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A unifying framework for watershed thermodynamics: balance equations for mass, momentum, energy and entropy, and the second law of thermodynamics

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The basic aim of this paper is to formulate rigorous conservation equations for mass, momentum, energy and entropy for a watershed organized around the channel network. The approach adopted is based on the subdivision of the whole watershed into smaller discrete units, called representative elementary watersheds (REW), and the formulation of conservation equations for these REWs. The REW as a spatial domain is divided into five different subregions: (1) unsaturated zone; (2) saturated zone; (3) concentrated overland flow; (4) saturated overland flow; and (5) channel reach. These subregions all occupy separate volumina. Within the REW, the subregions interact with each other, with the atmosphere on top and with the groundwater or impermeable strata at the bottom, and are characterized by typical flow time scales.

The balance equations are derived for water, solid and air phases in the unsaturated zone, water and solid phases in the saturated zone and only the water phase in the two overland flow zones and the channel. In this way REW-scale balance equations, and respective exchange terms for mass, momentum, energy and entropy between neighbouring subregions and phases, are obtained. Averaging of the balance equations over time allows to keep the theory general such that the hydrologic system can be studied over a range of time scales. Finally, the entropy inequality for the entire watershed as an ensemble of subregions is derived as constraint-type relationship for the development of constitutive relationships, which are necessary for the closure of the problem. The exploitation of the second law and the derivation of constitutive equations for specific types of watersheds will be the subject of a subsequent paper.

Keywords: representative elementary watersheds, subregions, balance equations.

NOMENCLATURE

- A mantle surface with horizontal normal delimiting the REW externally
- b external supply of entropy, $[L^2/T^{3o}]$
- C^A external boundary curve of the REW
- C^r length of the channel, $[L]$
- e mass exchange per unit surface area, $[M/TL^2]$
- E internal energy per unit mass, $[L^2/T^2]$
- f external supply term for ψ
- F entropy exchange per unit surface area projection, $[M/T^{3o}]$
- $\boldsymbol{g}$ 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 $[M/T^{3o}]$
- L rate of net production of entropy, $[M/T^{3o}L]$
- 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
- $\mathbf{n}^{jA}$ unit normal pointing from the j-subregion outward with respect to the mantle surface
- $\mathbf{n}^j$ unit normal pointing from the j-subregion into the atmosphere or into the ground

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n^{ji} unit normal pointing from the j-subregion into the i-subregion
n$^{\alpha\beta}$ unit normal pointing from the α-phase into the β-phase
N global outward normal to the mantle surface
N$_k$ number of REWs surrounding the kth REW
q heat vector, $[M/T^3]$
Q energy exchange per unit surface area projection, $[M/T^3]$
s the saturation function, [—]
S the time-invariant surface area of the REW, $[L^2]$
t microscopic stress tensor, $[M/T^2L]$
t time, $[T]$
T momentum exchange per unit surface area projection, $[M/T^2L]$
v velocity vector of the bulk phases, $[L/T]$
V the global reference volume, $[L^3]$
V^j volume occupied by the entire j-subregion, $[L^3]$
w velocity vector for phase and subregion boundaries, $[L/T]$
y^j average thickness of the i-subregion along the vertical, $[L]$

Greek symbols

γ	the phase distribution function
Δ	indicates an increment in time
ϵ^j	porosity of the j-subregion soil matrix,
ϵ^j_α	j-subregion α-phase volume fraction,
η	the entropy per unit mass, $[L^2/T^{2o}]$
θ	the temperature
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, $[L^2]$
Σ^j	horizontal projection of the surface area covered by the j-subregions, $[L^2]$
ψ	a generic thermodynamic property
ω^j	The time-averaged surface area fraction occupied by the j-subregion, [—]

Subscripts and superscripts

i	superscript indicating a subregion, the atmosphere or the underlying deep soil
j	superscript which indicates the various subregions within a REW
k	subscript which indicates the various REWs within the watershed
l	index which indicates the various REWs surrounding the kth REW
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

