Megascale thermodynamics in the presence of a conservative field: The watershed case

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ABSTRACT

In a series of earlier papers the authors have proposed a unique approach for watershed modelling, which is based on developing watershed-scale balance equations for mass, momentum, energy and entropy by averaging the point-scale (microscale) equations over appropriate averaging regions or control volumes (megascale). The regions are referred to as Representative Elementary Watersheds (REWs), as they are considered to be invariant with respect to the spatial scale. Here, the REW-approach is generalized by developing balance equations and constitutive relationships for sub-REW units, referred to as Elements. Similar to an REW, Elements are divided into a series of zones to accommodate typical flow processes. The subdivision of an REW into Elements supports sub-REW-scale process representation. The proposed procedure yields exchange terms for mass, forces and thermal energy across phase and Element boundaries. These terms constitute unknowns and require a systematic closure. The closure is addressed within a thermodynamic approach, in which the Clausius–Duhem inequality formulated for a watershed serves as a mathematical and physical constraint. The present paper represents a clear extension of earlier work, as it includes non-isothermal processes in presence of the conservative gravitational field. The subdivision of an REW into Elements also provides means for including sub-REW variability due to landuse, geology or presence of infrastructure in the watershed. The paper also shows how an REW Element-scale unsaturated flow equation and non-linear reservoir equations for overland and channel flow can be consistently derived within the thermodynamic theory framework.

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1. Introduction

Reggiani et al. (1999,1998,2000) proposed a novel approach for watershed modelling, whereby a watershed is subdivided into discrete three-dimensional units called Representative Elementary Watersheds (REWs). REWs are organized around the stream channel network and constitute control volumes. The boundaries of an REW coincide with topographic drainage divides. The REWs are defined in a way as to be identified at various scales of observation and are therefore scale-invariant. Nevertheless, as also pointed out by Beven (2006), the appropriate closure relationship remain scale-dependent and need to be developed case by case on the basis of a generalized constitutive theory.

A watershed for example may be considered a single large REW, or can be split into a finite number of smaller REWs. A REW fills a spatial region enclosed by a prismatic mantle surface delineated by the topographic REW boundary as shown in Fig. 1. On the top, the REW is delimited by the atmosphere, and at the bottom by an assumed depth boundary. The REW control volume contains the most common flow zones encountered in watersheds. In the original work by Reggiani et al. (1998) these were: *(1)* the unsaturated zone, *(2)* saturated zone, *(3)* saturated overland flow, *(4)* concentrated overland flow and *(5)* the river channel. In this extension of the REW approach we add two additional zones: *(6)* saturated subsurface storm flow layer and *(7)* snow/ice pack. Flows within the zones are characterised by vastly different time scales and include multiphase unsaturated and saturated porous media flow (subsurface zones, snow) and single phase flow (overland and channel flow).

In traditional distributed physically-based watershed models (Abbott et al., 1986a,b), partial differential equations governing water flow in various zones are discretized and solved at scales much smaller than the REW, i.e. at the nodal points of a computational grid. In the REW approach, conservation equations for mass, momentum, energy and entropy are averaged over each flow zone, yielding global balance laws. The governing equations are Ordinary

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Nomenclature

Latin symbols

A	Element or REW boundary
$\mathcal{A}$	Helmholtz free energy per unit mass
$\hat{A}$	Extensive Helmholtz free energy
B	First-order expansion coefficient for mass exchange
e	Megascopic mass exchange term
E	Internal energy per unit mass
$\hat{E}$	Extensive internal energy
f	External supply of generic property ψ
F	Megascopic entropy exchange term
G	Net production of generic property ψ
$\mathbf{g}$	Gravity vector
$\mathbf{i}$	Non-convective flux vector
$\mathbf{j}$	Entropy flux vector
$\mathbf{J}_\alpha^i$	Specific moment of mass the i-subregion α-phase
K	First-order expansion coefficient for thermal exchange
l	Length of the river channel
L	Length dimension
m	Channel average cross sectional area
M	Mass
$\mathbf{M}$	First-order expansion tensor for momentum exchange
$\bar{M}^{-1}$	Hydraulic conductivity of the soil
n	Manning hydraulic roughness
p	Phase pressure
P_w	Wetted perimeter of channel reach
$\mathbf{q}$	Heat vector
Q	Megascopic heat exchange term defined in equations
$\mathbf{R}$	Second-order expansion coefficient for momentum exchange
R_h	Hydraulic radius of channel reach
s	Phase saturation
S	Phase interface
S_0	Bed slope of channel reach
t	Time
T	Time dimension
$\mathbf{t}$	Stress tensor
$\mathbf{T}$	Momentum exchange term defined inequations (12a) and (12b)
$\mathbf{v}$	Velocity vector
V	Phase, Element or REW volume
$\mathbf{w}$	Interface and boundary surface velocity vector
W	Work exerted on a phase
$\mathbf{x}$	Position vector of a fluid particle with respect to a reference $\mathbf{x}_o$
y	Average vertical thickness of a zone
z	Vertical coordinate
z_o	Reference datum
$\mathbf{Z}_\Lambda$	Multi-dimensional system state variable

Greek symbols

Δ	Time increment
ϵ	Porosity
η	Microscopic entropy
$\hat{\eta}$	Extensive entropy
λ	Water retention scaling exponent (Brooks–Corey)
Λ	Entropy production
θ	Temperature
μ	Chemical potential
ρ	Mass density
Σ	Horizontal area projection for the various zones, Elements and REWs
τ	Time integration variable
ψ	Generic thermodynamic property mass, momentum, energy or entropy
Ω	Boundary surface of a generic volume

Superscripts and subscripts

α, β	Indices indicating different phases
i, j	Superscripts indicating different zones
I	Superscript indicating Elements
a	Superscript indicating the atmosphere
c	Superscript indicating the concentrated (Hortonian) overland flow zone
f	Superscript indicating the snow/ice pack
o	Superscript indicating the saturated overland flow zone
p	Superscript indicating the saturated subsurface stormflow zone
r	Superscript indicating the river channel
s	Superscript indicating the saturated zone
u	Superscript indicating the unsaturated zone

Special notation

$\Sigma_{\alpha \neq \beta}$	Summation over all phases different from the α-phase
$\Sigma_{i \neq j}$	Summation over all Elements different from the Element i

Differential Equations (ODEs) which can be cast in a general form (Reggiani et al., 1998):

$$\frac{d\psi}{dt} = \sum_i e_i^\psi + U + G \tag{1}$$

where ψ represents a generic thermodynamic property like mass, momentum, energy, or entropy, e_i^ψ is a generic exchange term for ψ, U is the external supply of ψ and G is the net production rate. The exchange terms account for the transfer of ψ among phases, and across zones and REWs. We emphasize that all equations of type (1) no longer contain any spatial information and are
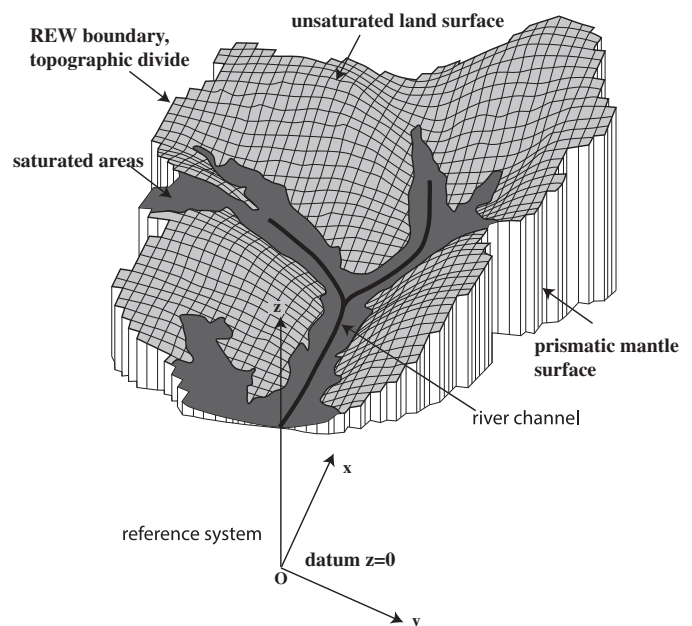

Fig. 1. An example of a single REW and the Cartesian reference system.

called megascale (or megascopic) equations by adopting the notation in Gray et al. (1993). This terminology is used to distinguish Eq. (1) from macroscale equations, which are commonly obtained in the porous media literature by averaging microscale conservation laws over a Representative Elementary Volume (REV). In this context, the e_i^ψ terms are called megascale (or megascopic) exchanges. These terms result from the averaging procedure, are unknown quantities, and need to be closed through constitutive relationships, in analogy to macroscale continuum mechanics. Such constitutive equations were obtained by Reggiani et al. (1999) trough a physically consistent procedure using the 2nd law of thermodynamics as a constraint. The REW-approach has been employed to simulate subsurface flow in a hillslope (Reggiani et al., 2000) and channel network flow in watersheds (Reggiani et al., 2001). Here we have refined the development of the REW-scale equations and added new features. The chief aims of this paper are:

- The formulation of balance laws and constitutive equations in terms of extensive quantities by introducing a generalised thermodynamic potential. The latter results in a more rigorous inclusion of gravity into the constitutive theory. The motivation behind this development is explained in Section 2.
- The division of REWs into a number of REW Elements based on the presence of sub-REW scale variability. The reason for this additional discretisation is the need to account for hydrological processes due to geological and topographical features or land-use pattern at the sub-REW scale, or to describe effects of reservoirs or hydraulic infrastructure.
- Two additional zones are introduced, which were not present in the original REW definition. These are the saturated subsurface stormflow zone, a shallow layer in the upper soil, which hosts fast saturated flow. According to the particular circumstances, this zone can also be interpreted as a shallow perched water-bearing body. Moreover, the presence of snowpack and/or ice in a separate surface layer is also taken into account.
- The exchange of thermal energy is included, allowing for phases and zones to be at the non-isothermal state. In this context, constitutive relationships for thermal energy fluxes among phases and across Element and REW boundaries are provided. This extension is required in studies of snow, ice and/or landsurface-atmosphere interaction processes.

In the following sections we describe how the system is conceptualised, introduce the necessary notation and the concept of REW Element, and show how spatio-temporal averaging is performed and constitutive equations for REW Elements are obtained.

2. Thermodynamics at the REW-scale

The development of equations for the thermodynamics of watersheds is complicated relative to smaller systems like porous media within an REV (Hassanizadeh and Gray, 1979). The difficulty lies in the presence of the conservative gravitational field and its thermodynamic effect at large spatial scales. This is because in averaging point-scale equations over a region, the centroids of different phases or zones may not be located at precisely the same elevation. The implications of this can be understood by considering two adjacent adiabatic vessels of unit depth, filled with an isothermal incompressible fluid at temperature θ (Fig. 2). The vessels contain the same fluid mass M and volume V and are isentropic at entropy η. The fluid is free-surface, but the vessels are assumed to be closed, in order to preclude mass exchange with the ambient. Due to the isothermal state and equal mass/volume the two vessels should have the same internal energy E, and when connected, they should be at equilibrium. But as we can see, their
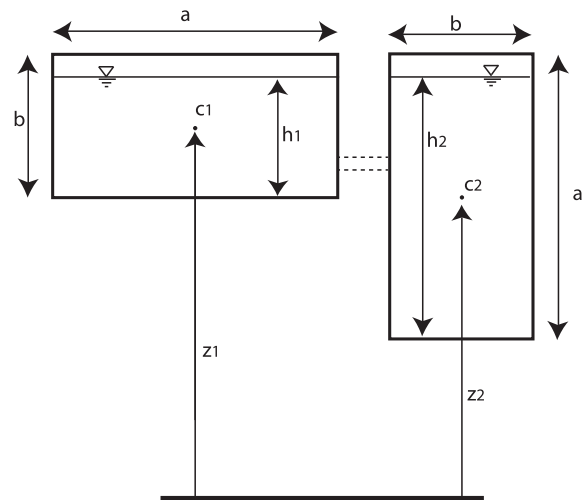

Fig. 2. Two closed adiabatic vessels containing equal quantities of an isothermal fluid.

centroids c_1, c_2 are positioned at different elevations. The average (hydrostatic) pressure $p_1 = (h_1 \rho g)/2$ in the left vessel is lower than the pressure $p_2 = (h_2 \rho g)/2$ in the right one, thus E_1 is apparently lower than E_2. This is made visible by writing the internal energy of a vessel in the Euler form (Callen, 1985):

$$E = \theta\,\eta + \mu\,M - p\,V \tag{2}$$

where μ is the chemical potential of the fluid. If the two vessels are suddenly interconnected so that fluid can be interchanged, the difference in internal energy should cause a flow across the connecting pipe to bring the two-vessel system to a new thermodynamic equilibrium. From experience we know that this is not the case. From this we deduce that the internal energy of the two vessels must be equal, and an additional constitutive dependency of E related to gravity must be included, to ensure that the two systems have the same internal energy. In this paper we address this issue and postulate a dependence of thermodynamic potentials at the megascale on gravity, when developing constitutive relationships for Elements or REWs. We note that the theory is general and applies to any megascopic system exposed to a conservative field.

