsymbol{\tau}}^i_\alpha = -\mathbf{R}^i_\alpha \cdot \mathbf{v}^i_\alpha, \tag{4.23}$$

where $\mathbf{R}^j$ is a tensor, which is a function of the remaining independent variables and parameters of the system. For the flow occurring on the land surface and in the channel, experimental observations suggest that the friction forces depend on the square of the velocity. This fact is evident from formulations such as Chezy's and Manning's law, which serve as parameterisations for the bottom friction at the local scale in situations of overland and channel flow. As a result, a second-order approximation in terms of the velocity is sought in the following fashion:

$$\bar{\boldsymbol{\tau}}^i_\alpha = -\mathbf{R}^i_\alpha \cdot \mathbf{v}^i_\alpha - |\mathbf{v}^i_\alpha| \cdot \mathbf{U}^i_\alpha \cdot \mathbf{v}^i_\alpha, \tag{4.24}$$

where, once again, $\mathbf{R}^i_\alpha$ and $\mathbf{U}^i_\alpha$ are tensors which depend on some of the remaining variables and parameters. We observe the necessity to take the absolute value of the second order velocity to preserve the sign of the flow resistance force, which is always directed opposite to the flow.

5. Closure of the equations

The balance equations for mass, momentum, energy and entropy for all five subregions of the watershed have been rigorously derived by Reggiani et al. [33]. Thanks to Assumption I we can generally omit the subscripts α, which indicate different phases, as we are dealing with water in all subregions as the only mobile phase. The balance equations and relative exchange terms for mass and momentum, reported throughout the subsequent sections, refer, therefore, to the water phase only. Subsequently, we need to find expressions for the momentum exchange terms in the balance of forces. Second, parameterisations for the mass exchange terms need to be proposed. These two issues are handled separately in the following sections.

5.1. Closure of the momentum balance equations

Unsaturated zone: The specific balance equation of momentum for the unsaturated zone water phase, stated in the form Eq. (2.10), is:

$$(\rho\epsilon y^{\mathrm{u}} s^{\mathrm{u}} \omega^{\mathrm{u}})\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{v}^{\mathrm{u}} - \rho\epsilon y^{\mathrm{u}} s^{\mathrm{u}} \mathbf{g}^{\mathrm{u}} \omega^{\mathrm{u}} = \mathbf{T}^{\mathrm{u}A}|_e + \mathbf{T}^{\mathrm{us}}|_e + \mathbf{T}^{\mathrm{uc}}|_e + \mathbf{T}^{\mathrm{u}}_{\mathrm{wg}}|_e + \mathbf{T}^{\mathrm{u}}_{\mathrm{wm}}|_e - \mathbf{R}^{\mathrm{u}} \cdot \mathbf{v}^{\mathrm{u}} \tag{5.1}$$

where y^{u} is the average thickness of the unsaturated zone, ϵ is the porosity of the soil matrix, s^{u} is the water phase saturation and ω^{u} is the area fraction covered by the unsaturated zone. The right-hand side terms are the equilibrium components of the following forces: $\mathbf{T}^{\mathrm{u}A}$ is the force exerted on the prismatic mantle surface, $\mathbf{T}^{\mathrm{uc}}$ is the force acting on the unsaturated zone water phase across the land surface, while $\mathbf{T}^{\mathrm{u}}_{\mathrm{wg}}$ and $\mathbf{T}^{\mathrm{u}}_{\mathrm{wm}}$ are the forces exchanged between water and gas and water and soil matrix, respectively. All quantities have been accurately defined by Reggiani et al. [33]. Furthermore, we have expanded the non-equilibrium components of these forces as a function, which is linear in the velocity, as suggested in Section 4.3.

To obtain expressions for the equilibrium forces, an appropriate condition of equilibrium for the unsaturated zone needs to be defined. We describe equilibrium as the situation where the forces acting on the water phase within the soil pores (gravity, capillary forces) and the forces acting between REWs across the lateral mantle surface are balanced. In this case the average water phase velocity is zero and the mass exchanges across the water table, the mantle and the land surface are all zero. The same is valid for the phase changes between water and vapour within the soil pores. By applying the equilibrium condition (4.21), the specific expressions for the force terms at equilibrium are obtained. First, we note the equilibrium force acting on the water phase through interaction with the soil matrix and the gaseous phase is equally zero for symmetry reasons:

$$\mathbf{T}^{\mathrm{u}}_{\mathrm{wg}}|_e = \mathbf{T}^{\mathrm{u}}_{\mathrm{wm}}|_e = 0. \tag{5.2}$$

Next, the force acting on the prismatic mantle surface is given by the expression:

$$\mathbf{T}^{\mathrm{u}A}|_e = [-p^{\mathrm{u}} + \rho(\phi^{\mathrm{u}}A - \phi^{\mathrm{u}})]\mathbf{A}^{\mathrm{u}A}. \tag{5.3}$$

We recall from Reggiani et al. [33] that the mantle surface is composed of a series of segments which form the boundary between the REW under consideration and neighbouring REWs or the external boundary of the watershed. Therefore, the total force $\mathbf{T}^{\mathrm{u}A}|_e$ needs to be separated into the various components acting on the respective mantle segments:

$$\mathbf{T}^{\mathrm{u}A}|_e = \sum_l \mathbf{T}^{\mathrm{u}A}_l|_e + \mathbf{T}^{\mathrm{u}A}_{\mathrm{ext}}|_e. \tag{5.4}$$

The force $\mathbf{T}^{\mathrm{uc}}|_e$, acting on the land surface, can be derived from Eq. (4.21) in complete analogy to Eq. (5.3). The total force $\mathbf{T}^{\mathrm{us}}|_e$, acting on the water phase along the phreatic surface is effectively zero, as the pressure is atmospheric in these locations. Thus we impose the condition:

$$[-p^{\mathrm{u}} + \rho(\phi^{\mathrm{us}} - \phi^{\mathrm{u}})]\mathbf{A}^{\mathrm{us}} = 0 \tag{5.5}$$

from which we obtain an expression, which can be employed for the evaluation of the equilibrium pressure in Eq. (5.3) and its counterpart for $\mathbf{T}^{\mathrm{uc}}|_e$:

$$p^{\mathrm{u}} = \rho(\phi^{\mathrm{us}} - \phi^{\mathrm{u}}). \tag{5.6}$$

After substituting the equilibrium forces into Eq. (5.1), the equation needs to be projected along the axes of the reference system O introduced in Section 3 to evaluate the actual components of the equilibrium forces. This task will be pursued in Section 6.

Saturated zone: The balance equation of momentum for the saturated zone is:

$$(\rho\epsilon y^{\mathrm{s}}\omega^{\mathrm{s}})\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{v}^{\mathrm{s}} - \rho\epsilon\mathbf{g}^{\mathrm{s}}y^{\mathrm{s}}\omega^{\mathrm{s}} = \mathbf{T}^{\mathrm{s}A}|_e + \mathbf{T}^{\mathrm{s\ bot}}|_e + \mathbf{T}^{\mathrm{su}}|_e + \mathbf{T}^{\mathrm{so}}|_e + \mathbf{T}^{\mathrm{sr}}|_e + \mathbf{T}^{\mathrm{s}}_{\mathrm{wm}}|_e - \mathbf{R}^{\mathrm{s}}\cdot\mathbf{v}^{\mathrm{s}}, \tag{5.7}$$

where y^{s} is the average thickness of the saturated zone and ω^{s} is the area fraction covered by the aquifer. The right-hand side terms are the respective equilibrium components of the REW-scale force exerted on the prismatic mantle surface, $\mathbf{T}^{\mathrm{s}A}$, the force acting on the bottom of the aquifer, $\mathbf{T}^{\mathrm{sbot}}$, on the water table, $\mathbf{T}^{\mathrm{su}}$, on the seepage face, $\mathbf{T}^{\mathrm{so}}$, on the channel bed, $\mathbf{T}^{\mathrm{sr}}$, and on the soil matrix within the porous medium, $\mathbf{T}^{\mathrm{s}}_{\mathrm{wm}}$. Also in this case the non-equilibrium component of the forces has been expressed as a linear function of the velocity.