Special notation

$\sum_{\beta\neq\alpha}$	summation over all phases except the α-phase
$\sum_{l}$	summation over all N_k REWs surrounding the kth REW
$\langle\rangle^j_\alpha$	average operator defined for the u- and the s-subregion α-phases
$\langle\rangle^j$	average operator defined for the o-, c- and the r-subregions
$^{-j}_{\alpha}$	mass-weighted average operator defined for the u- and the s-subregion α-phases
$^{-j}$	mass-weighted average operator defined for the o-, c- and the r-subregions
$^{\sim j}_{\alpha}$	deviation from the mass-weighted average within the u- and s-subregion α-phase
$^{\sim j}$	deviation from the mass-weighted average within the o-, c- and r-subregion
$^{j}_{\alpha}$	denotes a quantity within the u- and the s-subregion α-phase
^{j}	denotes a quantity within the o-, c- and the r-subregion
$^{j}_{\alpha}$	property for the u- and the s-subregion α-phase defined on a per unit area basis
^{j}	property for the o-, c- and the r-subregions defined on a per unit area basis
$\{\}_k$, $[]_k$, $()_k$, $\|_k$	denotes a quantity or expression relative to the kth REW

Particular combinations of super- and subscripts for the terms e, I, **T**, Q and F; u- and s-subregion:

$^{jA}_{\alpha}$	exchange from j-subregion α-phase across the mantle
$^{jA}_{\alpha,l}$	exchange from the j-subregion α-phase across the lth mantle segment
$^{jA}_{\alpha,\text{ext}}$	exchange from the j-subregion α-phase across the ext. watershed boundary
$^{j\,\text{top}}_{\alpha}$	exchange between α-phase and atmosphere
$^{j\,\text{bot}}_{\alpha}$	exchange between α-phase and underlying strata
$^{j}_{\alpha\beta}$	intra-subregion exchange between α-phase and β-phase
$^{ji}_{\alpha}$	inter-subregion exchange between j-subregion and i-subregion

c-, o- and r-subregions

^{jA}	exchange from j-subregion across the mantle
$^{jA}_{l}$	exchange from the j-subregion across the lth mantle segment
$^{jA}_{\text{ext}}$	exchange from the i-subregion across the external watershed boundary
^{ji}	inter-subregion exchange between j-subregion and i-subregion
$^{j\,\text{top}}$	exchange between j-subregion and atmosphere

1 INTRODUCTION

The study of the response of a watershed to atmospheric forcing is of critical importance to applied hydrology and remains a major challenge to hydrological research. Among the current generation of hydrological models we can distinguish two major categories which are called, in short, physically-based and conceptual models. Freeze[13] introduced the first of a generation of distributed physically-based watershed models founded on rigorous numerical solution of partial differential equations (PDE) governing flow through porous media (Richards' equation, Darcy's law), overland flow (kinematic wave equation) and channel flow (Saint–Venant equations). These equations also form the basis of other distributed watershed models such as the Système Hydrologique Européen (SHE) model described by Abbott *et al*.[1,2] Others to follow similar approaches were Binley and Beven[8] and Woolhiser *et al*.[35]

There has been considerable discussion regarding the advantages and disadvantages of such distributed physically-based models by Beven,[5] Bathurst[4] and O'Connell and Todini.[31] While these models have the advantage that they explicitly consider conservation of both mass and momentum (but expressed at the point or REV scale), their main shortcomings are the following: first, the numerical solution of the governing equations is a computationally overwhelming task, except for very small watersheds; the models also require detailed information about soil properties and geometry, which is not available for most real world watersheds. Even if the necessary input information was available, detailed results provided by distributed models are not needed for most practical purposes. Secondly, since these distributed watershed models are usually over parameterized, infinite combinations of parameter values can yield the same result, leading to a large parameter estimation problem (see e.g. Beven[6]).