3. Conceptualisation of the system and notation

In Reggiani et al. (1999,1998), a watershed is discretised into REWs (Representative Elementary Watersheds), which represent control volumes and serve as averaging regions for conservation equations. Here the approach is generalized by splitting the REW into smaller entities, called *REW Elements* (or in short, *Elements*). This procedure is necessary to describe parts of the REW in more detail and address sub-REW-scale variability. For example, one may define REW Elements on the basis of geological, landuse or other pattern that have a direct impact on soil properties or groundwater flow, and thus on the hydrological response of an entity. Fig. 3 shows how a single REW is separated into such Elements. We emphasise that the set of balance equations and constitutive relationships derived in this paper are similar to those obtained in Reggiani et al. (1999,1998), and identical, if an REW contains one Element only. Each Element can include the same hydrological entities found in an REW. These host particular hydrological processes and occupy own spatial regions, referred to as *zones*. The zones are denoted with superscripts as described below. The superscript u identifies the portion of the Element (or REW) occupied by the unsaturated zone, while the portion occupied by the saturated zone is indicated with s. The volume associated with the

Table 1
The seven zones within an REW or an Element.

| Zone	Phases	Phase volumes	Adjacent zones	Zone boundaries	Phase interfaces	Ext. boundaries
unsat. zone (u)	water solid air	V_w^u, V_g^u V_m^u	u, s, c, p, a	A^{us}, A^{uc} A^{up}, A^{ua}	S_{wg}^u, S_{wm}^u S_{gm}^{ug}	A^{uu}
sat. zone (s)	water solid	V_w^s, V_m^s	u, o, s, r	A^{su}, A^{so} A^{sr}	S_{wm}^s	A^{ss}
river (r)	water	V^r	s, o, p, a, r	A^{sr}, A^{ro} A^{rp}, A^{ra}	n/a	A^{rr}
sat. overland flow (o)	water	V^o	s, c, a, r	A^{so}, A^{oc} A^{oa}, A^{or}	n/a	n/a
Hortonian overland flow (c)	water	V^c	o, a, r	A^{oc}, A^{ca} A^{cr}	n/a	n/a
sat. subsurface stormflow (p)	water solid	V_w^p, V_m^p	c, f, r	A^{pc}, A^{pf} A^{pr}	S_{wm}^p	n/a
snow zone (f)	water solid air	V_w^f, V_g^f V_m^f	p, a	A^{pf}, A^{fa}	S_{wg}^f, S_{wm}^f S_{gm}^f	n/a
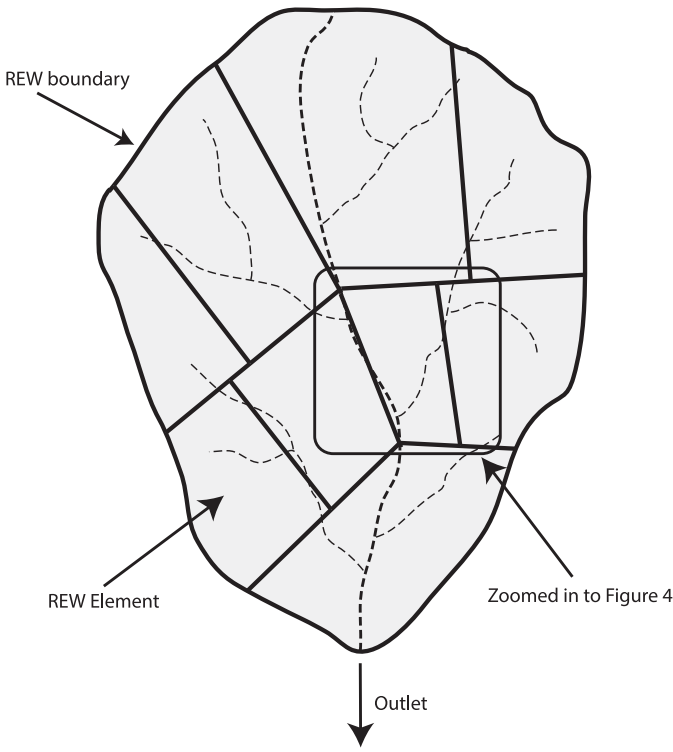
Fig. 3. An REW separated into a finite number of Elements.

channel carries the superscript *r*, the one occupied by the saturated overland flow the superscript *o*, the Hortonian overland flow the symbol *c*, the saturated subsurface stormflow the symbol *p* and the snow/ice pack the symbol *f*. On the land surface, the watershed is in direct contact with the atmosphere, denoted with the superscript *a*. All flow zones are summarised in Table 1. Fig. 4 shows a single Element and its zones. We also note that in the unsaturated zone *u* or the snowpack *f* water, solid and gas (air) coexist and are denoted with subscripts *w*, *m*, and *g*, respectively. The saturated zone *s* or the subsurface stormflow zone *p*, consist of two phases: water and solid. The remaining zones (*r*, *o* and *c*) contain water only. The total volume occupied by the whole watershed is the sum of volumes of all constituent REWs, Elements, zones and phases:

$$V = \sum_K \sum_I \sum_i \sum_\alpha V_\alpha^{ilK} = \sum_{K,I,i,\alpha} V_\alpha^{ilK} \qquad (3)$$

where α indicates a phase within a particular zone *i*, which forms part of an Element *I* within the *K*-th REW. We note that the indices *I* and *K* are mostly omitted for notational simplicity. We distinguish two types of boundaries for an Element: *internal boundaries* that separate either phases within a zone or zones within an Element; *external boundaries* that separate either Elements of an REW or coincide with REW or watershed boundaries. Two adjacent Elements are separated by surfaces indicated with A^{ij}. The portion of the surface occupied by the α-phase is indicated with A_α^{ij}. In the subsurface or the snowpack we are in presence of multiphase flow, where three phases meet and an equal number of interfaces is generated: the water-solid matrix interface S_{wm}^i, the water-gas interface S_{wg}^i, and the gas-solid interface S_{gm}^i. In the saturated zone and the subsurface stormflow layer, solid and water exist and are separated by the interface S_{wm}^s and S_{wm}^p respectively. In the channel and overland flow zones there are no phase interfaces. All possible internal or external boundaries as well as phases within a zone are summarized in Table 1.

4. Balance laws

General form: The averaged balance equation for a thermodynamic property ψ of the α-phase in the *i*-zone of an Element is obtained by integrating the microscale balance equation spatially over V_α^i and integrating from $t - \Delta t$ to $t + \Delta t$ in time (Reggiani et al., 1998):

$$\frac{1}{2\Delta t} \frac{d}{dt} \int_{t-\Delta t}^{t+\Delta t} \int_{V_\alpha^i} \rho \psi \, dV \, d\tau$$
$$+ \sum_{j \neq i} \frac{1}{2\Delta t} \int_{t-\Delta t}^{t+\Delta t} \int_{A_\alpha^{ij}} \mathbf{n}^{ij} \cdot [\rho \psi (\mathbf{v} - \mathbf{w}^{ij}) - \mathbf{i}] dA \, d\tau$$
$$+ \sum_{\beta \neq \alpha} \frac{1}{2\Delta t} \int_{t-\Delta t}^{t+\Delta t} \int_{S_{\alpha\beta}^i} \mathbf{n}^{\alpha\beta} \cdot [\rho \psi (\mathbf{v} - \mathbf{w}^{\alpha\beta}) - \mathbf{i}] dS \, d\tau$$
$$= \frac{1}{2\Delta t} \int_{t-\Delta t}^{t+\Delta t} \int_{V_\alpha^i} \rho f \, dV \, d\tau + \frac{1}{2\Delta t} \int_{t-\Delta t}^{t+\Delta t} \int_{V_\alpha^i} G \, dV \, d\tau \qquad (4)$$

In this equation all variables inside the integrals represent microscale quantities. The first term expresses the total rate of change of ψ. The second term is the sum of all convective and nonconvective exchanges of ψ across the internal boundaries A_α^{ij}; the sum is performed over all neighbouring zones and Elements. The third term accounts for phase changes within an Element; it is the sum of all exchanges of ψ across the phase interfaces $S_{\alpha\beta}^i$ within a zone. The interfaces $S_{\alpha\beta}^i$ form boundaries that exist exclusively
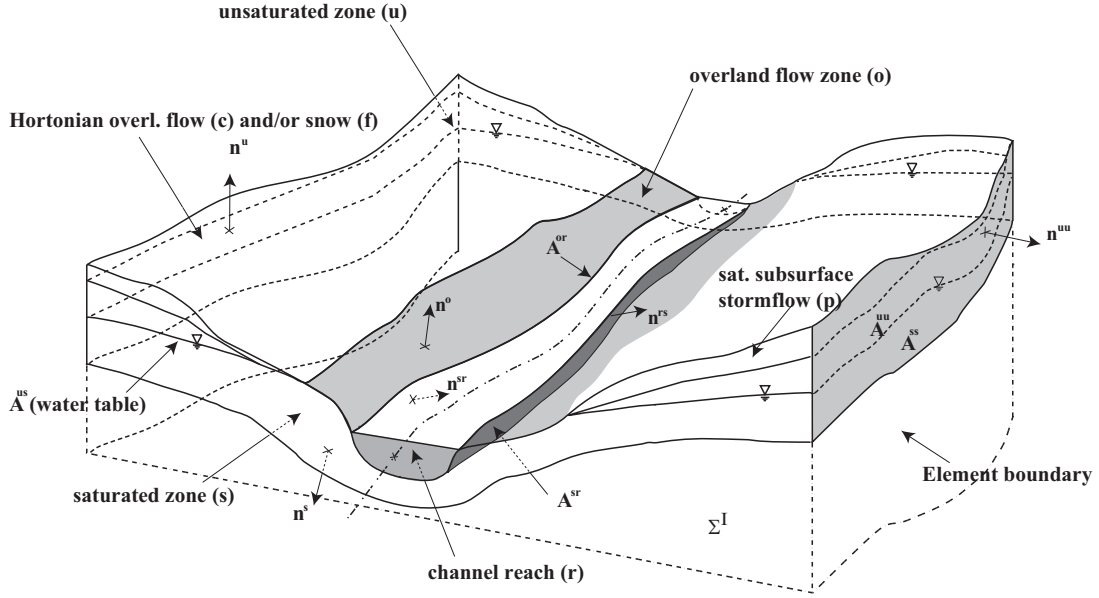
Fig. 4. Detailed view of an Element including the flow zones.

Table 2
Comparison of the flow pathways (based on data by Dunne, 1978).

Flow type	Temporal scale	Velocity [m/s]
Groundwater flow	days - years	$\leq 10^{-6}$
Hortonian overland flow	hours	$10^{-3} - 10^{-1}$
Subsurface flow	hours - days	$10^{-7} - 10^{-4}$
Saturated overland flow	hours	$10^{-2} - 10^{-1}$
Channel flow	hours - days	$1 - 10$

Table 3
Summary of the properties in the conservation equations.

Quantity	ψ	$\mathbf{i}$	f	G
Mass	1	0	0	0
Momentum	$\mathbf{v}$	$\mathbf{t}$	$\mathbf{g}$	0
Energy	$E + \frac{1}{2}v^2$	$\mathbf{t} \cdot \mathbf{v} + \mathbf{q}$	h	0
Entropy	η	$\mathbf{j}$	b	Λ

within a particular zone and need to be clearly separated from boundaries between zones or Elements.