The condition for mechanical equilibrium within the saturated zone is defined as the situation, where all forces acting on the water phase are balanced, and the mass exchanges across the water table and the prismatic mantle surface are zero. The mass exchanged across the bed surface of the channel is also zero because the difference in hydraulic potentials between the channel and the saturated zone is zero at equilibrium. With these considerations in mind, we first find that the equilibrium force exerted by the water on the soil matrix is zero for symmetry reasons:

$$\mathbf{T}^{\mathrm{s}}_{\mathrm{wm}}|_e = 0. \tag{5.8}$$

In analogy to previous cases, we obtain the equilibrium force acting on the mantle through application of Eq. (4.21):

$$\mathbf{T}^{\mathrm{s}A}|_e = [-p^{\mathrm{s}} + \rho(\phi^{\mathrm{s}A} - \phi^{\mathrm{s}})]\mathbf{A}^{\mathrm{s}A}. \tag{5.9}$$

This force needs, once again, to be separated into the components acting on the segments of the various segments of the mantle, which separate the aquifer form the aquifers of neighbouring watersheds or are part of the external watershed boundary. Similar expressions for the forces $\mathbf{T}^{\mathrm{so}}|_e$ and $\mathbf{T}^{\mathrm{sr}}|_e$, acting on the seepage face and the channel bed, respectively, can be obtained from Eq. (4.21). Finally, from the momentum balance Eq. (5.7) we obtain that the total equilibrium force $\mathbf{T}^{\mathrm{s\ bot}}|_e$, acting on the bottom of the aquifer, must balance the weight of the water contained within the saturated zone:

$$\mathbf{T}^{\mathrm{s\ bot}}|_e = -\rho\mathbf{g}^{\mathrm{s}}y^{\mathrm{s}}\epsilon\omega^{\mathrm{s}} = [-p^{\mathrm{s}} + \rho(\phi^{\mathrm{s\ bot}} - \phi^{\mathrm{s}})]\mathbf{A}^{\mathrm{s\ bot}}. \tag{5.10}$$

This equation can be employed to evaluate the average water pressure p^{s}, once it has been projected along the vertical direction through scalar multiplication with the unit vector $\mathbf{e}_z$.

Concentrated overland flow: The balance equation of momentum for the concentrated overland flow zone (in the form Eq. (2.10)) is:

$$(\rho y^{\mathrm{c}}\omega^{\mathrm{c}})\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{v}^{\mathrm{c}} - \rho y^{\mathrm{c}}\mathbf{g}^{\mathrm{c}}\omega^{\mathrm{c}} = \mathbf{T}^{\mathrm{c\ top}}|_e + \mathbf{T}^{\mathrm{cu}}|_e + \mathbf{T}^{\mathrm{co}}|_e - \mathbf{R}^{\mathrm{c}}\cdot\mathbf{v}^{\mathrm{c}} - |\mathbf{v}^{\mathrm{c}}|\cdot\mathbf{U}^{\mathrm{c}}\cdot\mathbf{v}^{\mathrm{c}}, \tag{5.11}$$

where y^c is the average thickness of the flow sheet and ω^c is the area fraction covered by the concentrated overland flow. The terms on the right-hand side are the equilibrium components of the forces exchanged with the atmosphere, $\mathbf{T}^{\mathrm{ctop}}$, with the unsaturated zone, $\mathbf{T}^{\mathrm{cu}}$ and with the saturated overland flow, $\mathbf{T}^{\mathrm{co}}$, respectively. The non-equilibrium component has been expanded as a second order function of the velocity. For the concentrated overland flow, we define equilibrium as the situation where there is no flow. Due to the fact that the water is flowing along a slope, no-flow conditions can only be achieved under complete absence of water altogether (dry land surface). In this case $\mathbf{v}^c$, y^c and the average pressure p^c are zero. Consequently Eq. (4.21) yields:

$$\mathbf{T}^{\mathrm{co}}|_e = \mathbf{T}^{\mathrm{cu}}|_e = 0. \tag{5.12}$$

After we neglect the first-order term in Eq. (5.11) and substitute Eq. (5.12), we obtain:

$$(\rho y^c \omega^c)\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{v}^c - \rho y^c \mathbf{g}^c \omega^c = -|\mathbf{v}^c| \cdot \mathbf{U}^c \cdot \mathbf{v}^c \tag{5.13}$$

Saturated overland flow: In complete analogy to the previous case, we define equilibrium as the situation of no flow, which eventuates in the absence of water on the saturated areas. This definition yields zero momentum exchange terms at equilibrium and the conservation of momentum reduces to:

$$(\rho y^o \omega^o)\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{v}^o - \rho y^o \mathbf{g}^o \omega^o = -|\mathbf{v}^o| \cdot \mathbf{U}^o \cdot \mathbf{v}^o. \tag{5.14}$$

We observe, that in different hydrologic situations, a different definition of equilibrium could have been adopted. In the case of wetlands, where the saturated overland flow zone consists of stagnant water with near-horizontal free surface covering the soil, equilibrium is equivalent to zero flow velocity $\mathbf{v}^o$ and non-zero water depth y^o. In this case non-zero equilibrium forces and pressure p^o would have been obtained.

Channel reach: The specific conservation equation for momentum for a single reach can be stated in the form (for reference see Eq. (2.10)):

$$\begin{aligned}(\rho m^r \xi^r)\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{v}^r - \rho m^r \mathbf{g}^r \xi^r \\ = \mathbf{T}^{rA}|_e + \mathbf{T}^{r\ \mathrm{top}}|_e + \mathbf{T}^{rs}|_e + \mathbf{T}^{ro}|_e - \mathbf{v}^r \cdot \mathbf{U}^r \cdot \mathbf{v}^r\end{aligned} \tag{5.15}$$

where m^r is the average cross sectional area of the reach and ξ^r is the length of the channel axis on a per-unit-area basis. The forces on the right-hand side are exchanged on the channel end sections, $\mathbf{T}^{rA}$, on the channel free surface with the atmosphere, $\mathbf{T}^{r\ \mathrm{top}}$, with the channel bed, $\mathbf{T}^{rs}$, and with the saturated overland flow on the channel edges, $\mathbf{T}^{ro}$. Also here the first order term of the frictional force has been omitted.

Equilibrium in a channel can be defined by assuming a near-horizontal free surface within the reach. Under these circumstances the flow velocity $\mathbf{v}^r$ is zero. A different equilibrium condition, such as a dry channel, could be imposed, if the situation would suggest it (e.g. case of a steep channel). From the equilibrium expression for the momentum exchange terms Eq. (4.21) we get the expression:

$$\mathbf{T}^{rA}|_e = [-p^r + \rho(\phi^{rA} - \phi^r)]\mathbf{A}^{rA} \tag{5.16}$$

for the total force acting on the end sections of the channel reach. We remind the reader (for reference see Reggiani et al. [33]) that the surface A^{rA} represented by the vector $\mathbf{A}^{rA}$ constitutes a single cross section at the outlet, if the REW under consideration is relative to a first order stream or includes two inlet sections (for each of the two reaches converging at the inlet from upstream) and an outlet section in the case of higher order streams:

$$\mathbf{T}^{rA}|_e = \sum_l \mathbf{T}_l^{rA}|_e + \mathbf{T}_{\mathrm{ext}}^{rA}|_e \tag{5.17}$$

$\mathbf{T}_{\mathrm{ext}}^{rA}|_e$ is non-zero only for the reach, whose end section coincides with the watershed outlet. In analogy to Eq. (5.16) we obtain an expression for $\mathbf{T}^{rs}|_e$ from Eq. (4.21). Finally, we recall that the atmospheric pressure force acting on the channel surface at equilibrium, $\mathbf{T}^{r\ \mathrm{top}}|_e$, is zero, yielding an equation which is useful for the evaluation of the average pressure p^r within the reach:

$$p^r = \rho(\phi^{r\ \mathrm{top}} - \phi^r). \tag{5.18}$$

5.2. Linearisation of the mass exchange terms

The mass exchange terms are unknown quantities of the problem. From the entropy inequality (4.13), a linearisation of the mass exchange terms as functions of differences in chemical potentials, gravitational potentials and average velocities within the adjacent subregions is suggested:

$$e_\alpha^{ij} = \mathscr{A}^{ij}\left[\mu_\alpha^j - \mu_\alpha^i + \phi_\alpha^j - \phi_\alpha^i\right] - \mathscr{B}^{ij}\frac{1}{2}(\mathbf{v}^i + \mathbf{v}^j) \cdot \mathbf{A}_\alpha^{ij} \tag{5.21}$$

where the areal vector $\mathbf{A}_\alpha^{ij}$ represents the fluid fraction of the interface and is defined through Eq. (2.4). The linearisation coefficients $\mathscr{A}^{ij}$ and $\mathscr{B}^{ij}$ in Eq. (5.21) are functions of the remaining independent variables and system parameters and are both positive. We point out, that the chemical potential can be expressed in terms of the internal energy, temperature and entropy (for reference see Eq. (4.7)):

$$\mu_\alpha^i = E_\alpha^i - \theta\eta_\alpha^i + \frac{p_\alpha^i}{\rho_\alpha^i} \tag{5.20}$$

For situations of unithermal, slow flow, where the differences in internal energy and entropy are negligible, the mass exchange term can be linearised in terms of difference in hydraulic potentials:

$$e^{ij}_{\alpha} = \mathscr{A}^{ij}\left[p^j_{\alpha} - p^i_{\alpha} + \rho^j_{\alpha}\phi^j_{\alpha} - \rho^i_{\alpha}\phi^i_{\alpha}\right] - \mathscr{B}^{ij}\frac{1}{2}(\mathbf{v}^i + \mathbf{v}^j)\cdot\mathbf{A}^{ij}_{\alpha} \tag{5.21}$$

Experimental effort is required in order to establish the various functional dependencies of the coefficients. Here we discuss the proposed parameterisations for all mass exchange terms on a case-by-case basis.