Parallel to these distributed models, a series of lumped conceptual watershed models have been developed. These do not take into account the detailed geometry of the system and the small-scale variabilities, rather they consider the watershed as an ensemble of interconnected conceptual storages. Examples are the Nash cascade[30] or the Stanford Watershed model[29]. The disadvantages of many of the current lumped conceptual models are listed as follows. First, they are based only on the mass balance and do not explicitly consider any balance of forces or energy. Secondly, the models use *ad hoc* parameterizations *in lieu* of derived constitutive relationships for the various mass exchange terms. As a result, the parameters lack physical meaning.

At present, there does not exist an accepted general framework for describing the response of a hydrologic system which is applicable directly at the spatial scale of a watershed and takes into account explicitly balances of mass, momentum and energy (i.e. without having to use point-scale equations) while serving as a guideline for model development, field data collection and design applications. The aim of the present work is to attempt to fill this gap by formulating an approach which aims to combine the advantages of the distributed and lumped approaches.

The procedure we present here has been motivated by the averaging approach for multi-phase flow in porous media, pioneered by Hassanizadeh and Gray, and published in a series of papers, e.g.[17–22]. the physics of porous media flow must consider fluid motions through an interconnected system of soil pores, and the physical and chemical interactions between the fluid phase, the gaseous phase and the solid phase representing the soil matrix. However, the details of the complex arrangement of soil grains and the geometry of the pore spaces are unknown, and generally unknowable. Also, predictions of flow through porous media are required, not at the scale of the pore (the microscale), but at scales much larger than the pore (the macroscale). For these reasons, Hassanizadeh and Gray[17–19] sought to develop a theory of porous media flow which is expressed in terms of balance equations for mass, momentum, energy, and entropy at the macroscale. At this scale the porous medium is then treated as a continuum. The averaging procedure has been successfully applied by Hassanizadeh and Gray to derive Darcy's law for single-phase flow[19] and for two-phase flow,[22] and the Fickian dispersion equation for multi-component saturated flow.[20] The averaging approach has also been referred to as 'hybrid mixture theory' by Achanta *et al*.[3] in a work regarding flow in clayey materials.

In the present paper, the averaging approach will be employed in order to derive watershed scale balance equations for mass, momentum, energy and entropy. The whole watershed is divided into smaller entities over which the conservation equations are averaged in space and time. The distributed description of the watershed is replaced by an ensemble of interconnected discrete points. The ensemble of points has subsequently to be assembled by imposing appropriate jump conditions for the transfer of mass, momentum, energy and entropy across the various boundaries of the system. Furthermore, the large range of time scales typical for the various flows within a watershed requires additional averaging of the equations in time.

The averaging approach presented here has never been pursued before in watershed hydrology. However, recently, Duffy[10] presented a hillslope model based on the global mass balance equations, formulated for a two-state (unsaturated and saturated store) system. Constitutive relationships were postulated for the mass exchange between the stores, and with the surroundings. The parameter calibration of the model was performed by using a numerical Richards' equation solver. In our approach constitutive equations will be derived with the aid of the second law of thermodynamics, explicitly taking into account the equations for conservation of momentum and energy.

As a concluding remark we emphasize that theories for flow and transport are usually derived in a separate manner for the saturated and the unsaturated zones, for the overland and the channel flows by writing flow equations for the various zones. The equations are later hooked together during modelling. In the present approach we obtain balance and constitutive equations for these zones within the framework of a single procedure by ensuring the compatibility of all constitutive relationships for the entire watershed with the second law of thermodynamics. We believe this will lead to more consistent models in the future.

2 OUTLINE OF THE UNIFYING FRAMEWORK

The purpose of the present work is to propose a general framework which can be recast to address specific problems among the entire spectrum of hydrologic situations. In a wider sense, a watershed constitutes an open thermodynamic system, where mass, momentum, energy and entropy are permanently exchanged with the atmosphere or surrounding regions. These exchanges are driven by mass input from the atmosphere during storms, by extraction of mass towards the atmosphere during interstorm periods, and by transfer of mass towards adjacent regions. Atmospheric forcing (rainfall, solar radiation) and gravity (run-off) play fundamental roles in these processes. It is important for the theoretical framework to be expandable, in order to handle other problems related to the hydrologic cycle. In this context one could think of terrestrial water and energy balances, transport of sediments and pollutants, land erosion, salinity problems and land–atmosphere interaction at the watershed scale, relevant for the implementation of global climate models (GCM). Even though the present work is restricted to the surface and subsurface zones and does not explicitly consider the presence of vegetation or the transport of sediments or chemical species, future inclusion of these issues is compatible with the developments pursued here.