The first term on the r.h.s. of (4) represents the external supply of ψ, while the second term expresses the net generation of ψ. The vectors $\mathbf{n}^{ij}$ and $\mathbf{n}^{\alpha\beta}$ are unit normal vectors to the surfaces A^{ij} and $S^i_{\alpha\beta}$, respectively, and are pointing outwards. The vector $\mathbf{i}$ denotes the non-convective flux of ψ. The symbol $\mathbf{v}$ denotes the microscale (or point-scale) velocity, while $\mathbf{w}^{ij}$ and $\mathbf{w}^{\alpha\beta}$ represent the velocities of A^{ij} and $S^i_{\alpha\beta}$ respectively. Further, ρ denotes the microscopic mass density, while f is the external supply of ψ. Finally, G is the net production of ψ, which is non-zero only in the balance of entropy.

Flow processes encountered within a zone can spread over a wide range of temporal and spatial scales. Examples for velocity and associated time scales are reported in Table 2 from data published by Dunne and Kirkby (1978). This wide spectrum of time scales must be acknowledged when upscaling balance equations or deriving constitutive relationships and requires temporal averaging. That is why Eq. (4) has been integrated over a characteristic time interval, where Δt has to be chosen in line with the particular problem to be analysed. For example, if one is interested in instantaneous events, the averaging period is set equal to zero. If annual values of dynamic variables need to be simulated, the interval must be chosen to be 6 months. Specific balance laws for mass, momentum, energy and entropy are obtained from Eq. (4) by substituting the microscopic quantities listed in Table 3.

Balance of mass: The megascale balance of mass for the α-phase in the i-zone is obtained by setting $\psi = 1$ and the non-convective flux $\mathbf{i}$, the external supply f and the net production G zero in the generic balance law (4). The result in terms of megas-

cale quantities becomes:

$$\frac{d}{dt}(\rho^i_\alpha V^i_\alpha) - \sum_{j \neq i} e^{ij}_\alpha - \sum_{\beta \neq \alpha} e^i_{\alpha\beta} = 0 \tag{5}$$

where the average density ρ^i_α is defined as:

$$\rho^i_\alpha = \frac{1}{2\Delta t} \frac{1}{V^i_\alpha} \int_{t-\Delta t}^{t+\Delta t} \int_{V^i_\alpha} \rho \, dV d\tau \quad \text{and} \quad V^i_\alpha = \frac{1}{2\Delta t} \int_{t-\Delta t}^{t+\Delta t} \int_{V^i_\alpha} dV d\tau \tag{6}$$

The second term on the left hand side of (5) are the sum of all α-phase mass fluxes across the boundary surfaces with adjacent zones within the same Element or in neighbouring Elements. The third term represents the mass exchanges (due to phase change) across phase interfaces within a zone. The mass exchange terms are defined in terms of time-averaged flux integrals:

$$e^{ij}_\alpha = \frac{1}{2\Delta t} \int_{t-\Delta t}^{t+\Delta t} \int_{A^{ij}_\alpha} \rho(\mathbf{w}^{ij} - \mathbf{v}) \cdot \mathbf{n}^{ij} \, dA d\tau \tag{7}$$

$$e^i_{\alpha\beta} = \frac{1}{2\Delta t} \int_{t-\Delta t}^{t+\Delta t} \int_{S^i_{\alpha\beta}} \rho(\mathbf{w}^{\alpha\beta} - \mathbf{v}) \cdot \mathbf{n}^{\alpha\beta} \, dS d\tau \tag{8}$$

It must be noted that the order of indices ij and/or $\alpha\beta$ is important. For example, e^{ij}_α indicates a flux of the α-phase from the j-zone to the i-zone, while $e^i_{\alpha\beta}$ indicates the phase change from the α to the β-phase. For modelling purposes it is useful to introduce the phase volume fraction ϵ^i_α, the ratio of phase volume V^i_α to total volume V^i of a zone. The total zone volume V^i can be expressed as the product of two quantities: the average depth y^i and the zone area projection Σ^i, with the exception of the channel zone. The channel volume is expressed as the product of the

Table 4
Element volumes, phase volumes and phase volume fractions.

Zone	Phase volume V_α^i	Zone volume V^i	Phase volume fraction ϵ_α^i
unsaturated zone (u)	$V_\alpha^s = \epsilon^u s_\alpha^u y^u \Sigma^u$	$V^u = y^u \Sigma^u$	$\epsilon^u s_\alpha^u$
saturated zone (s)	$V_\alpha^s = \epsilon^s y^s \Sigma^s$	$V^s = y^s \Sigma^s$	ϵ^s
river zone (r)	$V_\alpha^r = l^r m^r$	$V^r = l^r m^r$	1
sat. overland flow zone (o)	$V_\alpha^o = y^o \Sigma^o$	$V^o = y^o \Sigma^o$	1
Hortonian overland flow zone (c)	$V_\alpha^c = y^c \Sigma^c$	$V^c = y^c \Sigma^c$	1
sat. subsurface flow zone (p)	$V_\alpha^p = \epsilon^p y^p \Sigma^p$	$V^p = y^p \Sigma^p$	ϵ^p
snow zone (f)	$V_\alpha^f = \epsilon^f s_\alpha^f y^f \Sigma^f$	$V^f = y^f \Sigma^f$	$\epsilon^f s_\alpha^f$

average cross-section area m^r with the reach length l^l. These concepts are summarised in Table 4 for all seven zones. In this table, ϵ^u, ϵ^s, ϵ^p and ϵ^f denote the average porosities of the unsaturated (u), the saturated (s), the saturated subsurface stormflow (p) and the snow/icepack (f) zone, respectively. The variable s_α^i denotes the α-phase saturation of the i-zone; obviously $s_\alpha^i = 1$ in case of full saturation. To obtain the mass balance equations for a particular phase within a zone, we need to replace the phase volume in Eq. (5) by the products indicated in Table 4. For example, the megacale mass balance equation for water in the unsaturated zone is written as:

$$\frac{d}{dt}(\rho_w^u s_w^u \epsilon^u y^u \Sigma^u) = e_w^{uu} + e_w^{us} + e_w^{uc} + e_{wg}^u + e_{ws}^u \tag{9}$$

where e_w^{uu} represents the water influx from the unsaturated zone of all neighbouring Elements across A^{uu}, e_w^{us} is the influx from the saturated zone within the same Element across the water table A^{us}, and e_w^{uc} is the infiltration flux across the land surface A^{uc} from the Hortonian overland flow. The last two terms, e_{wg}^u and e_{ws}^u, represent the water-gas phase change (evaporation, condensation) across the water-gas interface S_{wg}^u, and the water- solid phase change (dissolution, deposition) across the corresponding interface S_{wm}^u, respectively. This last term is zero in most cases, unless dissolution or erosion is considered and freezing or thawing of soil water is occurring.

Balance of momentum: To obtain the balance equation for momentum, we substitute the appropriate microscopic properties $\mathbf{v}$, $\mathbf{t}$, and $\mathbf{g}$ from Table 3 into the generic balance Eq. (4). To obtain specific balance equations for the various zones, the integration needs to be carried out over the respective boundary surfaces, A_α^{ij}, and phase interfaces, $S_{\alpha\beta}^i$, as listed in Table 1. Next, we define the volume-average velocity $\mathbf{v}_\alpha^i$ as:

$$\mathbf{v}_\alpha^i = \frac{1}{2\Delta t} \frac{1}{\rho_\alpha^i V_\alpha^i} \int_{t-\Delta t}^{t+\Delta t} \int_{V_\alpha^i} \rho \mathbf{v} dV d\tau \tag{10}$$

For statistically stationary flows, the microscopic velocity at a point can be expressed as the sum $\mathbf{v}_\alpha^i$ plus a deviation term $\tilde{\mathbf{v}}$ with zero mean:

$$\mathbf{v} = \mathbf{v}_\alpha^i + \tilde{\mathbf{v}} \tag{11}$$

After invoking the definition of the mass exchanges (7) and (8), and collecting some terms, we obtain the following equation of momentum balance:

$$\frac{d}{dt}(\rho_\alpha^i \mathbf{v}_\alpha^i V_\alpha^i) = \sum_{j\neq i}\left[e_\alpha^{ij}\mathbf{v}_\alpha^i + \mathbf{T}_\alpha^{ij}\right] + \sum_{\beta\neq\alpha}\left[e_{\alpha\beta}^i\mathbf{v}_\alpha^i + \mathbf{T}_{\alpha\beta}^i\right] + \rho_\alpha^i \mathbf{g}_\alpha^i V_\alpha^i \tag{12}$$

where the megascale interaction forces $\mathbf{T}_\alpha^{ij}$ and $\mathbf{T}_{\alpha\beta}^i$ are defined as:

$$\mathbf{T}_\alpha^{ij} = \frac{1}{2\Delta t} \int_{t-\Delta t}^{t+\Delta t} \int_{A_\alpha^{ij}} \mathbf{n}^{ij} \cdot [\mathbf{t} - \rho\tilde{\mathbf{v}}(\mathbf{v} - \mathbf{w}^{ij})]dAd\tau \tag{13}$$

$$\mathbf{T}_{\alpha\beta}^i = \frac{1}{2\Delta t} \int_{t-\Delta t}^{t+\Delta t} \int_{S_{\alpha\beta}^i} \mathbf{n}^{\alpha\beta} \cdot [\mathbf{t} - \rho\tilde{\mathbf{v}}(\mathbf{v} - \mathbf{w}^{\alpha\beta})]dSd\tau \tag{14}$$

with $\rho\tilde{\mathbf{v}}(\mathbf{v} - \mathbf{w}^{\alpha\beta})$ apparent Reynolds stresses. Application of the chain rule of differentiation to the first term on the l.h.s. and exploitation of the mass balance Eq. (5) yields the following final form of the momentum balance:

$$(\rho_\alpha^i V_\alpha^i)\frac{d}{dt}\mathbf{v}_\alpha^i = \sum_{j\neq i}\mathbf{T}_\alpha^{ij} + \sum_{\beta\neq\alpha}\mathbf{T}_{\alpha\beta}^i + \rho_\alpha^i \mathbf{g}_\alpha^i V_\alpha^i \tag{15}$$

Balance of energy: In analogy to the momentum balance equation, the balance of energy is obtained by substituting the respective microscopic quantities from Table 3 into (4). Successive introduction of megascopic quantities yields:

$$\frac{d}{dt}\left\{\rho_\alpha^i\left[E_\alpha^i + \frac{(v_\alpha^i)^2}{2}\right]V_\alpha^i\right\}$$
$$= \sum_{j\neq i}e_\alpha^{ij}\left[E_\alpha^i + \frac{(v_\alpha^i)^2}{2}\right] + \sum_{\beta\neq\alpha}e_{\alpha\beta}^i\left[E_\alpha^i + \frac{(v_\alpha^i)^2}{2}\right]$$
$$+ \sum_{j\neq i}Q_\alpha^{ij} + \sum_{\beta\neq\alpha}Q_{\alpha\beta}^i + \sum_{j\neq i}\mathbf{T}_\alpha^{ij} \cdot \mathbf{v}_\alpha^i$$
$$+ \sum_{\beta\neq\alpha}\mathbf{T}_{\alpha\beta}^i \cdot \mathbf{v}_\alpha^i + \rho_\alpha^i(\mathbf{g}_\alpha^i \cdot \mathbf{v}_\alpha^i + h_\alpha^i)V_\alpha^i \tag{16}$$

where h_α^i is the external energy supply by radiation (see Table 3) and the terms arising from velocity and energy deviation have been accommodated as apparent heat fluxes in the thermal energy exchange terms:

$$Q_\alpha^{ij} = \frac{1}{2\Delta t} \int_{t-\Delta t}^{t+\Delta t} \int_{A_\alpha^{ij}} \mathbf{n}^{ij} \cdot \left[\mathbf{q} + \mathbf{t} \cdot \tilde{\mathbf{v}} - \rho\left(\tilde{E} + \frac{\tilde{v}^2}{2}\right)(\mathbf{v} - \mathbf{w}^{ij})\right]dAd\tau \tag{17}$$

$$Q_{\alpha\beta}^i = \frac{1}{2\Delta t} \int_{t-\Delta t}^{t+\Delta t} \int_{S_{\alpha\beta}^i} \mathbf{n}^{\alpha\beta}$$
$$\cdot \left[\mathbf{q} + \mathbf{t} \cdot \tilde{\mathbf{v}} - \rho\left(\tilde{E} + \frac{\tilde{v}^2}{2}\right)(\mathbf{v} - \mathbf{w}^{\alpha\beta})\right]dSd\tau \tag{18}$$

Substitution of the equations of mass and momentum balance in (16), after some manipulations, results in the conservation of thermal energy equation:

$$\frac{d\hat{E}_\alpha^i}{dt} = \sum_{j\neq i}\left[e_\alpha^{ij}E_\alpha^i + Q_\alpha^{ij}\right] + \sum_{\beta\neq\alpha}\left[e_{\alpha\beta}^i E_\alpha^i + Q_{\alpha\beta}^i\right] + \rho_\alpha^i h_\alpha^i V_\alpha^i \tag{19}$$

with $\hat{E}_\alpha^i = \rho_\alpha^i E_\alpha^i V_\alpha^i$ the extensive α-phase internal energy of the i-zone.