Unsaturated zone – concentrated overland flow (e^{uc}): The mass exchange term expressing the infiltration of water across the soil surface into the unsaturated zone is linearised in terms of the difference in hydraulic potentials between the concentrated overland flow (covering the unsaturated portion of the REW land surface) and the unsaturated zone. The average water pressure p^c in the concentrated overland flow subregion is comparable with atmospheric pressure, whereas the average water pressure p^u in the pores of the unsaturated zone is lower than the atmospheric pressure:

$$e^{uc} = -e^{cu} = \mathscr{A}^{uc}[p^c - p^u + \rho(\phi^c - \phi^u)] \tag{5.22}$$

The term e^{uc} acts as source for the unsaturated zone and as sink term for the concentrated overland flow. Consequently the constant $\mathscr{A}^{uc}$ needs to be always positive.

Unsaturated zone – saturated zone (e^{us}): The mass flux across the water table is linearised here in terms of the velocities $\mathbf{v}^u$ and $\mathbf{v}^s$ of the unsaturated and the saturated zones:

$$e^{us} = -e^{su} = -\mathscr{B}^{us}\frac{1}{2}(\mathbf{v}^u + \mathbf{v}^s)\cdot\mathbf{A}^{us} \tag{5.23}$$

where $\mathbf{A}^{us}$ is the area vector representing the water table as defined by Eq. (2.4) (the subscript w indicating the water fraction of the interface has been omitted). In this fashion, the mass exchange term can change sign according to the direction of the average velocity (upwards and downwards) and can switch between recharge of the saturated zone and capillary rise from the water table towards the unsaturated zone. The linearisation parameter $\mathscr{B}^{us}$ is thus required to be positive.

Unsaturated zone: water–vapour phase change (e^{u}_{wg}): Within the unsaturated zone water can change phase, turn into vapour, and leave the system through the soil surface after exhaustion of the concentrated overland flow, leading to soil water evaporation. The transition from water to water vapour is dependent on the difference in chemical potentials between the two phases, while their difference in gravitational potentials is zero within the same subregion:

$$e^{u}_{wg} = -e^{u}_{gw} = \mathscr{A}^{u}_{wg}(\mu^u_g - \mu^u_w). \tag{5.24}$$

The chemical potentials of the two phases are functions the respective pressures of the water and the gas phases, the vapour mass fraction in the gas phase and the temperature. The analysis of this term is beyond the scope of this work and will be pursued in the future. For more in-depth knowledge about this subject the reader is referred to specific literature in the field of soil physics, e.g. Nielsen et al. [31] or Hillel [25].

Unsaturated and saturated zones, mass exchange across the mantle (e^{uA}, e^{sA}): With respect to the linearisation of the mass exchange across the mantle surface A surrounding the REW laterally, a series of preliminary considerations are necessary. We recall that the REW is surrounded by a number N_k of neighbouring REWs. The REW under consideration exchanges mass with the surrounding REWs across respective segments A_l of the mantle surface and across the external boundary of the watershed. The mantle surface A can, therefore, be written as a sum of segments:

$$A = \sum_l A_l + A_{ext} \tag{5.25}$$

where A_l forms the boundary with the lth neighbouring REW and A_{ext} coincides with the external watershed boundary. For example, REW 1 in Fig. 3 has a number of $N_k = 3$ neighbouring REWs and one mantle segment in common with the external watershed boundary. The index l assumes the values 2, 3, and 4. As explained by Reggiani et al. [33], the latter term is non-zero only for REWs which have one or more mantle segments in common with the watershed boundary. A typical contact zone between two neighbouring REWs through the mantle is depicted schematically shown in Fig. 5. As a result, the total mass flux e^{iA}, $i = u, s$, can be written as the sum of the respective flux components relative to the various mantle segments:

$$e^{iA} = \sum_l e^{iA}_l + e^{iA}_{ext} \quad i = u, s \tag{5.26}$$

We propose a constitutive parameterisation for e^{iA}, by assuming a dependence of the exchange term on the the area A_l of the prismatic mantle segment and the velocities in the REW under consideration and in the lth neighbouring REW, $\mathbf{v}^i$ and $\mathbf{v}^i|_l$, respectively:

$$e^{iA}_l = -\mathscr{B}^{iA}_l\frac{1}{2}(\mathbf{v}^i + \mathbf{v}^i|_l)\cdot\mathbf{A}_l \tag{5.27}$$

where the vector $\mathbf{A}_l$ is defined through Eq. (2.4) and expresses the fluid fraction of the lth mantle segment. In a similar fashion, the mass exchange terms for the subsurface zones of the kth REW across the external watershed boundary A_{ext} can be expressed as:

$$e^{iA}_{ext} = -\mathscr{B}^{iA}_{ext}\frac{1}{2}(\mathbf{v}^i + \mathbf{v}^i|_{ext})\cdot\mathbf{A}_{ext} \tag{5.28}$$

where $\mathbf{v}^i|_{ext}$ is depending on boundary conditions.

Saturated zone – channel (e^{sr}): The saturated zone can be recharged from the channel through seepage across the bed surface or can drain water towards the channel. Recharge/drainage should be possible even when the average velocity within the saturated zone is zero. Therefore, we propose a linearisation, which is dependent only on the difference in hydraulic potentials

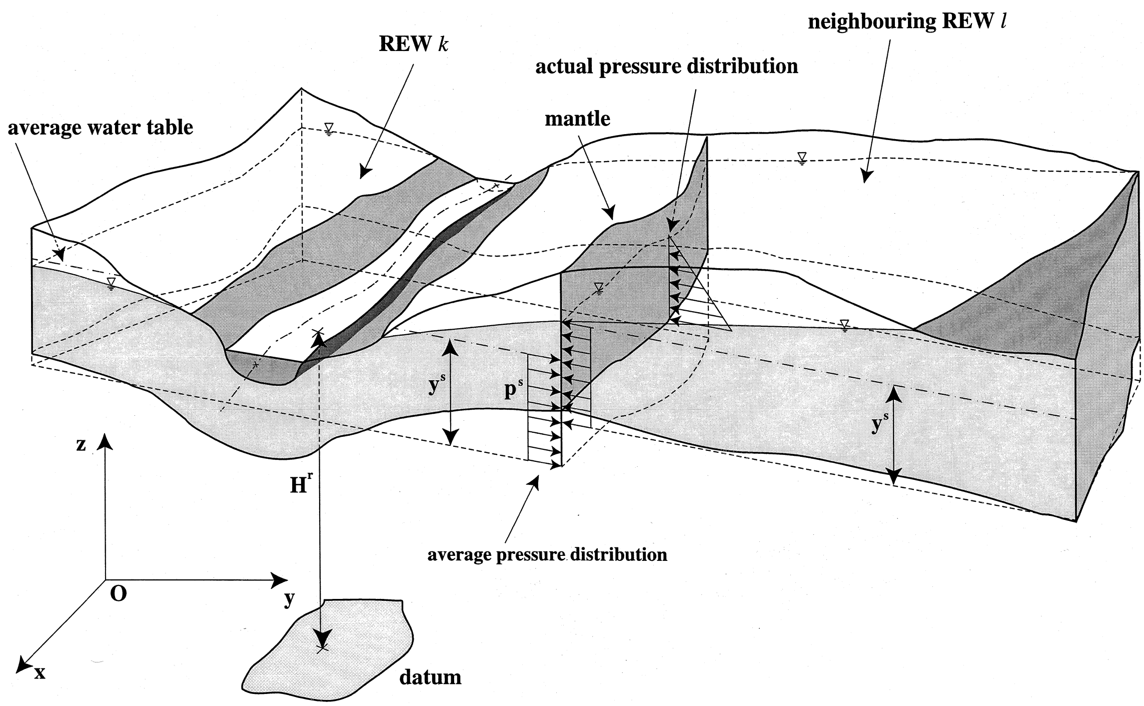

Fig. 5. Detailed view of the contact zone between two adjacent REWs.

between the channel and the saturated zone, and is independent of the velocity:

$$e^{\mathrm{sr}} = -e^{\mathrm{rs}} = \mathscr{A}^{\mathrm{rs}}[p^{\mathrm{r}} - p^{\mathrm{s}} + \rho(\phi^{\mathrm{r}} - \phi^{\mathrm{s}})] \tag{5.29}$$

Saturated zone – saturated overland flow (*seepage*) (e^{so}): As in the case of exchange with the channel, the seepage from the saturated zone also can eventuate in the absence of an average motion within the aquifer. Hence, the seepage outflow is parameterised in analogy to Eq. (5.29) in terms of the hydraulic potentials difference between the two subregions:

$$e^{\mathrm{so}} = -e^{\mathrm{os}} = \mathscr{A}^{\mathrm{rs}}[p^{\mathrm{o}} - p^{\mathrm{s}} + \rho(\phi^{\mathrm{o}} - \phi^{\mathrm{s}})] \tag{5.30}$$

Concentrated overland flow – saturated overland flow (e^{co}): The mass exchange between the regions of concentrated and saturated overland flow is occurring along the perimeter, circumscribing the saturated areas externally. This perimeter is defined by the line of intersection of the water table with the land surface. The cross sectional areas, across which the flow from uphill connects with the saturated overland flow, are denoted with A^{oc}, and are represented by an appropriate vector $\mathbf{A}^{\mathrm{co}}$. The mass exchange term between the two subregions is proposed as a linear function of the mean velocity $(\mathbf{v}^{\mathrm{c}} + \mathbf{v}^{\mathrm{o}})/2$:

$$e^{\mathrm{co}} = -e^{\mathrm{oc}} = -\mathscr{B}^{\mathrm{co}} \frac{1}{2}(\mathbf{v}^{\mathrm{c}} + \mathbf{v}^{\mathrm{o}}) \cdot \mathbf{A}^{\mathrm{co}} \tag{5.31}$$

where $\mathscr{B}^{\mathrm{co}}$ is a positive coefficient.