As pointed out by Gupta and Waymire,[16] the most striking feature observed in a watershed is the interconnected system of hillslopes organized around the river network. Hillslopes convert a fraction of the rainfall into run-off while the remainder becomes part of the soil moisture storage. Run-off generated from hillslopes is transferred by the channel network towards a common point, called the watershed outlet. A part of the soil moisture held within the hillslopes percolates down to recharge the regional groundwater reservoir. The remaining part is removed as evapotranspiration (bare soil evaporation and plant transpiration), providing for a return of water vapour and latent thermal energy back into the atmosphere and so contributing to the maintenance of the global hydrologic cycle. In a simplistic view one might envisage the watershed as a large funnel which in turn is composed of a number of smaller funnels. Each one of these smaller funnels can be decomposed again into even smaller ones and so forth. In pursuing an averaging approach, these sub-watershed scale funnels form natural averaging regions.

With these considerations in mind, in our work the whole watershed is divided into a number of smaller sub-watersheds which we refer to as representative elementary watersheds (REWs). The averaging of the conservation equations is carried out over the REW. Clearly, the system contains a large amount of spatial variability at scales smaller than the REW. By choosing the REW as the fundamental unit of discretization in space, we incorporate the effects of such small-scale variabilities in an effective manner and contemplate variability only between various REWs.

Another important issue to be considered in the context of such a framework is the range of time scales characterizing the hydrology of a watershed. It is clear that hydrological processes associated with the two fundamental components of a watershed, i.e. hillslopes and the channel network, typically operate over vastly different time scales. This is due to the variety of media in which water movement takes place. Even within a single hillslope there are different time scales associated with the various pathways the water takes to travel through the hillslope and exit the system. These include surface (overland flow) and subsurface pathways (unsaturated and saturated zone, regional groundwater system), and evapotranspiration. In Table 1 typical velocities associated with the various flow pathways are listed. The problem of dealing with a large range of time scales becomes especially apparent when balance equations used to describe the different hydrological processes (e.g. infiltration, surface run-off, channel flow, evapotranspiration) need to be combined together. Moreover, for the same watershed, one may be interested in short-term or long-term events. The time scale associated with the response of a watershed to a single rainfall event is much smaller than that of seasonal events (e.g. snowmelt, droughts) or long-term water yield. This implies that in the first case some processes occurring at very low velocities (e.g. filtration through the unsaturated zone) become unimportant with respect to the faster processes (e.g. surface run-off or flow in the channel network) which determine the behaviour of the system within the time frame of the event. In the second and third cases, fluctuations of the dynamic variables due to forcing events which are short with respect to the time scale under consideration can be averaged out without obscuring the long-term variations.

Vis à vis the wide range of time scales at which the system can operate, we propose to average the governing equations over a time interval which is chosen according to the particular application. The 'rapid' fluctuations of the system at time scales smaller than the averaging interval will not be accounted for and are filtered out. This approach is widely

Table 1. Comparison of the flow pathways (based on data by Dunne, 1978[11])

Flow type	Temporal scale	Velocity [m s^{-1}]
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

used in the study of turbulent flows, where time averages of the fluctuating variables (e.g. pressure, density, velocity) are performed over a characteristic time interval. The averaging procedure developed here results in a set of conservation equations of mass, momentum, energy and entropy for each subregion of the REW. The conservation equations will have the following general form:

$$\frac{d\psi}{dt} = \sum_i e_i^\psi + R + G \qquad (1)$$

where ψ can be such properties as soil water saturation, water mass density, flow velocity, water energy, water depth etc., e_i^ψ is the exchange of mass, force, or heat among various phases and subregions, R is a possible external supply, and G accounts for internal generation. The forms of these general balance equations are of course well known. The difficulty lies in the determination of relationships between the exchange terms and ψ-quantities. The approach presented here provides a framework for developing such relationships based on physical laws, as will be shown in a sequel paper. Substitution of these relationships in the balance laws will result in equations governing various flow mechanisms. Relationships analogous to well-known formulas such as Darcy's law or Chezy's formula are expected to be obtained at the watershed scale as results of our approach.