Balance of entropy: The balance of entropy is obtained by substituting the corresponding microscopic properties from Table 3 into the general balance Eq. (4). After introducing appro-

priate symbols for the megascale properties, we obtain:

$$\frac{d\hat{\eta}_\alpha^i}{dt} = \sum_{j \neq i} \left[e_\alpha^{ij} \eta_\alpha^i + F_\alpha^{ij} \right] + \sum_{\beta \neq \alpha} \left[e_{\alpha\beta}^i \eta_\alpha^i + F_{\alpha\beta}^i \right] + \rho_\alpha^i b_\alpha^i V_\alpha^i + \rho_\alpha^i \Lambda_\alpha^i V_\alpha^i \tag{20}$$

where $\hat{\eta}_\alpha^i = \rho_\alpha^i \eta_\alpha^i V_\alpha^i$ denotes the extensive entropy of the phase and b_α^i is the external entropy supply (see Table 3). The terms F_α^{ij} and $F_{\alpha\beta}^i$ are the megascale exchange terms for entropy across the Element boundary A_α^{ij} and the phase interfaces $S_{\alpha\beta}^i$, respectively. These are defined via the following two integrals respectively:

$$F_\alpha^{ij} = \frac{1}{2\Delta t} \int_{t-\Delta t}^{t+\Delta t} \int_{A_\alpha^{ij}} \mathbf{n}^{ij} \cdot [\mathbf{j} - \rho \tilde{\eta} (\mathbf{v} - \mathbf{w}^{ij})] dA d\tau \tag{21}$$

$$F_{\alpha\beta}^i = \frac{1}{2\Delta t} \int_{t-\Delta t}^{t+\Delta t} \int_{S_{\alpha\beta}^i} \mathbf{n}^{\alpha\beta} \cdot [\mathbf{j} - \rho \tilde{\eta} (\mathbf{v} - \mathbf{w}^{\alpha\beta})] dS d\tau \tag{22}$$

5. Jump conditions

The flux continuity of a thermodynamic property across Element, zone or phase boundaries must be correctly accounted for, when combining phases, zones, Elements and REWs in the entropy inequality. To derive these relationships, which are as important as the balance laws, we adopt the approach by Eringen (1980). He states the general balance law for two portions of a continuum separated by a surface of discontinuity. The two portions are subsequently assembled, yielding megascopic jump conditions for the balance equations across an interface. The detailed derivations are omitted here for reasons of brevity, and only the final results are presented.

Jump condition for mass: The jump condition for mass across an interface A_α^{ij} simply states that:

$$e_\alpha^{ij} + e_\alpha^{ji} = 0 \tag{23}$$

An analogous expression holds for the mass exchange across phase interfaces $S_{\alpha\beta}^i$:

$$e_{\alpha\beta}^i + e_{\beta\alpha}^i = 0 \tag{24}$$

Jump condition for momentum: The jump condition for momentum across a boundary A_α^{ij} is expressed as follows:

$$(e_\alpha^{ij} \mathbf{v}_\alpha^i + \mathbf{T}_\alpha^{ij}) + (e_\alpha^{ji} \mathbf{v}_\alpha^i + \mathbf{T}_\alpha^{ji}) = 0 \tag{25}$$

Upon substituting from (23) we can recast this equation into the form:

$$\mathbf{T}_\alpha^{ij} + \mathbf{T}_\alpha^{ji} = -e_\alpha^{ij} \mathbf{v}_\alpha^{i,j} \tag{26}$$

whereby a comma in the indices denotes a relative quantity, defined as follows:

$$\mathbf{v}_\alpha^{i,j} = \mathbf{v}_\alpha^i - \mathbf{v}_\alpha^j \tag{27}$$

Similarly, a jump condition for momentum across a phase interface is obtained by using (24):

$$\mathbf{T}_{\alpha\beta}^i + \mathbf{T}_{\beta\alpha}^i = -e_{\alpha\beta}^i \mathbf{v}_{\alpha,\beta}^i \tag{28}$$

where:

$$\mathbf{v}_{\alpha,\beta}^i = \mathbf{v}_\alpha^i - \mathbf{v}_\beta^i \tag{29}$$

Jump condition for energy: The jump condition for total energy across a boundary A_α^{ij} is expressed as:

$$\mathbf{T}_\alpha^{ij} \cdot \mathbf{v}_\alpha^i + Q_\alpha^{ij} + e_\alpha^{ij} \left[E_\alpha^i + \frac{(v_\alpha^i)^2}{2} \right] + \mathbf{T}_\alpha^{ji} \cdot \mathbf{v}_\alpha^j + Q_\alpha^{ji}$$
$$+ e_\alpha^{ji} \left[E_\alpha^j + \frac{(v_\alpha^j)^2}{2} \right] = 0 \tag{30}$$

The use of the jump conditions for mass (23) and (24) and those for momentum (25) and (28) allows to recast Eq. (30) into the form:

$$Q_\alpha^{ij} + Q_\alpha^{ji} = -\mathbf{T}_\alpha^{ij} \cdot \mathbf{v}_\alpha^{i,j} - e_\alpha^{ij} \left[E_\alpha^{i,j} + \frac{(v_\alpha^{i,j})^2}{2} \right] \tag{31}$$

where $E_\alpha^{i,j}$ is defined similarly to $\mathbf{v}_\alpha^{i,j}$ in Eq. (27). The jump condition across a phase interface $S_{\alpha\beta}^i$ becomes:

$$Q_{\alpha\beta}^i + Q_{\beta\alpha}^i = -\mathbf{T}_{\alpha\beta}^i \cdot \mathbf{v}_{\alpha,\beta}^i - e_{\alpha\beta}^i \left[E_{\alpha,\beta}^i + \frac{(v_{\alpha,\beta}^i)^2}{2} \right] \tag{32}$$

with $E_{\alpha,\beta}^i$ defined similarly to $\mathbf{v}_{\alpha,\beta}^i$ in Eq. (29).

Jump condition for entropy: As entropy is not a conservative quantity, the jump condition across the generic boundary surface A_α^{ij} would require:

$$(e_\alpha^{ij} \eta_\alpha^i + F_\alpha^{ij}) + (e_\alpha^{ji} \eta_\alpha^i + F_\alpha^{ji}) \geq 0 \tag{33}$$

Substitution from (23) gives:

$$F_\alpha^{ij} + F_\alpha^{ji} + e_\alpha^{ij} \eta_\alpha^{i,j} \geq 0 \tag{34}$$

with $\eta_\alpha^{i,j}$ defined in analogy to Eq. (27). Similarly, the jump condition across a phase interface $S_{\alpha\beta}^i$ becomes:

$$F_{\alpha\beta}^i + F_{\beta\alpha}^i + e_{\alpha\beta}^i \eta_{\alpha,\beta}^i \geq 0 \tag{35}$$

6. Entropy inequality

The 2nd law of thermodynamics states that the total entropy production of the system must be non-negative. The entropy production of the i-zone α-phase of Element I and REW K is the quantity Λ_α^i appearing in Eq. (20). To obtain the entropy production of the entire watershed, Eq. (20) must be added over all phases, zones, Elements, and REWs to obtain:

$$\Lambda = \sum_{K,I,i,\alpha} \theta_\alpha^i \rho_\alpha^i \Lambda_\alpha^i V_\alpha^i = \sum_{K,I,i,\alpha} \theta_\alpha^i \frac{d\hat{\eta}_\alpha^i}{dt} - \sum_{K,I,i,\alpha} \sum_{j \neq i} \theta_\alpha^i e_\alpha^{ij} \eta_\alpha^i$$
$$- \sum_{K,I,i,\alpha} \sum_{\beta \neq \alpha} \theta_\alpha^i e_{\alpha\beta}^i \eta_\alpha^i - \sum_{K,I,i,\alpha} \sum_{j \neq i} \theta_\alpha^i F_\alpha^{ij} - \sum_{K,I,i,\alpha} \sum_{\beta \neq \alpha} \theta_\alpha^i F_{\alpha\beta}^i$$
$$- \sum_{K,I,i,\alpha} \theta_\alpha^i \rho_\alpha^i b_\alpha^i V_\alpha^i \geq 0 \tag{36}$$

In arriving at this result, each single entropy conservation equation is multiplied by the absolute temperature θ_α^i of the phase and then added. Moreover the intensive Helmholtz free energy potential for the i-zone α-phase, $\mathcal{A}_\alpha^i$, is introduced:

$$\mathcal{A}_\alpha^i = E_\alpha^i - \theta_\alpha^i \eta_\alpha^i \tag{37}$$

Similarly, the extensive Helmholtz free energy $\hat{\mathcal{A}}_\alpha^i$ is defined as:

$$\rho_\alpha^i V_\alpha^i \mathcal{A}_\alpha^i = \hat{\mathcal{A}}_\alpha^i = \hat{E}_\alpha^i - \theta_\alpha^i \hat{\eta}_\alpha^i \tag{38}$$

To express the entropy inequality in terms of $\hat{\mathcal{A}}_\alpha^i$, the thermal energy Eq. (19) is summed over all system components and then added to the inequality (36). Then (38) and the chain rule of dif-

ferentiation are employed to yield:

$$
\Lambda = \sum_{K,I,i,\alpha} \theta_\alpha^i \rho_\alpha^i \Lambda_\alpha^i V_\alpha^i =
$$

$$
- \sum_{K,I,i,\alpha} \left(\frac{d\hat{\mathcal{A}}_\alpha^i}{dt} + \hat{\eta}_\alpha^i \frac{d\theta_\alpha^i}{dt} \right) + \sum_{K,I,i,\alpha} \sum_{j\neq i} e_\alpha^{ij} \mathcal{A}_\alpha^i + \sum_{K,I,i,\alpha} \sum_{\beta\neq\alpha} e_{\alpha\beta}^i \mathcal{A}_\alpha^i
$$

$$
+ \sum_{K,I,i,\alpha} \sum_{j\neq i} \left[Q_\alpha^{ij} - \theta_\alpha^i F_\alpha^{ij} \right] + + \sum_{K,I,i,\alpha} \sum_{\beta\neq\alpha} \left[Q_{\alpha\beta}^i - \theta_\alpha^i F_{\alpha\beta}^i \right]
$$

$$
+ \sum_{K,I,i,\alpha} \theta_\alpha^i \rho_\alpha^i \left(\frac{h_\alpha^i}{\theta_\alpha^i} - b_\alpha^i \right) V_\alpha^i \geq 0
$$

(39)

Following common practice in thermodynamics (for reference see Eringen (1980)), the external supply of entropy b_α^i is assumed to be attributable only to external supply of internal energy h_α^i:

$$
b_\alpha^i = \frac{h_\alpha^i}{\theta_\alpha^i}
$$

(40)

Eq. (40) and the jump conditions (23), (24) for mass, (31), (32) for energy and (34), (35) for entropy are used to further manipulate (39) and eliminate the thermal exchanges Q_α^{ij}, $Q_{\alpha\beta}^i$:

$$
\Lambda = - \sum_{K,I,i,\alpha} \left(\frac{d\hat{\mathcal{A}}_\alpha^i}{dt} + \hat{\eta}_\alpha^i \frac{d\theta_\alpha^i}{dt} \right) - \sum_{K,I,i,\alpha} \sum_{j\neq i} \mathbf{T}_\alpha^{ij} \cdot \mathbf{v}_\alpha^i - \sum_{K,I,i,\alpha} \sum_{\beta\neq\alpha} \mathbf{T}_{\alpha\beta}^i \cdot \mathbf{v}_\alpha^i
$$

$$
+ \sum_{K,I,i,\alpha} \sum_{j\neq i} e_\alpha^{ij} \left[\frac{(v_\alpha^j)^2}{2} - \frac{(v_\alpha^i)^2}{2} \right]
$$

$$
+ \sum_{K,I,i,\alpha} \sum_{\beta\neq\alpha} e_{\alpha\beta}^i \left[\frac{(v_\beta^i)^2}{2} - \frac{(v_\alpha^i)^2}{2} \right]
$$

$$
+ \sum_{K,I,i,\alpha} \sum_{j\neq i} \theta_\alpha^{j,i} F_\alpha^{ij} - \sum_{K,I,i,\alpha} \sum_{\beta\neq\alpha} \theta_{\beta,\alpha}^i F_{\alpha\beta}^i \geq 0
$$

(41)

where $\theta_\alpha^{j,i}$ and $\theta_{\beta,\alpha}^i$ are the differences of phase temperature across the zone boundaries or phase interfaces. The following step is the development of constitutive equations.