Saturated overland flow – channel (e^{sr}): The lateral inflow from the areas of saturated overland flow into the channel occurs along the channel edge. the flow cross section in these zones is denoted with A^{or} and is represented by a respective areal vector $\mathbf{A}^{\mathrm{or}}$ defined by Eq. (2.4). The mass exchange can be assumed as linear in average velocity $\mathbf{v}^{\mathrm{o}}$ (the velocity in the channel is directed parallel to the edge and does not contribute to e^{sr}):

$$e^{\mathrm{or}} = -e^{\mathrm{ro}} = -\mathscr{B}^{\mathrm{or}}\mathbf{v}^{\mathrm{o}} \cdot \mathbf{A}^{\mathrm{or}} \tag{5.32}$$

where $\mathscr{B}^{\mathrm{or}}$ is a positive coefficient.

Channel inflow and outflow ($e^{\mathrm{r}A}$): The channel network constitutes a bifurcating tree. The total mass exchange $e^{\mathrm{r}A}$ of the channel reach across the mantle of the kth REW can be separated into the two counterparts attributable to the REWs converging at the inlet section and the mass exchange with the REW further downstream. In the case of REWs associated with first order streams, the reach has only one outflow. This can be seen best in Fig. 3. For example, the channel reach of REW 7 communicates with the reaches of REW 5 and 6 at the inlet section and with REW 9 at the outlet ($N_k = 3$). REW 1 has only one outflow towards REW 4 ($N_k = 1$). As a result, we write the total mass exchange in a general fashion as the sum of the following constituent parts:

$$e^{\mathrm{r}A} = \sum_{l} e_{l}^{\mathrm{r}A} + e_{\mathrm{ext}}^{\mathrm{r}A} \tag{5.33}$$

where the second term on the right-hand side is nonzero only for the REW located at the outlet (e.g. REW 13 in Fig. 3). The sum extends over a single neighbouring REW in the case of first order streams and over three REWs in the case of higher order streams.

The proposed linearisation of the mass exchange terms is expressed through the cross sectional area vector $\mathbf{A}_l^{rA}$ and the mean velocity $(\mathbf{v}^r + \mathbf{v}^r|_l)/2$ between the reach of the kth REW and the reach of the lth neighbouring REW:

$$e_l^{rA} = -\mathscr{B}_l^{rA} \frac{1}{2} (\mathbf{v}^r + \mathbf{v}^r|_l) \cdot \mathbf{A}_l^{rA} \tag{5.34}$$

The coefficients $\mathscr{B}_l^{rA}$ are positive. A similar equation may be given for e_{ext}^{rA}:

$$e_{ext}^{rA} = -\mathscr{B}_{ext}^{rA} \frac{1}{2} (\mathbf{v}^r + \mathbf{v}^r|_{ext}) \cdot \mathbf{A}_{ext}^{rA} \tag{5.35}$$

where $\mathbf{v}^r|_{ext}$ is assumed to be known. For example, in the case of a river flowing into a lake $\mathbf{v}^r|_{ext}$ may be set equal to zero.

Rainfall or evaporation ($e^{c\ top}$, $e^{o\ top}$, $e^{r\ top}$): The mass exchange between the concentrated and the saturated overland flow and the atmosphere can be expressed as linear functions of the respective area fraction of the subregion and the rate J of mass input (rainfall intensity) or extraction (evaporation rate):

$$e^{i\ top} = \omega^i J \quad i = c, o \tag{5.36}$$

The mass exchange with the atmosphere on the channel free surface can be expressed as a linear function of the mass input or extraction J and the area of the channel free surface $A^{r\ top} = w^r \xi^r$, where w^r is the average channel top width, to be defined in Section 7:

$$e^{r\ top} = w^r \xi^r J. \tag{5.37}$$

6. Parameterised balance equation

In the previous section we have proposed possible parameterisations of the mass and momentum exchange terms. Here we project the momentum balance equations along the reference system introduced in Section 3, and substitute the respective exchange terms for mass and momentum into the respective conservation equations. The mass balance equations have been derived by Reggiani et al. [33] and are written in the general form Eq. (2.2). For reason of simplicity of the final set of equations, we state a series of assumptions regarding the geometry of the REW:

Assumption V. The water table within the REW is near-horizontal and the slope of the land surface is small. As a result we obtain that the horizontal components of the vectors $\mathbf{A}^{ij}$ defined through Eq. (2.4) for the unsaturated land surface, $\mathbf{A}^{uc}$, the seepage face, $\mathbf{A}^{so}$, and the water table, $\mathbf{A}^{us}$, are negligible. The same is valid for the cannel bed surface, $\mathbf{A}^{sr}$:

$$\mathbf{A}^{uc} \cdot \mathbf{e}_\lambda = \mathbf{A}^{so} \cdot \mathbf{e}_\lambda = \mathbf{A}^{us} \cdot \mathbf{e}_\lambda = \mathbf{A}^{sr} \cdot \mathbf{e}_\lambda \approx 0; \quad \lambda = x, y \tag{6.1}$$

Assumption VI. The bottom boundary of the aquifer is impermeable. As a result the vertical flow across the saturated zone is zero:

$$\mathbf{v}^s \cdot \mathbf{e}_z = 0 \tag{6.2}$$

Assumption VII. The tangential component of the vector relative to the channel bed area, $\mathbf{A}^{rs}$, is negligible:

$$\mathbf{A}^{rs} \cdot \mathbf{n}_t^r \approx 0 \tag{6.3}$$

We emphasise that these assumptions can be relaxed if required by the particular circumstances.

6.1. Unsaturated zone

Balance of mass: In view of Assumption V and from definition Eq. (2.4) we find that the fluid component of the horizontal exchange surface is:

$$\mathbf{A}^{uc} \cdot \mathbf{e}_z = \epsilon \omega^u \Sigma \tag{6.4}$$

Subsequently, we introduce the linearised mass exchange terms Eqs. (5.22)–(5.24) and Eq. (5.27) into the unsaturated zone mass balance in the form Eq. (2.2) and obtain:

$$\overbrace{\frac{d}{dt}(\rho y^u \omega^u s^u)}^{\text{storage}} = \overbrace{\mathscr{A}^{uc}[p^c - p^u + \rho(\phi^c - \phi^u)]}^{\text{infiltration}} + \overbrace{\mathscr{B}^{us} \omega^u v_z^u}^{\text{exchg. with sat. zone}} + \overbrace{\mathscr{A}_{wg}^u(\mu_g^u - \mu_w^u)}^{\text{evaporation}} + \overbrace{\sum_l \mathscr{B}_l^{uA} \frac{1}{2}\left[\pm A_{l,x}^{uA}(v_x^u + v_x^u|_l) + \pm A_{l,y}^{uA}(v_y^u + v_y^u|_l)\right] + e_{ext}^{uA}}^{\text{exchange across mantle segments}} \tag{6.5}$$

where the signs in the last term are positive or negative according to the orientation of A_l^{uA} with respect to the global reference system O. The mass exchange e_{ext}^{uA} across the mantle segment overlapping with the watershed boundary needs to be imposed according to the boundary conditions, e.g. by Eq. (5.28) or by zero-flux boundary conditions, $e_{ext}^{uA} = 0$.