3 THE REPRESENTATIVE ELEMENTARY WATERSHED (REW)

The present section is dedicated to the definition of the fundamental discretization units, the REWs, for which conservation equations will be derived. Since we want to study hydrological processes in watersheds, we need to define the averaging volume in such a way as to preserve an autonomous, functional watershed unit. In this respect it is natural to refer to the drainage network as the basic organizing structure for subdividing the watershed into smaller entities. This can be achieved by first disaggregating the channel network into single reaches which connect two internal nodes of the network (classified as higher-order streams by the Horton-Strahler network ordering system[27,33]). In the case of source streams (first-order streams according to the Horton–Strahler system), they will have an isolated endpoint at their upper end and merge with another stream at a node further downstream. One can associate with every reach a certain patch of land-surface, which drains water towards it. This patch of land-surface is delimited externally by ridges and thus remains a separate sub-watershed in itself. We call the sub-watershed a representative elementary watershed (REW) for the following reasons:

1. The REW includes all the basic functional components of a watershed (channels, hillslopes) and constitutes, therefore, a single functional unit, which is representative of other sub-entities of the entire watershed due to its repetitive character.
2. The REW is the smallest, and therefore the most elementary unit, into which we discretize the watershed for a given scale of interest.

The REW can also be assumed as being self-similar to the larger basin to which it is subordinated, in the sense that it reveals similar structural patterns independently of the scale of observation. This assumed self-similarity implies that certain aspects of composition and structure are invariant with respect to the change in spatial scale. This property can, for example, be recognized most clearly in the channel network. With increasing magnification, new branches and treelike structures can be recognized, which are reminiscent of the same geometrical patterns manifested at a larger scale. These fine network branches cover even single hillslope faces in the form of rills and gullies and are, therefore, part of the whole drainage network. The intrinsic self-similarity of the network and the related scaling properties are the subject of extensive, ongoing research. Ample discussion of the topic and respective references to related literature can be found in a recent treatise by Rodriguez-Iturbe and Rinaldo.[32]

It is relevant in this context to note that our definition of the fundamental unit, the REW, contemplates the self-similar structure of the system and preserves the geometric invariance with respect to change of spatial scale. This suggests that, for a given watershed, the REW can be chosen, for example, to be the entire watershed, or any smaller sub-watershed. The smallest admissible size of the REW is one in which the subregions, to be defined later in Section 4, are still identifiable. Furthermore, the size of the REW is one in which the subregions are also dependent on the spatial and temporal resolution one wants to achieve and on the spatial and temporal detail of the available data sets.

Fig. 1(a)–(c) show examples of how a real world watershed (Sabino Canyon, Santa Catalina Mountains, SE-Arizona) can be discretized into different sized REWs. Each time, we identify a main channel reach (solid grey line) associated with the REW and a sub-REW-scale network (dashed lines). The REW boundaries are indicated with a solid black line. In the first case (Fig. 1(a)) the REW coincides with the whole watershed. There is only a single main stream and the catchment boundaries overlap with the REW boundaries. In the second and third cases (Fig. 1(b) and (c)) the watershed has been subdivided into a finite number M of smaller REWs: We decide to label the REWs with an index k, $k = 1,\ldots,M$. Some REWs have a first order channel associated with them and possess, therefore, only one outlet. Other REWs are associated with higher order streams. As a result they have an inlet as well as an outlet. It is important to note that the main channel reach in a given REW may become part of a sub-REW-scale network in a larger REW, associated with a coarser discretization of the watershed.