7. Constitutive equations

The equations of conservation of mass, momentum, and energy presented in the previous sections are very general and in fact apply to any arbitrary volume, whether part of a watershed or just a continuum body. These equations must be supplemented with constitutive relationships for mass, force and thermal exchange terms defined in Section 4. This is also needed because the number of equations is much less than the number of unknowns. For example, for the water phase of the unsaturated zone, there are three equations (1 mass balance, 1 (vectorial) momentum balance and 1 energy balance), whereas there are 25 unknowns (ρ_w^u, V_w^u, e_w^{uu}, e_w^{us}, e_w^{uc}, e_{wg}^u, e_{wm}^u, $\mathbf{v}_w^u$, $\mathbf{T}_w^{uu}$, $\mathbf{T}_w^{us}$, $\mathbf{T}_w^{uc}$, $\mathbf{T}_{wg}^u$, $\mathbf{T}_{wm}^u$, $\hat{E}_w^u$, Q_w^{uu}, Q_w^{us}, Q_w^{uc}, Q_{wg}^u, Q_{wm}^u, $\hat{\eta}_w^u$, F_w^{uu}, F_w^{us}, F_w^{uc}, F_{wg}^u and F_{wm}^u), where we count vectorial quantities as one unknown too. Thermodynamically consistent constitutive relationships can be found by using the entropy inequality as a constraint. This requires us to focus on the internal energy of the system first.

In classical thermodynamics, the total energy available to perform "useful" work by a system is considered to depend on extensive system properties such as total mass, volume, and entropy. Consequently the internal energy potential can be stated as a function of independent extensive state variables:

$$
\hat{E}_\alpha^i = \hat{E}_\alpha^i (\hat{\eta}_\alpha^i, V_\alpha^i, M_\alpha^i, \dots)
$$

(42)

whereby the internal energy (or for that matter any other extensive thermodynamic potential) is additive. For example, if the mass

of the system is doubled, then $\hat{E}_\alpha^i$ will also double. This is known to be valid for small-scale systems (for example at the scale of REV for porous media flow) or for homogeneous large-scale systems. For a homogeneous system, a given amount of mass has the same volume, entropy and energy, regardless of where in the system it is located. Obviously, this does not hold for a heterogeneous system. For example, in a large body of fluid, which is under the influence of gravity, a given volume of the fluid can have a larger mass density at a lower depth than higher up; this is because of the pressure gradient over depth due to gravity. For such a system as a whole, the assumption of additivity no longer holds (Landberg et al., 1978). A REW (or any i-zone or Element for that matter) is effectively a large-scale system within a gravitational field. As such, it may be considered as a system featuring microstructure. Eringen and Suhubi (1964) have studied such systems and have suggested to include various moments to account for the effect of such microstructure. With the aim to address effects of gravity, we include an additional extensive property in the list of internal energy dependencies (42). For this purpose we first recall the definition of the centroid position of a phase with respect to a reference point $\mathbf{x}_0$:

$$
\mathbf{x}_\alpha^i - \mathbf{x}_0 = \frac{1}{\rho_\alpha^i V_\alpha^i} \frac{1}{2\Delta t} \int_{t-\Delta t}^{t+\Delta t} \int_{V_\alpha^i} \rho (\mathbf{x} - \mathbf{x}_0) \, dV d\tau
$$

(43)

Then we introduce the specific moment of mass denoted as $\mathbf{J}_\alpha^i$, effectively a moment of volume with dimension $[L^4]$:

$$
\mathbf{J}_\alpha^i = (\mathbf{x} - \mathbf{x}_0) V_\alpha^i
$$

(44)

The moment $\mathbf{J}_\alpha^i$ is a vectorial property characterizing the phase on the basis of its spatial mass distribution with respect to a reference point. The differential $d\mathbf{J}_\alpha^i$ represents the moment change by moving the ensemble of phase particles along a distance $d\mathbf{x}$. The property is extensive and directly proportional to the volume of the system. An infinitesimal work dW exerted on the system by the gravitational force can be written as the inner product of $d\mathbf{J}_\alpha^i$ with $\mathbf{g}$, i.e. $dW = \rho_\alpha^i \mathbf{g} \cdot d\mathbf{J}_\alpha^i$. Here, $\rho_\alpha^i \mathbf{g}$ $[ML^{-2}T^{-2}]$ is the volume-specific gravity, an intensive parameter conjugate (Callen, 1985) of the extensive property $\mathbf{J}_\alpha^i$. Including the work of a conservative force as a component of the megascale internal energy is analogous to considering the energy state change of a phase due to the orientation of the magnetic dipole moment of its particles in a direction parallel to an external magnetic field. The total dipole moment of a system is in that case analogous to the moment $\mathbf{J}_\alpha^i$, a generalized thermodynamic force, while the magnetic flux density assumes the same role as the gravity density $\rho_\alpha^i \mathbf{g}$. In light of this analysis, we propose the following constitutive relation for the extensive Helmholtz free energy, which is a thermodynamic potential. It was defined by Eq. (38) and introduced in the inequality (41) instead of the internal energy, to replace entropy with temperature as the independent variable:

$$
\hat{\mathcal{A}}_\alpha^i = \hat{\mathcal{A}}_\alpha^i (\theta_\alpha^i, M_\alpha^i, V_\alpha^i, \mathbf{J}_\alpha^i)
$$

(45)

All other system unknowns (that is, all mass, momentum, energy, and entropy exchange terms) are assumed to be functions of flow velocity $\mathbf{v}_\alpha^i$, as well as θ_α^i, M_α^i, V_α^i, $\mathbf{J}_\alpha^i$. A dependence of $\hat{\mathcal{A}}_\alpha^i$ on the phase velocity is ruled out a priori as it would violate the 2nd law (Eringen, 1980). The first term on the r.h.s. of (41) is expanded by applying the chain rule of differentiation to (45):

$$
\frac{d\hat{\mathcal{A}}_\alpha^i}{dt} = \frac{\partial \hat{\mathcal{A}}_\alpha^i}{\partial \theta_\alpha^i} \bigg|_{M,V,\mathbf{J}} \frac{d\theta_\alpha^i}{dt} + \frac{\partial \hat{\mathcal{A}}_\alpha^i}{\partial M_\alpha^i} \bigg|_{\theta,V,\mathbf{J}} \frac{dM_\alpha^i}{dt} + \frac{\partial \hat{\mathcal{A}}_\alpha^i}{\partial V_\alpha^i} \bigg|_{\theta,M,\mathbf{J}} \frac{dV_\alpha^i}{dt}
$$

$$
+ \frac{\partial \hat{\mathcal{A}}_\alpha^i}{\partial \mathbf{J}_\alpha^i} \bigg|_{\theta,M,V} \cdot \frac{d\mathbf{J}_\alpha^i}{dt}
$$

(46)

To simplify the notation we introduce a series of symbols for the conditional partial derivatives, so that (46) can be written as:

$$\frac{d\hat{\mathcal{A}}_\alpha^i}{dt} = \partial_\theta \hat{\mathcal{A}}_\alpha^i \frac{d\theta_\alpha^i}{dt} + \partial_M \hat{\mathcal{A}}_\alpha^i \frac{dM_\alpha^i}{dt} + \partial_V \hat{\mathcal{A}}_\alpha^i \frac{dV_\alpha^i}{dt} + \partial_J \hat{\mathcal{A}}_\alpha^i \cdot \frac{d\mathbf{J}_\alpha^i}{dt} \qquad (47)$$

The term dM_α^i/dt is replaced using the mass conservation Eq. (5) and, as common in thermodynamics, we assume that the entropy fluxes are only due to thermal energy exchange (for reference see Eringen (1980)), eliminating these from the entropy inequality:

$$F_\alpha^{ij} = \frac{Q_\alpha^{ij}}{\theta_\alpha^i} \qquad (48)$$

$$F_{\alpha\beta}^i = \frac{Q_{\alpha\beta}^i}{\theta_\alpha^i} \qquad (49)$$

Substitution of (47)–(49) into the inequality (41) and application of the jump conditions (23) and (24) for mass yields:

$$\Lambda = - \sum_{K,I,i,\alpha} \left(\partial_\theta \hat{\mathcal{A}}_\alpha^i + \hat{\eta}_\alpha^i \right) \frac{d\theta_\alpha^i}{dt} - \sum_{K,I,i,\alpha} \partial_V \hat{\mathcal{A}}_\alpha^i \frac{dV_\alpha^i}{dt} - \sum_{K,I,i,\alpha} \partial_J \hat{\mathcal{A}}_\alpha^i \cdot \frac{d\mathbf{J}_\alpha^i}{dt}$$

$$- \sum_{K,I,i,\alpha} \left[\sum_{j \neq i} \mathbf{T}_\alpha^{ij} + \sum_{\beta \neq \alpha} \mathbf{T}_{\alpha\beta}^i \right] \cdot \mathbf{v}_{\alpha,o}^i$$

$$+ \sum_{K,I,i,\alpha} \sum_{j \neq i} e_\alpha^{ij} \left[\partial_M \hat{\mathcal{A}}_\alpha^j - \partial_M \hat{\mathcal{A}}_\alpha^i + \frac{(v_{\alpha,o}^j)^2}{2} - \frac{(v_{\alpha,o}^i)^2}{2} \right]$$

$$+ \sum_{K,I,i,\alpha} \sum_{\beta \neq \alpha} e_{\alpha\beta}^i \left[\partial_M \hat{\mathcal{A}}_\beta^i - \partial_M \hat{\mathcal{A}}_\alpha^i + \frac{(v_{\beta,o}^i)^2}{2} - \frac{(v_{\alpha,o}^i)^2}{2} \right]$$

$$+ \sum_{K,I,i,\alpha} \sum_{j \neq i} \frac{\theta_\alpha^{j,i}}{\theta_\alpha^i} Q_\alpha^{ij} - \sum_{K,I,i,\alpha} \sum_{\beta \neq \alpha} \frac{\theta_{\beta,\alpha}^i}{\theta_\alpha^i} Q_{\alpha\beta}^i \geq 0 \qquad (50)$$

with $\mathbf{v}_{\alpha,o}^i = \mathbf{v}_\alpha^i - \mathbf{v}_o$ the relative velocity of the phase with respect to the velocity $\mathbf{v}_o$ of the reference frame in Fig. 1, to express the total entropy production Λ independently of a potentially moving observer. As a next step the term $d\mathbf{J}_\alpha^i/dt$ is expanded by applying the following equation:

$$\frac{d\mathbf{J}_\alpha^i}{dt} = (\mathbf{x}_\alpha^i - \mathbf{x}_o) \frac{dV_\alpha^i}{dt} + (\mathbf{v}_\alpha^i - \mathbf{v}_o) V_\alpha^i \qquad (51)$$

where $\mathbf{x}_\alpha^i$ has been defined via Eq. (43). The proof of this equality is provided in Appendix A. Eq. (51) is substituted back into the inequality (50) and terms are collected. By applying the mass conservation Eq. (5) to eliminate the rate of change of volume, the inequality can be cast into the following form:

$$\Lambda = - \sum_{K,I,i,\alpha} \left(\partial_\theta \hat{\mathcal{A}}_\alpha^i + \hat{\eta}_\alpha^i \right) \frac{d\theta_\alpha^i}{dt} + \sum_{K,I,i,\alpha} \left[\partial_V \hat{\mathcal{A}}_\alpha^i + \partial_J \hat{\mathcal{A}}_\alpha^i (\mathbf{x}_\alpha^i - \mathbf{x}_o) \right] \frac{d\rho_\alpha^i}{dt}$$

$$- \sum_{K,I,i,\alpha} \left[\sum_{j \neq i} \mathbf{T}_\alpha^{ij} + \sum_{\beta \neq \alpha} \mathbf{T}_{\alpha\beta}^i + \partial_J \hat{\mathcal{A}}_\alpha^i V_\alpha^i \right] \cdot \mathbf{v}_{\alpha,o}^i$$

$$+ \sum_{K,I,i,\alpha} \sum_{j \neq i} e_\alpha^{ij} \left[\partial_V \hat{\mathcal{A}}_\alpha^{j,i} + \partial_J \hat{\mathcal{A}}_\alpha^{j,i} + \partial_M \hat{\mathcal{A}}_\alpha^{j,i} + \frac{(v_{\alpha,o}^j)^2}{2} - \frac{(v_{\alpha,o}^i)^2}{2} \right]$$

$$+ \sum_{K,I,i,\alpha} \sum_{\beta \neq \alpha} e_{\alpha\beta}^i \left[\partial_V \hat{\mathcal{A}}_{\beta,\alpha}^i + \partial_J \hat{\mathcal{A}}_{\beta,\alpha}^i + \partial_M \hat{\mathcal{A}}_{\beta,\alpha}^i \right.$$

$$\left. + \frac{(v_{\beta,o}^i)^2}{2} - \frac{(v_{\alpha,o}^i)^2}{2} \right]$$

$$+ \sum_{K,I,i,\alpha} \sum_{j \neq i} \frac{\theta_\alpha^{j,i}}{\theta_\alpha^i} Q_\alpha^{ij} - \sum_{K,I,i,\alpha} \sum_{\beta \neq \alpha} \frac{\theta_{\beta,\alpha}^i}{\theta_\alpha^i} Q_{\alpha\beta}^i \geq 0 \qquad (52)$$

This expression constitutes the megascopic (or REW-scale) Clausius–Duhem inequality for a watershed, which can be used as a framework to verify the thermodynamic consistency of constitutive equations in continuum mechanics (Coleman and Noll, 1963).