Balance of momentum: Considering that the flow in the unsaturated zone is directed mainly along the vertical, we first project the conservation equation of momentum (5.1) through scalar multiplication with the unit vector $\mathbf{e}_z$. We also note that the z-coordinate is positive upward so that $\mathbf{g}^u \cdot \mathbf{e}_z = -g$. Thus we obtain in view of Eq. (6.4) the linearised form of the momentum balance along $\mathbf{e}_z$:

$$\overbrace{[-p^u + \rho(\phi^{uc} - \phi^u)]\epsilon\omega^u}^{\text{force top}} - \overbrace{\rho\epsilon s^u y^u \omega^u g}^{\text{gravity}} = \overbrace{-R^u\, v_z^u}^{\text{resistance force}} \tag{6.6}$$

where the inertial term has been considered negligible and the resistivity is isotropic. Along the horizontal directions pointed to by $\mathbf{e}_x$ and $\mathbf{e}_y$, the components of the gravity are zero. In view of Assumption V, the momentum balance along $\mathbf{e}_x$ and $\mathbf{e}_y$ becomes:

$$\overbrace{\pm\sum_l A^{\mathrm{u}A}_{l,\lambda}\left[-p^{\mathrm{u}}+\rho(\phi^{\mathrm{u}A}_l-\phi^{\mathrm{u}})\right]}^{\text{inter-REW driving force}} + \overbrace{\pm A^{\mathrm{u}A}_{\mathrm{ext},\lambda}\left[-p^{\mathrm{u}}+\rho(\phi^{\mathrm{u}A}_{\mathrm{ext}}-\phi^{\mathrm{u}})\right]}^{\text{force acting on the external boundary}} = \overbrace{-R^{\mathrm{u}}\,v^{\mathrm{u}}_{\lambda}}^{\text{resistance to flow}} \quad \lambda = x,y \tag{6.7}$$

where the signs are either positive or negative according to the orientation of $A^{\mathrm{u}A}_l$ and $A^{\mathrm{u}A}_{\mathrm{ext}}$ with respect to the reference system O. We note that, in the case of fast flows, where the resistance no longer varies linearly with velocity, second or higher order approximations for the resistance term can be sought. The force $\mathbf{T}^{\mathrm{u}A}_{\mathrm{ext}}$ is non-zero only for REWs with a mantle segment in common with the external watershed boundary and have to be imposed according to the actual boundary conditions (e.g. zero force, constant or time-varying pressure force acting on the boundary). The momentum balance equations given here are equivalent to a generalised Darcy's law for the unsaturated zone at the scale of the REW.

6.2. Saturated zone

Balance of mass: The flow in the saturated zone is assumed to occur only in a horizontal plane parallel to the $x-y$ plane of the global reference system O (See Assumption VI). We introduce the linearised mass exchange terms Eqs. (5.23), (5.27) and (5.29) and Eq. (5.30) into the equation of conservation of mass for the saturated zone (stated in the form Eq. (2.2). The substitution yields:

$$\overbrace{\frac{\mathrm{d}}{\mathrm{d}t}(\rho\epsilon y^{\mathrm{s}}\omega^{\mathrm{s}})}^{\text{storage}} = \overbrace{\mathscr{A}^{\mathrm{so}}[p^{\mathrm{o}}-p^{\mathrm{s}}+\rho(\phi^{\mathrm{o}}-\phi^{\mathrm{s}})]}^{\text{seepage}} - \overbrace{\mathscr{B}^{\mathrm{us}}v^{\mathrm{u}}_z\omega^{\mathrm{u}}}^{\text{exchange with unsat. zone}} + \overbrace{\mathscr{A}^{\mathrm{sr}}[p^{\mathrm{r}}-p^{\mathrm{s}}+\rho(\phi^{\mathrm{r}}-\phi^{\mathrm{s}})]}^{\text{sat. zone -- river exchange}} + \overbrace{\sum_l \mathscr{B}^{\mathrm{s}A}_l\frac{1}{2}\left[\pm A^{\mathrm{s}A}_{l,x}(v^{\mathrm{s}}_x+v^{\mathrm{s}}_x|_l)\pm A^{\mathrm{s}A}_{l,y}(v^{\mathrm{s}}_y+v^{\mathrm{s}}_y|_l)\right]+e^{\mathrm{s}A}_{\mathrm{ext}}}^{\text{exchange across mantle segments}}, \tag{6.8}$$

where $e^{\mathrm{s}A}_{\mathrm{ext}}$ is given according to the boundary conditions. The signs in the last term on the right-hand side become positive or negative according to the orientation of the surfaces with respect to the global reference system O. It can be no flux, or a specified mass inflow or outflow as given for example by Eq. (5.28). The last line in this equation allows the integration of regional groundwater flow into the watershed equations.

Balance of momentum: The balance equation of momentum is obtained from Eq. (5.25) through scalar multiplication with the unit vectors $\mathbf{e}_x$ and $\mathbf{e}_y$. Recalling Assumption V we obtain:

$$\overbrace{\pm\sum_l A^{\mathrm{s}A}_{l,\lambda}\left[-p^{\mathrm{s}}+\rho(\phi^{\mathrm{s}A}_l-\phi^{\mathrm{s}})\right]}^{\text{inter-REW driving force}} \overbrace{\pm A^{\mathrm{s}A}_{\mathrm{ext},\lambda}\left[-p^{\mathrm{s}}+\rho(\phi^{\mathrm{s}A}_{\mathrm{ext}}-\phi^{\mathrm{s}})\right]}^{\text{force on the external boundary}} + \overbrace{\pm A^{\mathrm{s\,bot}}_{\lambda}\left[-p^{\mathrm{s}}+\rho(\phi^{\mathrm{s\,bot}}-\phi^{\mathrm{s}})\right]}^{\text{force at the bottom boundary}} = \overbrace{-R^{\mathrm{s}}\,v^{\mathrm{s}}_{\lambda}}^{\text{resistance to flow}} \quad \lambda = x,y \tag{6.9}$$

This equation can be interpreted as a REW-scale Darcy's law for the saturated zone.

6.3. Concentrated overland flow zone

Conservation of mass: We introduce the mass exchange terms Eqs. (5.22) and (5.31) and the term accounting for rainfall input Eq. (5.36) into the appropriate equation of conservation of mass presented by Reggiani et al. [33]:

$$\overbrace{\frac{\mathrm{d}}{\mathrm{d}t}(\rho y^{\mathrm{c}}\omega^{\mathrm{c}})}^{\text{storage}} = \overbrace{-\mathscr{A}^{\mathrm{uc}}[p^{\mathrm{c}}-p^{\mathrm{u}}+\rho(\phi^{\mathrm{c}}-\phi^{\mathrm{u}})]}^{\text{infiltration into unsat.zone}} - \overbrace{\frac{1}{4}\mathscr{B}^{\mathrm{co}}\Lambda^{\mathrm{co}}(y^{\mathrm{o}}+y^{\mathrm{c}})(v^{\mathrm{o}}+v^{\mathrm{c}})}^{\text{flow to sat. overl. flow}} + \overbrace{\omega^{\mathrm{c}}J}^{\text{rainfall or evap.}} \tag{6.10}$$

We note that the projection of the cross sectional area A^{co} has been approximated by the product:

$$A^{\mathrm{co}} \approx \Lambda^{\mathrm{co}}\frac{1}{2}(y^{\mathrm{o}}+y^{\mathrm{c}}) \tag{6.11}$$

where Λ^{co} is the length of the contour curve forming the perimeter of the saturated areas. The length of the curve is subject to variations due to possible expansions and contractions of the seepage faces. A plausible geometric relationship will be presented in Section 7.

Conservation of momentum: The flow has been assumed to occur along an *effective* direction tangent to a flow plane with an inclination angle γ^{c} with respect to the horizontal, as explained in Section 4. A unit vector $\mathbf{n}^{\mathrm{c}}_t$, pointing along the effective direction, has been introduced, as shown in Fig. 4. We now project the equation of conservation of momentum derived from Eq. (5.11) by scalar multiplication with $\mathbf{n}^{\mathrm{c}}_t$:

$$\overbrace{(\rho y^{\mathrm{c}}\omega^{\mathrm{c}})\frac{\mathrm{d}}{\mathrm{d}t}v^{\mathrm{c}}}^{\text{inertial term}} - \overbrace{\rho y^{\mathrm{c}}\omega^{\mathrm{c}}g\sin\gamma^{\mathrm{c}}}^{\text{gravity}} = -\overbrace{U^{\mathrm{c}}v^{\mathrm{c}}|v^{\mathrm{c}}|}^{\text{resistance to flow}} \tag{6.12}$$

If we also neglect the inertial term, we obtain a REW-scale Chezy formula for the concentrated overland flow:

$$\rho y^{\mathrm{c}}\omega^{\mathrm{c}}g\sin\gamma^{\mathrm{c}} = -U^{\mathrm{c}}v^{\mathrm{c}}|v^{\mathrm{c}}|. \tag{6.13}$$

6.4. Saturated overland flow zone

Conservation of mass: The conservation of mass for the saturated overland flow subregion is linearised by introducing the parameterised mass exchange terms Eqs. (5.30) and (5.32) and the term Eq. (5.36) accounting for the rainfall input into the appropriate mass balance equation:

$$\overbrace{\frac{\mathrm{d}}{\mathrm{d}t}(\rho y^{\mathrm{o}}\omega^{\mathrm{o}})}^{\text{storage}} = \overbrace{-\mathscr{B}^{\mathrm{or}}\Lambda^{\mathrm{or}}y^{\mathrm{o}}\ v^{\mathrm{o}}}^{\text{lat. channel inflow}} + \overbrace{\mathscr{A}^{\mathrm{so}}[p^{\mathrm{o}} - p^{\mathrm{s}} + \rho(\phi^{\mathrm{o}} - \phi^{\mathrm{s}})]}^{\text{seepage}}$$

$$+ \overbrace{\mathscr{B}^{\mathrm{co}}\frac{1}{4}\Lambda^{\mathrm{co}}(y^{\mathrm{o}} + y^{\mathrm{c}})(v^{\mathrm{o}} + v^{\mathrm{c}})}^{\text{inflow from conc. overl. flow}} + \overbrace{\omega^{\mathrm{o}}J}^{\text{rainfall or evap.}} \tag{6.14}$$

where the area A^{or} has been approximated by the product:

$$A^{\mathrm{or}} \approx \Lambda^{\mathrm{or}}y^{\mathrm{o}} \tag{6.15}$$

with Λ^{or} is the contour curve forming the edge of the channel, to be addressed in Section 7.