8. Equilibrium analysis

The entropy inequality (52) needs to be analysed in a situation of thermodynamic equilibrium. Equilibrium is reached when velocities of various phases are zero, the volumes are no longer subject to expansion or contraction, the system is isothermal at a reference temperature, and mass exchanges are zero. This means that at thermodynamic equilibrium the following set of variables vanishes:

$$\mathbf{Z}_\Lambda = \left(e_\alpha^{ij}, e_{\alpha\beta}^i, \mathbf{v}_{\alpha,o}^i, \theta_\alpha^{i,j}, \theta_{\alpha,\beta}^i, \frac{d\theta_\alpha^i}{dt}, \frac{d\rho_\alpha^i}{dt} \right) = \mathbf{0} \qquad (53)$$

Closer examination of (52) reveals that the net entropy production is zero at equilibrium. As Λ cannot be negative, it reaches its absolute minimum at equilibrium. There are two necessary and sufficient conditions for Λ to be at its absolute minimum: *i)* the first derivative of Λ with respect to $\mathbf{Z}_\Lambda$ must be zero:

$$\frac{\partial \Lambda}{\partial \mathbf{Z}_\Lambda} \bigg|_{\mathbf{Z}_\Lambda = 0} = 0 \qquad (54)$$

and *ii)* the Hessian matrix of the associated quadratic form

$$\left| \frac{\partial^2 \Lambda}{\partial^2 \mathbf{Z}_\Lambda} \right| \qquad (55)$$

must be positive semi-definite. Application of (54) shows that the first term between brackets in the inequality (52) yields an identity between entropy and partial derivative of the Helmholtz free energy with respect to temperature:

$$\frac{\partial \hat{\mathcal{A}}_\alpha^i}{\partial \theta_\alpha^i} = \partial_\theta \hat{\mathcal{A}}_\alpha^i = -\hat{\eta}_\alpha^i \qquad (56)$$

This is a relationship of classical thermodynamics (Callen, 1985). For the second term in brackets, the following relationship holds at equilibrium:

$$\left[\partial_V \hat{\mathcal{A}}_\alpha^i + \partial_J \hat{\mathcal{A}}_\alpha^i \cdot (\mathbf{x}_\alpha^i - \mathbf{x}_o) \right] = 0 \qquad (57)$$

We also recall that the partial derivative of the Helmholtz free energy with respect to volume equals the pressure:

$$\partial_V \hat{\mathcal{A}}_\alpha^i = p_\alpha^i \qquad (58)$$

Also, on the basis of the dependency of the free energy on $\mathbf{J}_\alpha^i$, the partial derivative with respect to $\mathbf{J}_\alpha^i$ must equate the product of mass density and gravity vector, $\rho_\alpha^i \mathbf{g}$, an intrinsic thermodynamic property of the phase defined in analogy to magnetic systems, as explained in Section 7:

$$\partial_J \hat{\mathcal{A}}_\alpha^i = -\rho_\alpha^i \mathbf{g} \qquad (59)$$

The negative sign indicates that the free energy $\hat{\mathcal{A}}_\alpha^i$ increases by displacing the centre of mass of the phase against the orientation of the conservative field $\mathbf{g}$. In association with (57) and in view of the fact that $\mathbf{g} = -g \mathbf{e}_z$, the latter two relationships indicate that the average phase pressure at equilibrium is as expected, equal to the hydrostatic pressure:

$$p_\alpha^i = \rho_\alpha^i g (z_\alpha^i - z_o) \qquad (60)$$

with $z_\alpha^i = \mathbf{x}_\alpha^i \cdot \mathbf{e}_z$ the vertical position of the phase centroid and $z_o = \mathbf{x}_o \cdot \mathbf{e}_z$ is a reference datum.

Next, we analyse the third term in (52). At equilibrium, when all relative velocities are zero, the stress tensor in the megascopic momentum exchange terms $\mathbf{T}_\alpha^{ij}$ and $\mathbf{T}_{\alpha\beta}^i$ reduces to $\mathbf{t} = p_\alpha^i \mathbf{I}$, where

p_α^i is the average phase pressure. The sum of all terms between square brackets must therefore satisfy the relation:

$$\sum_{j\neq i} p_\alpha^i \, \mathbf{A}_\alpha^{ij} + \sum_{\beta\neq\alpha} p_\alpha^i \, \mathbf{S}_{\alpha\beta}^i = \mathbf{g}\, \rho_\alpha^i V_\alpha^i \tag{61}$$

where $\mathbf{A}_\alpha^{ij}$ and $\mathbf{S}_{\alpha\beta}^i$ are areal vectors. Eq. (61) states that at equilibrium the weight of the phase must be balanced by the pressure forces acting on the phase boundaries. Finally, the last four terms in the inequality are all zero at equilibrium due to absence of mass fluxes and the isothermal state of the system, at which no thermal fluxes are admissible.

9. Near-equilibrium analysis

Under non-equilibrium conditions, yet close to thermodynamic equilibrium, closure expressions for mass, momentum and thermal exchange terms need to be sought, which respect the entropy inequality and ensure for condition (55) to be met. This can be achieved by expanding the various exchange terms to the first or higher order terms around equilibrium.

Linearization of mass exchange terms: Under non-equilibrium conditions, the mass exchange terms become non-zero and the system is non-isothermal, thus we need to examine the fourth and fifth term in (52). First we expand the second term in (52) by exploiting the mass balance Eq. (5) with the aim to eliminate dV_α^i/dt. We substitute into (52) and collect the mass exchange terms to obtain:

$$\Lambda = -\sum_{K,I,i,\alpha} \left(\partial_\theta \hat{\mathcal{A}}_\alpha^i + \hat{\eta}_\alpha^i\right)\frac{d\theta_\alpha^i}{dt} - \sum_{K,I,i,\alpha}\left[\frac{p_\alpha^i}{\rho_\alpha^i} + g(z_\alpha^i - z_o)\right]V_\alpha^i \, \frac{d\rho_\alpha^i}{dt}$$

$$-\sum_{K,I,i,\alpha}\left[\sum_{j\neq i}\mathbf{T}_\alpha^{ij} + \sum_{\beta\neq\alpha}\mathbf{T}_{\alpha\beta}^i - \mathbf{g}\,\rho_\alpha^i V_\alpha^i\right]\cdot\mathbf{v}_{\alpha,o}^i$$

$$+\sum_{K,I,i,\alpha}\sum_{j\neq i}e_\alpha^{ij}\left[\frac{p_\alpha^j}{\rho_\alpha^j} - \frac{p_\alpha^i}{\rho_\alpha^i} + gz_\alpha^{j,i} + \mu_\alpha^{j,i} + \frac{(v_{\alpha,o}^j)^2}{2} - \frac{(v_{\alpha,o}^i)^2}{2}\right]$$

$$+\sum_{K,I,i,\alpha}\sum_{\beta\neq\alpha}e_{\alpha\beta}^i\left[\frac{p_\beta^i}{\rho_\beta^i} - \frac{p_\alpha^i}{\rho_\alpha^i} + gz_{\beta,\alpha}^i + \mu_{\beta,\alpha}^i\right.$$

$$\left.+\frac{(v_{\beta,o}^i)^2}{2} - \frac{(v_{\alpha,o}^i)^2}{2}\right]$$

$$+\sum_{K,I,i,\alpha}\sum_{j\neq i}\frac{\theta_\alpha^{j,i}}{\theta_\alpha^i}Q_\alpha^{ij} - \sum_{K,I,i,\alpha}\sum_{\beta\neq\alpha}\frac{\theta_{\beta,\alpha}^i}{\theta_\alpha^i}Q_{\alpha\beta}^i \geq 0 \tag{62}$$

where $\mu_\alpha^{j,i}$ and $\mu_{\beta,\alpha}^i$ express the differences in chemical potentials (or molar Gibbs free energies) of the phases across the respective interfaces. We recall that in classical thermodynamics the chemical potential is defined as $\mu_\alpha^i = \partial\hat{\mathcal{A}}_\alpha^i / \partial M_\alpha^i|_{\theta,V,\mathbf{J}}$ in (46). The quantities $z_\alpha^{j,i}$ and $z_{\beta,\alpha}^i$ are the differences of the centroid elevation of the phase relative to those in adjacent zones or phases. In summary, under non-equilibrium conditions, mass exchanges between phases and zones are driven by differences in total piezometric heads $p_\alpha^i/\rho_\alpha^i + g(z_\alpha^i - z_o)$, chemical potentials, and kinetic energy across interfaces. We note that under non-equilibrium conditions, when mass exchanges, phase motion and compression/decompression occur, z_α^i varies in time, and the pressure is as a result non-hydrostatic. By looking at the multipliers of the mass exchange terms, it is natural for those to be approximated at the first-order through linearisation in terms of the thermodynamic forces driving the exchange:

$$e_\alpha^{ij} = B^{ij}\left[\frac{p_\alpha^j}{\rho_\alpha^j} - \frac{p_\alpha^i}{\rho_\alpha^i} + gz_\alpha^{j,i} + \mu_\alpha^{j,i} + \frac{(v_{\alpha,o}^j)^2}{2} - \frac{(v_{\alpha,o}^i)^2}{2}\right] \tag{63}$$

$$e_{\alpha\beta}^i = B_{\alpha\beta}\left[\frac{p_\beta^i}{\rho_\beta^i} - \frac{p_\alpha^i}{\rho_\alpha^i} + gz_{\beta,\alpha}^i + \mu_{\beta,\alpha}^i + \frac{(v_{\beta,o}^i)^2}{2} - \frac{(v_{\alpha,o}^i)^2}{2}\right] \tag{64}$$

where the linearisation coefficients B^{ij} and $B_{\alpha\beta}$ need to be positive and can depend non-linearly on independent system variables such as saturation, mass density, velocity or temperature.

Closure of force terms: Under non-equilibrium conditions we can approximate the deviatoric part of the stress tensor acting on the respective interfaces at the second-order by expanding around the hydrostatic equilibrium pressure (61) in terms of the phase velocity $\mathbf{v}_\alpha^i$:

$$\sum_{j\neq i}\mathbf{T}_\alpha^{ij} + \sum_{\beta\neq\alpha}\mathbf{T}_{\alpha\beta}^i = \mathbf{g}\,\rho_\alpha^i V_\alpha^i + \mathbf{M}_\alpha^i\cdot\mathbf{v}_\alpha^i + \mathbf{R}_\alpha^i\cdot\mathbf{v}_\alpha^i\,|\mathbf{v}_\alpha^i| \tag{65}$$

The tensors $\mathbf{M}_\alpha^i$ and $\mathbf{R}_\alpha^i$ relate to first- and second-order flow resistivities, which can be non-linear functions of the remaining independent variables such as saturation, temperature etc.:

$$\mathbf{M}_\alpha^i = \mathbf{M}_\alpha^i(s_\alpha^i, \theta_\alpha^i, \dots.) \tag{66}$$

The inclusion of the second-order term may be required to accommodate situations, in which there is a clearly non-linear dependence of the resistance on the velocity, such as for overland and/or channel flow. For subsurface flows a linear approximation may suffice, as enshrined by Darcy's law (Hassanizadeh and Gray, 1980).