Conservation of momentum: The momentum balance equation Eq. (5.32) needs to be projected along the tangent to the respective flow plane (see Fig. 4) through scalar multiplication with $\mathbf{n}_t^{\mathrm{o}}$. The result is:

$$(\rho y^{\mathrm{o}}\omega^{\mathrm{o}})\frac{\mathrm{d}}{\mathrm{d}t}v^{\mathrm{o}} - \rho y^{\mathrm{o}}\omega^{\mathrm{o}}g\sin\gamma^{\mathrm{o}} = -U^{\mathrm{o}}v^{\mathrm{o}}|v^{\mathrm{o}}|. \tag{6.16}$$

Omission of the inertial term leads to a REW-scale Chezy-formula.

6.5. Channel reach

Conservation of mass: The conservation equation of mass for the channel reach belonging to the kth REW is parameterised by introducing the linearised mass exchange terms Eqs. (5.29) and (5.32) and Eq. (5.34) into the appropriate mass balance equation for the reach presented by Reggiani et al. [33]:

$$\overbrace{\frac{\mathrm{d}}{\mathrm{d}t}(\rho m^{\mathrm{r}}\xi^{\mathrm{r}})}^{\text{storage}} = \overbrace{\mathscr{B}^{\mathrm{or}}\Lambda^{\mathrm{or}}y^{\mathrm{o}}\ v^{\mathrm{o}}}^{\text{lateral inflow}} - \overbrace{\mathscr{A}^{\mathrm{sr}}[p^{\mathrm{r}} - p^{\mathrm{s}} + \rho(\phi^{\mathrm{r}} - \phi^{\mathrm{s}})]}^{\text{channel - sat. zone exch.}} +$$

$$\overbrace{\pm\sum_{l}\mathscr{B}_l^{\mathrm{r}A}\frac{1}{2}A_l^{\mathrm{r}A}(v^{\mathrm{r}} + v^{\mathrm{r}}|_l) + e_{\mathrm{ext}}^{\mathrm{r}A}}^{\text{inflow, outflow}} + \overbrace{\xi^{\mathrm{r}}w^{\mathrm{r}}J}^{\text{rainfall, evap. on free surf.}} \tag{6.17}$$

where the sign of the second-last term is positive for inlet sections (source of mass for the reach) and negative for outlet sections (mass sink). The term $e_{\mathrm{ext}}^{\mathrm{r}A}$ is non-zero only for the last REW whose outlet coincides with the outlet of the entire watershed (e.g. REW 13 in Fig. 3) and is given by Eq. (5.35). Eq. (6.17) is in complete agreement with the mass conservation equation for a binary tree forming a channel network, as derived by Gupta and Waymire [20]. In the present work we go further by formulating the corresponding momentum balance equation for the network, as described below.

Conservation of momentum: The conservation equation for momentum is obtained from Eq. (5.15) through projection of each reach along its effective tangent to the channel bed $\mathbf{n}_t^{\mathrm{r}}$, shown in Fig. 4. Consequently, we consider Assumption VII and employ simply the symbol v^{r} to denote average along-slope channel velocity:

$$\overbrace{(\rho m^{\mathrm{r}}\xi^{\mathrm{r}})\frac{\mathrm{d}}{\mathrm{d}t}v^{\mathrm{r}}}^{\text{inertial term}} = \overbrace{\rho g\xi^{\mathrm{r}}m^{\mathrm{r}}\sin\gamma^{\mathrm{r}}}^{\text{gravitational force}} - \overbrace{U^{\mathrm{r}}v^{\mathrm{r}}|v^{\mathrm{r}}|}^{\text{Chezy resistance}} +$$

$$\overbrace{\pm\sum_{l}A_l^{\mathrm{r}A}\cos\delta_l\left[-p^{\mathrm{r}} + \rho(\phi_l^{\mathrm{r}A} - \phi^{\mathrm{r}})\right]}^{\text{pressure forces exchanged among REWs}}$$

$$+ \overbrace{A_{\mathrm{ext}}^{\mathrm{r}A}\left[-p^{\mathrm{r}} + \rho(\phi_{\mathrm{ext}}^{\mathrm{r}A} - \phi^{\mathrm{r}})\right]}^{\text{pressure force at watershed outlet}} \tag{6.18}$$

where the last term is non-zero only for the REW situated at the watershed outlet and depends on the local boundary conditions.The sign of the second-last term is negative for the inlet and positive for the outlet sections of the reaches. The angle δ_l is the local angle between the reach of the REW l and the reach of the REW under consideration, as can be seen from Fig. 6. The angle δ_l can be estimated from topographic data. In this way the momentum of the two upstream reaches converging at the REW inlet is projected along the direction of the downstream reach The two components of momentum normal to the axis of the down-stream reach are assumed to cancel each other. We also observe, that the above equation is equivalent to the *Saint–Venant* equation stated for a tree-like structure of zero-dimensional inter-connected buckets, where channel curvature effects have been neglected. The pair of Eqs. (6.17) and

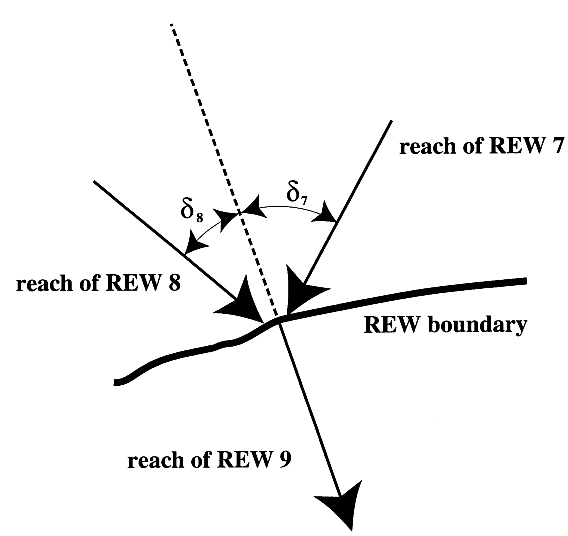

Fig. 6. Confluence angles of two reaches at the inlet of a REW.

(6.18) together govern the response of the channel network.

7. Discussion of the equation system

In the previous section we have obtained a system of 13 non-linear, coupled balance equations for mass and momentum for each subregion in the kth REW, which respect the jump conditions for mass and momentum across the inter-phase, inter-subregion and inter-REW boundaries. The 19 unknowns of the system are:

$$Z_k = (v_x^u, v_y^u, v_z^u, v_x^s, v_y^s, v^o, v^c, v^r, s^u, y^u\omega^u, y^s\omega^s, y^c\omega^c, y^o\omega^o, m^r\xi^r, p^u, p^s, p^c, p^o, p^r)_k \tag{7.1}$$

The 13 balance equations in Section 5 are supplemented with Eqs. (5.6), (5.10) and (5.18) for the evaluation of the pressures. Based on the equilibrium assumptions made for the overland flow zones (see Section 6) the pressures $p^c = 0$ and $p^o = 0$. As a result, the number of unknowns in Eq. (7.1) is reduced to 14 (one excess unknown with respect to the available equations). Nevertheless, the balance equations allow us only to evaluate the products of variables, such as $\omega^i y^i$ or $m^r\xi^r$, while the area fractions ω^i, the average channel cross-sectional area m^r, the channel top width w^r or the depth y^r appear in the equations (or are needed indirectly for the evaluation of the pressures) and are necessary for the evaluation of the mass exchange terms. The same is valid for Λ^{oc} and Λ^{or}. Consequently, 9 additional unknowns have been introduced. In total, there is a need of 10 additional constitutive relationships, to obtain a determinate system. These need to take explicitly into account the geometry of the REW.