Linearization of thermal energy exchanges: Under non-isothermal conditions, the thermal energy fluxes can be linearised in terms of temperature differences across the phase boundaries:

$$Q_\alpha^{ij} = K^{ij}\,\theta_\alpha^{j,i} \tag{67}$$

$$Q_{\alpha\beta}^i = K_{\alpha\beta}\,\theta_{\beta,\alpha}^i \tag{68}$$

The linearisation coefficients K^{ij} and $K_{\alpha\beta}$ are known as thermal conductivities which can also depend on remaining system state variables.

By inserting the expanded exchange terms into (62), it is easy to prove that r.h.s. terms 3 through 7 are always non-negative, while the non-negativity of the 1st term is ensured by equality (56), which is valid also under non-equilibrium conditions. The 2nd term is only relevant for compressible fluids; to ensure non-negativity outside equilibrium, the pressure must adjust in a situation of density variations to changes of z_α^i, such that the expression between brackets remains always zero, as $d\rho_\alpha^i/dt$ can assume arbitrarily large positive or negative values. The substitution of the linearised terms (63)–(68) and the quadratic term (65) into the balance equations for mass (5), momentum (15) and thermal energy (19), leads to a set of fully parametrised and thermodynamically consistent megascopic equations.

10. Geometrical relationships

The proposed equation system includes for each Element 7 zones, two of which contain 3 phases (*u* and *f*-zone), other two have 2 phases (*s* and *p*-zone) and the remaining three include only a single phase (*o*, *c*, and *r*-zone). It is also assumed that the solid matrix of the subsurface flow zones as well as snow and ice are immobile, and that all solid phases, except snow/ice, do not change phase, thus are not subject to either deformation or solution. This is equivalent to stating:

$$\mathbf{v}_m^u = \mathbf{v}_m^s = \mathbf{v}_m^p = \mathbf{v}_m^f = \mathbf{0} \tag{69}$$

$$e_{mg}^u = e_{mw}^u = e_{mw}^s = e_{mw}^p = 0 \tag{70}$$

We continue studying only the motion of the fluid phases and consider solid phases only for mass and thermal energy balance purposes. As a result, we obtain a system of 35 independent equations

consisting of 9 mass, 9 (vectorial) momentum and 13 thermal energy balance equations as well as the ideal gas law for the u and the f zone air pressure, in 35 unknowns:

$$(p_g^u, p_g^f, \rho_g^u, \rho_g^f, s_w^u, s_w^f, V^y, V^s, V^o, V^c, V^r, V^p, V^f, \mathbf{v}_w^u, \mathbf{v}_g^u, \mathbf{v}_w^s, \tag{71}$$
$$\mathbf{v}^o, \mathbf{v}^c, \mathbf{v}^r, \mathbf{v}_w^p, \mathbf{v}_w^f, \mathbf{v}_g^f, \theta_g^u, \theta_w^u, \theta_m^u, \theta_w^s, \theta_m^s, \theta^o, \theta^c, \theta^r, \theta_w^p, \theta_m^p,$$
$$\theta_g^f, \theta_w^f, \theta_m^f)$$

The system of equations is in principle fully determined. We note however that in most cases it is not practical to calculate the zone volume V^i, but it is desirable to evaluate a conjugate property such as the flow depth y^i or the channel cross sectional area, as indicated in Table 4. As a result 7 additional geometrical unknowns are considered, which we use to derive the desired property from the volume V^i:

$$(\Sigma^u, \Sigma^s, \Sigma^c, \Sigma^o, \Sigma^p, \Sigma^f, l^r) \tag{72}$$

The quantities Σ^i are defined as the horizontal projections of the areas covered by the respective i-zone, while l^r is the length of the channel reach in the Ith Element and Kth REW. These 7 unknowns require the introduction of additional geometrical relationships for each Element. First we assume that l^r is constant and the number of unknowns drops to 6. Secondly we can state that the sum of the unsaturated and the saturated zone volume adds up to the (constant) total volume of the entire subsurface zone in an Element:

$$V^u + V^s = y^u \Sigma^u + y^s \Sigma^s = const \tag{73}$$

Similarly, the sum of the area projections of the concentrated and the saturated overland flow add up to a constant value, equal to the known area projection Σ^I of the Element onto the horizontal plane (for reference see Fig. 4):

$$\Sigma^c + \Sigma^o = \Sigma^I \tag{74}$$

After the Hortonian overland flow sheet, which is ephemeral, has vanished, Σ^c becomes zero and the entire unsaturated land surface becomes exposed to the atmosphere, in which case:

$$\Sigma^u + \Sigma^o = \Sigma^I \tag{75}$$

The snow pack is supposed to be spread over the Element surface, thus $\Sigma^f = \Sigma^I$, while the saturated subsurface storm flow zone is assumed to underlie the Hortonian overland flow zone within the Element, thus $\Sigma^p = \Sigma^c$. Situations, in which no saturated subsurface storm flow zone underlies the Hortonian overland flow zone ($\Sigma^p = 0, \Sigma^c \neq 0$) or vice versa ($\Sigma^p \neq 0, \Sigma^c = 0$) are also possible. Finally, the surface area projection of the saturated overland flow zone is expressed as a function of the saturated zone volume:

$$\Sigma^o = \Sigma^o(V^s) = \Sigma^o(y^s \Sigma^s) \tag{76}$$

If we assume that the saturated zone underlies the entire Element, then $\Sigma^s = \Sigma^I$ for each Element and (76) reduces to the relationship:

$$\Sigma^o = \Sigma^o(y^s) \tag{77}$$

The outlined geometric relationships determine the remaining 6 unknowns and allow resolving the entire system of equations in terms of hydrologically meaningful quantities. Preliminary attempts to apply these relationships in modelling real-world systems have been proposed in Reggiani et al. (2000,2014a,b) and Reggiani and Rientjes (2010).

11. Examples

To show how two familiar governing equations can be obtained from the previous equations, we consider the momentum balance equation along the main axes of a Cartesian reference system depicted in Fig. 1. These are identified by three unit vectors, $\mathbf{e}_x$, $\mathbf{e}_y$
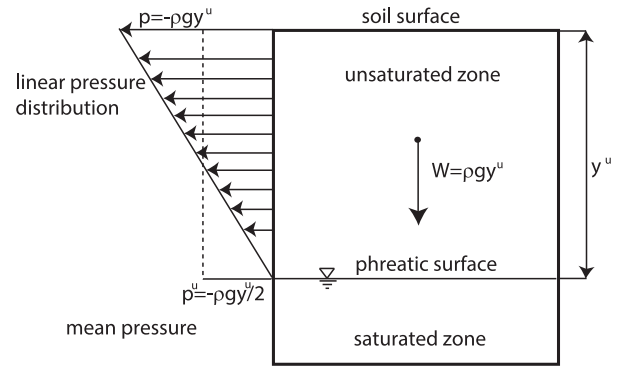

Fig. 5. Pressure distribution and forces acting in the unsaturated zone Element.

and $\mathbf{e}_z$, pointing along the two horizontal axes and the vertical axis of the reference system. The vectorial momentum equation can be projected by taking the internal product with a unit vector. This is carried out next under the assumption of constant mass density to obtain i) Darcy's law for the vertical movement through the unsaturated zone and ii) the non-linear reservoir equation for channel routing.

Unsaturated zone Darcy's law: Darcy's law governing the vertical motion through the unsaturated zone is obtained from (15) by neglecting the inertial term and retaining zone boundary forces $\mathbf{T}_w^{uc}$ and $\mathbf{T}_w^{us}$. The vertical projections of all other boundary forces, $\mathbf{T}_w^{uu}$, as well as $\mathbf{T}_{wg}^u$ and $\mathbf{T}_{wm}^u$, acting on the phase interfaces, either cancel or are negligible:

$$\left[\mathbf{T}_w^{uc} + \mathbf{T}_w^{us} - \rho \, \mathbf{g} V_w^i\right] \cdot \mathbf{e}_z = \mathbf{M} \cdot \mathbf{v}_w^u \cdot \mathbf{e}_z \tag{78}$$

At equilibrium only pressure forces act to balance the weight of pore water:

$$[\, p_w^u A_w^{uc} \mathbf{n}^{uc} + p_w^u A_w^{us} \mathbf{n}^{us}] \cdot \mathbf{I} \cdot \mathbf{e}_z = \rho \, s_w^u \epsilon^u V^u \mathbf{g} \cdot \mathbf{e}_z \tag{79}$$

with A_w^{uc} the upper zone boundary, i.e. the soil surface, and A_w^{us} the water table, while p_w^u is the average water pressure of the u-zone. After taking the inner products and assuming that the zone is prismatic, $A_w^{uc} = A_w^{us}$, and we obtain:

$$2 \, p_w^u s_w^u \epsilon^u \Sigma^u = -\rho \, g s_w^u \epsilon^u y^u \Sigma^u \tag{80}$$

In this equation $s_w^u \epsilon^u \Sigma^u$ is to be interpreted as the horizontal projection of the water portion $A_w^{uc} \mathbf{n}^{uc} \cdot \mathbf{e}_z$ of the soil surface or the horizontal projection of the water table $A_w^{us} \mathbf{n}^{us} \cdot \mathbf{e}_z$, while V^u has been written as product indicated in Table 4. The average u-zone water pressure is thus:

$$p_w^u = -\frac{1}{2} \, \rho \, g y^u \tag{81}$$

This implies that in presence of an atmospheric air pressure p_a, for the megascopic equilibrium forces acting on the upper and lower zone boundaries to balance the weight $\rho \, g \epsilon^u s^u V^u$ of water, the vertical pressure distribution across the unsaturated zone must be hydrostatic, with a minimum value of $p_w^{uc} = -\rho \, g y^u + p_a$ at the soil surface A_w^{uc}, and a value of $p_w^{us} = p_a$ at the water table A_w^{us}. The average (negative) capillary pressure in the u-zone becomes $p_{cap}^u = p_a - p_w^u = -\rho \, g y^u /2$ (for reference see Fig. 5). Under non-equilibrium conditions the pressure at the upper boundary A_w^{uc} is given by an expression different from hydrostatic:

$$p_a - p_w^{uc} = p_{cap}^{uc} \, (s_w^u, y^u, \lambda, s_0, p_0) \tag{82}$$

where λ is a soil-dependent pressure-saturation scaling parameter, s_0 and p_0 are soil-dependent maximum soil saturation and the air entry pressure. These can be found via a Brooks and Corey (1964) or, in slightly modified form, through the Van Genuchten (1980) water retention curve. Similar considerations apply to the

unsaturated hydraulic conductivity. In summary, the megascopic Darcy' law valid for unsaturated vertical flow becomes:

$$v_z^u = -\bar{M}^{-1}[(p_a - p_w^{uc}) - \rho g y^u]s_w^u \epsilon^u \Sigma^u \tag{83}$$

with $\bar{M}^{-1}$ the scalar hydraulic conductivity, which is a function of soil saturation.

Non-linear reservoir equation: As a second example we derive the non-linear reservoir equations, which are used for overland flow and channel routing on steep slopes with typically kinematic behaviour, where backwater effects are unimportant. First we take the mass balance (5) for a channel reach with zero upstream inflow and downstream outflow e^r:

$$\rho \frac{d V^r}{dt} = e^r \tag{84}$$

Additional indices I and K referring to Elements and REWs have been omitted for notational simplicity. The momentum balance equation for a reach segment is obtained from (15) by projecting the parametrized vectorial equation in a direction parallel to the channel axis. The result is a scalar equation with a second-order resistance term:

$$\rho V^r \frac{dv^r}{dt} = \rho g V^r S_0 - R v^r |v^r| \tag{85}$$

with S_0 the reach bed slope, which can vary between Elements and REWs. We note that the pressure terms acting at the channel head sections and the first-order friction term in (65) are neglected in line with the classical kinematic wave model assumptions. On the other hand Manning's formula states:

$$v^r = \frac{1}{n} R_h^{2/3} S_0^{1/2} \tag{86}$$

with $R_h = m^r/P_w$ the hydraulic radius of the reach and P_w the wetted perimeter, properties which are in principle all variable between Elements and REWs. Substitution of v^r from (86) into (85) under assumption of steady state (i.e. $dv^r/dt = 0$), yields an expression for the second-order resistivity parameter R $[ML^{-1}]$ in terms of hydrodynamic properties of the reach:

$$R = \rho g n^2 V^r R_h^{-4/3} \tag{87}$$

Next we multiply both sides in (86) by the average reach cross-section area m^r and rearrange conveniently. By noting that one can approximate $e^r \approx \rho v^r m^r$ we substitute back into (84) to obtain the non-linear reservoir equation:

$$\frac{dV^r}{dt} = \frac{S_0^{1/2}}{n} \frac{P_w}{(P_w \, l^r)^{5/3}} (V^r)^{5/3} \tag{88}$$

This lumped model has been derived independently by integrating the kinematic wave model equations over a channel segment Liu and Todini (2004) and can be solved either numerically or integrated analytically after approximating $(V^r)^{5/3}$ through a second-order Taylor series polynomial Reggiani et al. (2014a).

12. Discussion and conclusions

This paper is an extension of the original work by the authors (Reggiani et al., 1999, 1998). The concept of Representative Elementary Watersheds introduced earlier has been revised and extended to include novel features. First we recall that an REW effectively is a "mixture" of zero-dimensional contiguous phases filling separate portions of space. Following the definitions by Gray et al. (1993) we adopt a "megascopic" perspective of the system. Through spatial and temporal averaging and zero-dimensional representation, the state variables and physical properties for an entity remain only time-dependent. This leads to a system of coupled ordinary differential governing equations (ODEs), which are computationally cheaper to solve than conventional distributed models

(Abbott et al., 1986a,b). This can be a major advantage in probabilistic applications that require multiple consecutive model executions, as in real-time or long-term climate forecasting.

To extend earlier work, we now accommodate a more flexible modelling of watersheds by allowing for a subdivision of an REW into Elements, for which we provide conservation equations and constitutive relationships. The sub-division of REWs can be dictated by either topographic features or geological formations, by landcover or landuse patterns, or by anthropic factors such as urbanization, all of which influence flow behaviour.

In zero-dimensional (megascopic) systems exposed to gravity, the free energy potential of a phase, an REW or Element, depends on standard extensive properties (mass, volume and entropy) as well as on a density-specific moment of mass. The dependency of the energy potential on the moment of mass is necessary, because the vertical pressure distribution due to gravity within a particular phase needs to be correctly addressed in the zero-dimensional system components. Accounting for this additional dependency of the energy potential results in a natural, thermodynamically admissible inclusion of gravity in the constitutive theory, which is congruent with the physical behaviour described in Section 2. Mass exchanges between phases, elements and REWs must always be driven by total energy differences. Without the use of such generalized potential, this behaviour can only be represented on the basis of ad-hoc assumptions (Reggiani et al., 1999).

Typical dynamic effects encountered in natural systems, such as hysteresis between filling and emptying of channel reach segments during a transiting flood wave, or between wetting and drying of soils (Davies and Beven, 2015; Martina et al., 2011) can also be addressed in the zero-dimensional upscaling approach. As an example, we name the recent analysis and application of the variable parameter Muskingum method for channel routing (Reggiani et al., 2014b), which consists of zero-dimensional reach segments arranged in series. Through non-linear closure of in- and outgoing mass fluxes at the head sections of a reach, the dynamic effects in a looped stage-discharge relationship can be captured, while fully conserving mass and momentum. It constitutes an example of a solution of the closure problem $Q(t) = H(S, R, \Delta t) \cdot A$, highlighted by Beven (2006).

Another important aspect is the linearisation of the entropy inequality in proximity of the equilibrium state in a multidimensional state space. A relevant point that needs further clarification is the meaning of thermodynamic equilibrium for a watershed. While this concept is well-defined for classical thermodynamic systems it needs to be defined properly in our case. We envisage hydrological equilibrium as a system state akin to a hypothetical isothermal wetland with standing ponded water. If flow is induced by energy gradients, the system departs from the state of equilibrium. The departure increases as flow accelerates. Acceleration eventually induces turbulence in surface and channel flow, while groundwater movement supposedly remains laminar. Also in the case of turbulent flows, the velocity is represented through averages, such as the mean velocity over a cross section, and can be treated in analogy to laminar flow. Turbulent shear stresses are closed through a second-order dependency on mean flow velocity, in agreement with the second law of thermodynamics (Ozawa et al., 2001).

In this work, we also have relaxed some fundamental assumptions underlying the development of constitutive relationships in earlier work (Reggiani et al., 1999), such as the prior assumption of incompressible phases and an isothermal state. This is necessary for future applications, where compressible phases like water vapour and air, non-isothermal processes in snow and ice ablation or landsurface-atmosphere interaction need to be modelled. Here, we allow for compressible, non-isothermal phases as well as for exchange of thermal energy among system components.

Finally, we have shown that the equations are directly applicable for watershed modelling by presenting two examples. We obtain thermodynamically consistent REW-scale versions of Darcy's law for the unsaturated subsurface flow and the non-linear reservoir equation for modelling channel and overland flow processes.

Acknowledgement

Appendix A. Proof

To prove relationship (51), the time derivative is applied to the definition of $\mathbf{J}_\alpha^i$ given by Eq. (44):

$$\frac{d\mathbf{J}_\alpha^i}{dt} = \frac{dV_\alpha^i}{dt}(\mathbf{x}_\alpha^i - \mathbf{x}_0) + V_\alpha^i \frac{d}{dt}(\mathbf{x}_\alpha^i - \mathbf{x}_0) \tag{A.1}$$

To complete the proof we need to verify that:

$$\frac{d}{dt}(\mathbf{x}_\alpha^i - \mathbf{x}_0) = \mathbf{v}_\alpha^i - \mathbf{v}_0 \tag{A.2}$$

where $\mathbf{v}_\alpha^i$ is given by Eq. (10) while $\mathbf{v}_0$ is a potentially non-zero velocity of the reference framework. It is easy to show that (A.2) always holds for an incompressible phase. Here we demonstrate that it holds for compressible phases as well. From the definition of the centre of mass position, $\mathbf{x}_\alpha^i - \mathbf{x}_0$, it follows that:

$$(\rho_\alpha^i V_\alpha^i)\frac{d}{dt}(\mathbf{x}_\alpha^i - \mathbf{x}_0)$$

$$= (\rho_\alpha^i V_\alpha^i)\frac{d}{dt}\left[\frac{1}{\rho_\alpha^i V_\alpha^i}\frac{1}{2\Delta t}\int_{t-\Delta t}^{t+\Delta t}\int_{V_\alpha^i}\rho\,(\mathbf{x} - \mathbf{x}_0)\,dV d\tau\right]$$

$$= \frac{1}{2\Delta t}\frac{d}{dt}\int_{t-\Delta t}^{t+\Delta t}\int_{V_\alpha^i}\rho\,(\mathbf{x} - \mathbf{x}_0)\,dV d\tau - \frac{d(\rho_\alpha^i V_\alpha^i)}{dt}(\mathbf{x}_\alpha^i - \mathbf{x}_0) \tag{A.3}$$

The term $d(\mathbf{x}_\alpha^i - \mathbf{x}_0)/dt$ is given by the rate of change of total moment minus a term depending on the rate of change of mass. We recast the integral in (A.3) by noting that $\mathbf{x}$ can be split into the sum of the centroid position, $\mathbf{x}_\alpha^i$, and a deviation $\mathbf{x}'$:

$$\mathbf{x} = \mathbf{x}' + \mathbf{x}_\alpha^i \tag{A.4}$$

We substitute and then expand the integral to obtain:

$$\frac{1}{2\Delta t}\frac{d}{dt}\int_{t-\Delta t}^{t+\Delta t}\int_{V_\alpha^i}\rho\,(\mathbf{x} - \mathbf{x}_0)\,dV d\tau$$

$$= \frac{d(\rho_\alpha^i V_\alpha^i)}{dt}(\mathbf{x}_\alpha^i - \mathbf{x}_0) + \frac{1}{2\Delta t}\frac{d}{dt}\int_{t-\Delta t}^{t+\Delta t}\int_{V_\alpha^i}\rho\,\mathbf{x}'\,dV d\tau \tag{A.5}$$

Now we apply the mean value theorem to evaluate the function at a time point $c(t) \in (t - \Delta t, t + \Delta t)$, which depends on the centre t of the time averaging window and always exists for a function that is continuous in $[t - \Delta t, t + \Delta t]$ and differentiable in $(t - \Delta t, t + \Delta t)$, such that:

$$\frac{1}{2\Delta t}\frac{d}{dt}\int_{t-\Delta t}^{t+\Delta t}\int_{V_\alpha^i}\rho\,\mathbf{x}'\,dV d\tau = \frac{1}{2\Delta t}\frac{d}{dt}\mathbf{F}[c(t)] \tag{A.6}$$

where $\mathbf{F}[c(t)]$ is evaluated at $\tau = c(t)$ and is defined as:

$$\mathbf{F}[c(t)] = 2\Delta t\int_{V_\alpha^i(c(t))}\rho[\mathbf{x}, c(t)]\,\mathbf{x}'[\mathbf{x}, c(t)]\,dV \tag{A.7}$$

and $\mathbf{F}[c(t)]/2\Delta t$ is the moving average of the volume integral over the sliding window $(t - \Delta t, t + \Delta t)$. We combine (A.3), (A.5) and (A.6) and use Reynolds transport theorem to convert $d\mathbf{F}[c(t)]/dt$ in

(A.6) into a surface integral:

$$(\rho_\alpha^i V_\alpha^i)\frac{d}{dt}(\mathbf{x}_\alpha^i - \mathbf{x}_0) = \frac{d\mathbf{F}[c(t)]}{dt}$$

$$= \frac{d}{dt}\int_{V_\alpha^i(c(t))}\rho[\mathbf{x}, c(t)]\,\mathbf{x}'[\mathbf{x}, c(t)]\,dV$$

$$= \int_{V_\alpha^i(c(t))}\mathbf{x}'\left.\frac{\partial\rho}{\partial t}\right|_x dV + \int_{\Omega_\alpha^i(c(t))}\rho\,\mathbf{x}'\,(\mathbf{v} - \mathbf{v}_0)\cdot\mathbf{n}^*\,d\Omega \tag{A.8}$$

where Ω_α^i is the boundary of V_α^i with unit normal $\mathbf{n}^*$ pointing outward, $\mathbf{v}_0$ is the velocity of a moving reference frame and $|_x$ indicates that the partial derivative is evaluated with the spatial coordinate held constant (i.e. $\Rightarrow \partial\mathbf{x}'/\partial t|_x = 0$). The last surface integral on the r.h.s. can be converted into a volume integral by applying Gauss theorem:

$$\int_{\Omega_\alpha^i(c(t))}\rho\,\mathbf{x}'\,(\mathbf{v} - \mathbf{v}_0)\cdot\mathbf{n}^*\,d\Omega = \int_{V_\alpha^i(c(t))}\nabla\cdot[\rho\,\mathbf{x}'\,(\mathbf{v} - \mathbf{v}_0)]\,dV \tag{A.9}$$

The divergence operator is expanded further:

$$\int_{V_\alpha^i(c(t))}\nabla\cdot[\rho\,\mathbf{x}'\,(\mathbf{v} - \mathbf{v}_0)]\,dV$$

$$= \int_{V_\alpha^i(c(t))}\rho\,(\mathbf{v} - \mathbf{v}_0)\,dV + \int_{V_\alpha^i(c(t))}\mathbf{x}'\nabla\cdot[\rho\,(\mathbf{v} - \mathbf{v}_0)]\,dV$$

$$= \rho_\alpha^i V_\alpha^i\,(\mathbf{v}_\alpha^i - \mathbf{v}_0) - \int_{V_\alpha^i(c(t))}\mathbf{x}'\left.\frac{\partial\rho}{\partial t}\right|_x dV \tag{A.10}$$

whereby the microscale mass conservation equation has been used to substitute the divergence operator (see Eq. (9.3) in Gray et al. (1993)). Finally we combine (A.8) with (A.10) and obtain equality (A.2), proving its validity also for the compressible case.

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