7.1. Constitutive relationships for geometric variables

To overcome the remaining deficiency of equations, we introduce a set of 10 geometric relationships. The first relationship is based on the conservation of volume for the entire subsurface region of the REW, including the saturated and the unsaturated zones. This relationship takes into account the fact that the total volume of the subsurface zone of REW (the saturated and the unsaturated zones) is constant. An increase or decrease of the saturated zone due to fluctuations of the water table results in an equal decrease or increase of the volume of the unsaturated zone, respectively. This consideration leads to a constitutive function which relates the rate of change of volume $y^u\omega^u$ of the unsaturated zone to the rate of change of volume $y^s\omega^s$ of the saturated zone:

$$(\dot{y^u\omega^u}) + (\dot{y^s\omega^s}) = 0. \tag{7.2}$$

In the parameterised equations, we find that a knowledge of the area fractions ω^j, the depths y^j, the drainage density ξ^r or the cross sectional area m^r is necessary for the evaluation of the terms accounting for rainfall input and evaporation ($e^{o\ top}$, $e^{c\ top}$, $e^{r\ top}$), and the mass and momentum exchange terms within the REW (e^{cu}, e^{os}, e^{us}, e^{or}, e^{oc}, e^{rA}, e^{sA}, e^{uA}, e^{u}_{wg}, $\bar{\boldsymbol{\tau}}^u$, $\bar{\boldsymbol{\tau}}^s$, $\bar{\boldsymbol{\tau}}^o$, $\bar{\boldsymbol{\tau}}^c$, $\bar{\boldsymbol{\tau}}^r$). To overcome this obstacle, we state another assumption:

Assumption VIII. The saturated zone underlies the whole REW, and therefore, $\Sigma^s = \Sigma$. This implies that:

$$\omega^s = 1. \tag{7.3}$$

For the area fraction of the saturated overland flow ω^o, we postulate a dependence on the average depth of the saturated zone y^s and the rate of change of depth $\dot{y}^s$:

$$\dot{\omega}^o = \dot{\omega}^o(y^s, \dot{y}^s). \tag{7.4}$$

This functional dependence is related to the local topography of the REW. Such relationships can be derived by approaches similar to the topography-based framework adopted by TOPMODEL of Beven and Kirkby [1]. For example, the saturated area fraction of the catchment may be expressed as a function of the statistical distribution of the topographic index $\ln(a)/\tan\beta$ and the average depth of the water table, which is equivalent to the variable y^u in the present approach. The area covered by the saturated overland flow (seepage faces) is complementary with the area covered by the concentrated overland flow zone, such that:

$$\Sigma^o + \Sigma^c = \Sigma \tag{7.5}$$

We observe that by assuming this relationship between area projections, we have regarded the projection of the free surface area $A^{r\ top}$ of the channel as negligible. The equality (7.4) yields, after division by Σ and differentiation with respect to time, another useful relationship between the rate of change of area fractions:

$$\dot{\omega}^o + \dot{\omega}^c = 0 \tag{7.6}$$

Another relationship derives from the fact, that the area projection of the concentrated overland flow region is overlapping with the horizontal projection of the unsaturated zone, i.e. $\Sigma^u = \Sigma^c$. This leads to a relationship between the two respective area fractions:

$$\omega^u = \omega^c \tag{7.7}$$

Finally, the drainage density ξ^r can be assumed to be a function of the average cross sectional area of the channel m^r and its rate of change:

$$\dot{\xi}^r = \dot{\xi}^r(m^r, \dot{m}^r) \tag{7.8}$$

We observe that this relationship is only valid for REWs related to *first order* channels which are allowed to vary their length through uphill expansion. If the REW is associated with a *higher order* channel, the drainage density remains constant and may be obtained from topographical data:

$$\xi^{\mathrm{r}} = \text{known constant} \tag{7.9}$$

The knowledge of the average channel top width, w^{r} and the average depth y^{r} are convenient for the evaluation of the channel free surface area $A^{\mathrm{rtop}} = \xi^{\mathrm{r}} w^{\mathrm{r}}$ and the channel pressure p^{r} defined in Eq. (5.18). The average width w^{r} (or alternatively the average depth y^{r}) can be obtained according to Leopold and Maddock [29] through a power law relationship in terms of the discharge D^{r} given the product of m^{r} and the velocity v^{r} (at-a-station hydraulic geometry):

$$y^{\mathrm{r}} = a(D^{\mathrm{r}})^{b} = a(m^{\mathrm{r}} v^{\mathrm{r}})^{b} \tag{7.10}$$

$$w^{\mathrm{r}} = c(D^{\mathrm{r}})^{d} = c(m^{\mathrm{r}} v^{\mathrm{r}})^{d} \tag{7.11}$$

The coefficients a, c and the exponents b, d need to be evaluated from field data. The length Λ^{co} of the intersection curve between the water table and the land surface changes with expansion or contraction of the area of the seepage faces:

$$\Lambda^{\mathrm{co}} = \Lambda^{\mathrm{co}}(\omega^{\mathrm{o}}). \tag{7.12}$$

This function could be obtained from topographic maps. The length of the channel edge Λ^{or} is a function of the top width of the channel and the total length:

$$\Lambda^{\mathrm{or}} = \Lambda^{\mathrm{or}}(w^{\mathrm{r}}, \xi^{\mathrm{r}}) \tag{7.13}$$

Inclusion of the geometric relationships (7.1)–(7.12) yields a determinate system of 13 governing equations plus 10 geometric relationships in as many unknowns. In these equations we have considered rates of change of area fractions with time rather than the area fractions. This approach seems more convenient from an experimental point of view, because it requires the experimentalist to monitor only the rate at which the various subregions expand or contract, without having to measure the actual values of the various area fractions and of the drainage density with changes of the respective independent variables. The form of the functional dependence has to be determined through field experiments and can vary from site to site according to the local topographic and geological circumstances.

8. Conclusions

This work is a sequel to a previous paper by Reggiani et al. [33] in which a systematic approach for the derivation of a physically-based theory of watershed thermodynamic responses is developed. In this approach, a watershed is divided into a number of subwatersheds, called *Representative Elementary Watersheds* (REWs). Each REW is, in turn subdivided into five subregions: unsaturated zone, saturated zone, concentrated overland flow zone, saturated overland flow zone, and a channel reach. A systematic averaging procedure is applied to derive watershed-scale equations of conservation of mass, momentum, energy, and entropy for each and every subregion of all REW's. The balance equations need to be supplemented with constitutive relationships for the averaged thermodynamic quantities. In the present paper, the procedure for the development of the constitutive theory is presented and it is illustrated by applying it to a generic watershed.

The paper first introduces a global reference system and effective directions of flow for the five distinct and interacting subregions contained within the REW. Next, the closure problem is tackled by making use of the Coleman–Noll procedure for the exploitation of the second law of thermodynamics (i.e., entropy inequality) leading to a set of constitutive relationships which are thermodynamically admissible and physically consistent. The procedure is implemented uniformly and in a consistent manner across all subregions and REWs making up the watershed. As a first attempt, linear parameterisations of the mass exchange terms between phases, subregions and REWs, are postulated as functions of pressure head differences, velocities and chemical potentials, in such a way that they do not violate the entropy inequality. These lead, via the entropy inequality, to equivalent parameterisations of the momentum exchange terms under equilibrium conditions. The non-equilibrium component of the momentum exchange terms are obtained through first or second order Taylor series expansions around equilibrium, guided by previous field evidence. For example, the momentum exchange term relating to subsurface flow uses a first order expansion, leading to a REW-scale Darcy's law, while the resistance terms relating to overland flow are expressed in terms of a REW-scale Chezy formula. For the channels an equivalent of the Saint-Venant equations has been obtained for a tree-like branching network of river reaches. The end result is a set of REW-scale balance equations for mass and momentum, comprising 13 balance equations in 23 unknowns.

An additional 10 constitutive relationships are introduced, based on geometric considerations, in order to obtain a determinate system of equations; these are also required to satisfy the entropy inequality. The resulting set of 23 equations (13 balance equations plus 10 geometric relationships) in 23 unknown REW-scale variables (velocities, depths, area fractions, saturation etc. which do not vary spatially within REWs, and change only *between* REWs), represent a system of coupled non-linear *ordinary differential equations* (ODE). The flow within a single REW can influence, and be influenced by, the flow fields in neighbouring REWs, through the exchange of groundwater and soil moisture across the mantle, and via backwater effects along the channel reaches constituting the river channel network. The above-mentioned coupling amongst the REWs necessitates a solution algorithm which takes into account the whole ensemble of REWs simultaneously.

The solution of 13 non-linear ODEs for 30 or more REWs may appear overwhelming. However, compared to the finite element or finite difference numerical schemes associated with traditional distributed models with thousands of nodes, our proposed system of equations is still very modest. On the other hand, compared to traditional conceptual models of watershed response, the parameterisations developed here are physically-based, and more importantly, they are parsimonious.

The momentum exchange terms derived in this paper are linearised with respect to velocity and/or total head differences. The linearisation parameters $\mathscr{A}$ and $\mathscr{B}$ are functions of the remaining variables of the system. These functions can be either linear or non-linear and need to be estimated from field experiments or through detailed numerical models.

Aside from the summary presented above, the overriding message to come out of this work is that a comprehensive set of physically-based, watershed-scale governing equations, which respects the presence of a stream network, can indeed be constructed based on first principles. With appropriate simplifying assumptions, the equations do give rise to a watershed-scale Darcy's law and Chezy law; yet the equations are also flexible enough so that when field evidence warrants it we can go beyond the constraints of these traditional models and use other more general parameterisations appropriate to the field situation. Issues such as macropore flow in soils, and rills and gullies in overland flow, come to mind in this regard. In this and other respects, the derivation of the governing equations also provides the motivation to design new field and remote measurement techniques to advance the development of a new hydrologic theory.

The key to such a development is to keep the theoretical aspects as general as possible with a minimum of assumptions. However, being a first attempt, complete generality was not the goal in this study, for pragmatic reasons. While the overall aim has been to develop a general, unifying thermodynamic framework for describing watershed responses, the constitutive theory development presented has made a number of simplifying assumptions to keep the problem at a manageable level. In particular, we have focussed on runoff processes at the expense of processes related to evapotranspiration. Evapotranspiration makes up over 60% of the water balance worldwide, and it is important that the theory presented in this paper be generalised to take it into account. To fully describe evapotranspiration, we should include thermal effects, movement of both water vapour as well as liquid water in the soil, vegetation effects (both root water uptake and plant physiology), and turbulent transport processes in the atmospheric boundary layer above the land surface. The needed extensions of the theory to include these aspects, which are quite considerable, are left for future research.

9. Future perspectives

In concluding this paper, we feel the need to present an outline of where we believe the present work may be heading, and what we hope to achieve in the future. This seems appropriate, in order to give the readers a farsighted, although somewhat biased and very much speculative vision of the long-term perspectives of our research, and to stimulate their interest and participation in some of the future goals.

In contrast to watershed hydrologists, fluid mechanicians have at their disposal well established equations governing fluid movement. Their main research efforts, at the present time, focus on improving closure schemes for turbulence, on understanding particular phenomena such as mixing, dispersion, density driven flows, natural convection, internal waves, and interactions between hydrodynamics and chemical and biological processes, and on developing and improving computational algorithms for the solution of the governing partial differential equations. The basic governing equations they deal with routinely, namely, the point-scale conservation equations for mass, linear and rotational momentum, as well as energy, were derived roughly two centuries ago and form the very foundation of their work to which they could always fall back on for guidance or insight.

This is not the case in watershed hydrology. The common practice in surface hydrology has been to assemble the equations governing individual hydrologic processes (such as infiltration, overland flow, channel flow), which have been derived independently, at small scales, often in different contexts (e.g., infiltration equations derived by soil physicists), and based on more or less restrictive a priori assumptions (e.g., uniform soils). Examples include, among others, Darcy's law and its extension to unsaturated flow, the Richards equation, its approximate analytical solutions for infiltration such as the Green-Ampt model or Philip's equation, the Saint-Venant equations and the kinematic wave approximation. To describe watershed response, the common practice has been to assemble these equations together rather mechanically, regardless of the differences in context and in scales, i.e., between the scales at which they were developed and the watershed scale at which predictions are sought. Currently there is no agreed set of conservation equations for mass, momentum and energy balances, at the scale of a watershed; certainly not derived within the framework of a single and systematic procedure, as done in the present work.

In line with our own limited perception of how the research field of fluid mechanics has developed in the past and is developing at present, we attempt to give an overview of the research tasks which will be needed to complete the development of a hydrologic theory based on the set of governing balance equations presented earlier in this paper. We also try to indicate how these can be employed in the future to model general situations related to watershed hydrology, including long-term water balance, hydrologic extremes (floods and droughts), erosion and sediment transport, water quality, and the general problem of *prediction of ungauged basins* (the PUB problem discussed by Gupta and Waymire [20]). Possible steps involved in a generalisation of our approach and its implementation to solve these problems can be listed as follows.

Inclusion of evapotranspiration. Similar to the Navier–Stokes equations in fluid mechanics, we have obtained a set of *watershed-scale balance equations* for mass and momentum, supplemented with appropriate *constitutive relationships*. These allow us to evaluate the responses of the various subregions of the watershed, i.e. in the subsurface zones, the overland flow zones and the channel network, to generate space-time fields of storages and velocities everywhere across the watershed. Various extensions of the work we have done can be envisaged. One important example is the inclusion of both bare soil evaporation and plant transpiration. To do this, two things need to be done: first, a new zone has to be defined and added to the five zones of REW defined so far. This zone would represent the atmospheric boundary layer, including vegetation. Averaged equations of conservation of mass, momentum, energy and entropy for the atmospheric boundary layer need to be developed following the procedure outlined and applied by Reggiani et al. [33]. Exchange of properties between this zone and all the other zones and the external world will have to be properly accounted for. Next, following the procedure of the present paper, constitutive relationships describing thermal energy exchanges between the various subregions, water vapour diffusion, root water uptake, plant physiology, and above all mass, momentum and energy exchanges between the land surface and the atmospheric boundary layer have to be developed. Our contention is that the governing equations derived above (including extensions to include evapotranspiration) can form the basis for predictive models of watershed response. As a first effort in that direction, a model of rainfall-runoff response for a bifurcating stream network has been constructed (Reggiani et al. [34]), and has been used to estimate space-time fields of velocity and storage in the network. This model is currently being extended to include hillslope processes.

Improvement of constitutive relationships. The constitutive relationships presented in this paper are quite basic, and need to be considerably improved and tested under various climatic and geographic circumstances, and the effects of variabilities of the hydrologic processes at scales smaller than the REW need also to be incorporated in the parameterisations. This can be achieved by means of both field experiments and detailed numerical models based on traditional small-scale governing equations (e.g. Duffy [6]). Indeed, much of the previous work which has been carried out on spatial variability, scale and similarity (Wood et al. [39], Blöschl and Sivapalan [2], Kubota and Sivapalan [28], Kalma and Sivapalan [27]) can be placed in this context. The added value of the present work is that with the availability now of a proper set of balance equations, these need no longer be ad hoc and should be seen as proper closure schemes similar to those investigated in fluid mechanics. Data collection is important for all modelling efforts, to serve as climatic inputs and as landscape parameters, and to validate model predictions. However, in the context of the present work, new types of data and new observational strategies are needed to assist in the development of constitutive relationships, especially to quantify the effects of sub-grid variability.

Inclusion of sediment transport, chemistry and biology. The set of balance equations for mass, momentum, and energy derived by Reggiani et al. [33] govern the transport of water within and over the watershed. However, we know that water is also the carrier for sediments, chemical constituents and living organisms through the various subregions of the watershed. Therefore, the governing equations need to be coupled with general equations for *sediment transport* to account for erosion, transport and deposition of sediments. These can later be coupled with transport equations for various chemical constituents such as nutrients, in streams, on the land surface, and in the soil pores, for the purpose of water quality studies. The same procedure can be repeated for *biological* components by combining the equations governing the growth and decline of living organisms in the water and in soils (e.g., algae and bacteria) with equations governing streamflow, sediments, nutrients (balance of water mass and momentum, and mass transport), as well as temperature (balance of energy).

Space-time fields, flood scaling, flood forecasting. Numerical models of the governing equations of mass and momentum balance at the watershed scale can also open up further exciting possibilities for the investigation of space-time variability of *runoff fields*, including the extremes of floods and droughts, and their process controls (for reference see e.g. Gupta and Waymire [20], Robinson and Sivapalan [35] and Blöschl and Sivapalan [2], [3]). Areas where these will have a direct impact are *the scaling behaviour of floods* and the implementation of *flood forecasting systems*. In addition, due to the formulation of constitutive relationships which are physically based and meaningful, the need for calibration is significantly reduced, especially when combined with innovative field measurements of critical variables. Therefore, this can make a significant contribution to the classical problem of *prediction of ungauged basins* discussed by Gupta and Waymire [20].

Long-term water balances. Once the evapotranspiration part of the hydrologic cycle is fully incorporated in the governing equations, and provided they are averaged over a suitable averaging time, these can then be used to investigate long-term water balances, and in particular, the effect of climate–soil–vegetation interactions on the dynamics of water balance, as an extension to the pioneering work of Eagleson [7–13,37]. Water balance is a simple principle, yet it reflects many complex interactions which are driven by a competition between the two primary driving forces of gravity and solar energy, with a mediating role played by soils and plant physiology. All natural hydrologic variability (e.g., extremes) is underlain by the variability of water balance, and hence understanding water balance variability is a fundamental problem. The set of governing equations which incorporate these physical processes can go a long way towards understanding and predicting the observed natural variability of water balances, and any changes to these due to human intervention.

Search for hydrologic theory. Finally, we expect that our approach would deliver appropriate equations and would then be used to formulate and test fundamental principles which could guide our understanding of the organisation of landscapes and watersheds (including climate, soil and vegetation). Work is needed to investigate possible manifestations of these organising principles on hydrologic variability, and to validate these against observed data. Examples of such principles include the *principle of minimum energy expenditure* governing hydraulic geometry in channel networks (See Refs. [36,30]), and the *ecological optimality hypothesis* governing climate–soil–vegetation interactions (See Refs. [8–15,24]).

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