As mentioned earlier, every REW is lumped into a single discrete point in the process of the averaging proposed here. The original watershed will be substituted by

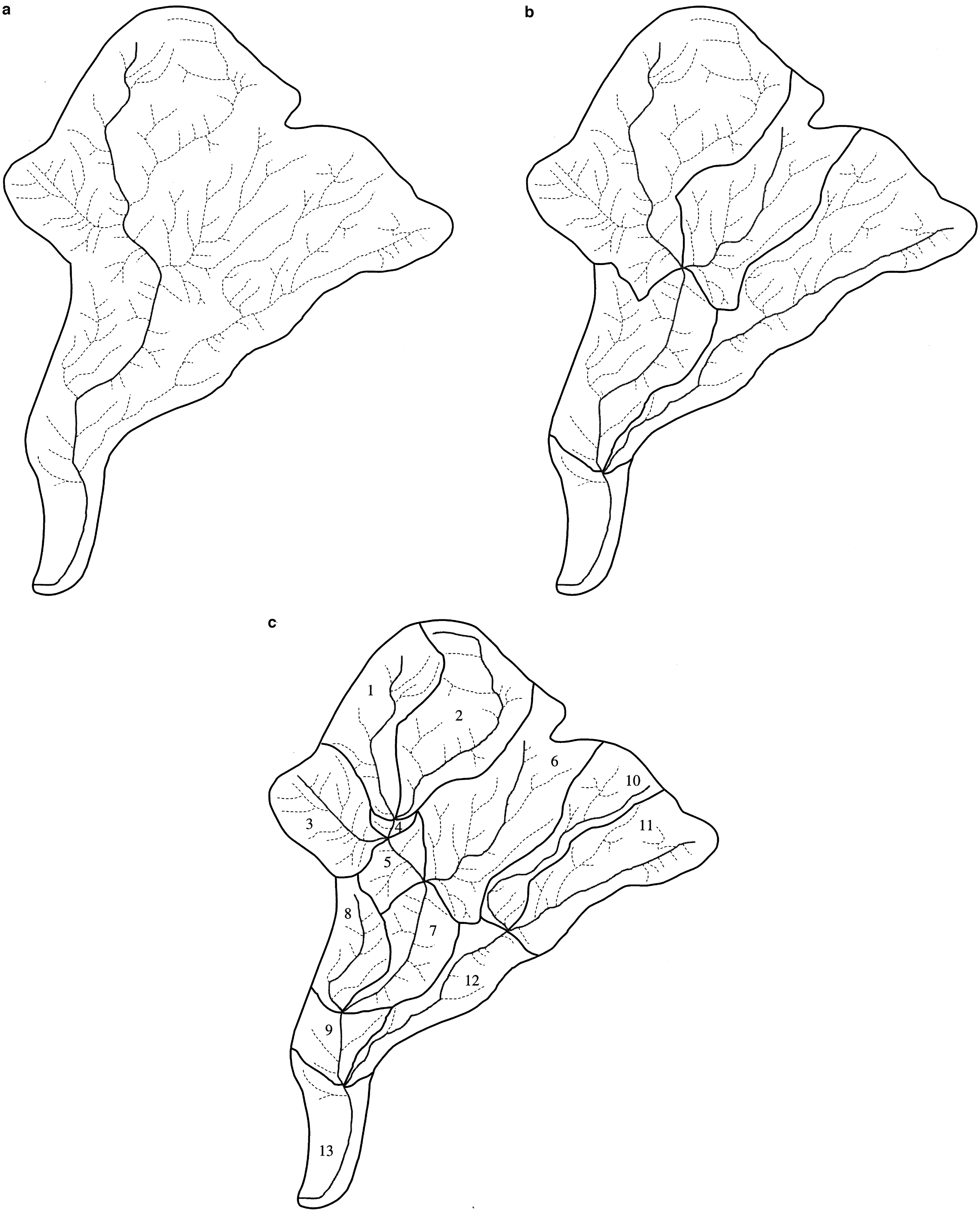

Fig. 1. (a) A real world watershed constituting a single REW (Sabino Canyon, Santa Catalina Mountains, SE-Arizona), reproduced from 36). (b) The watershed of (a) discretized into 5 REWs; and (c) the watershed of (a), discretized into 13 REWs.

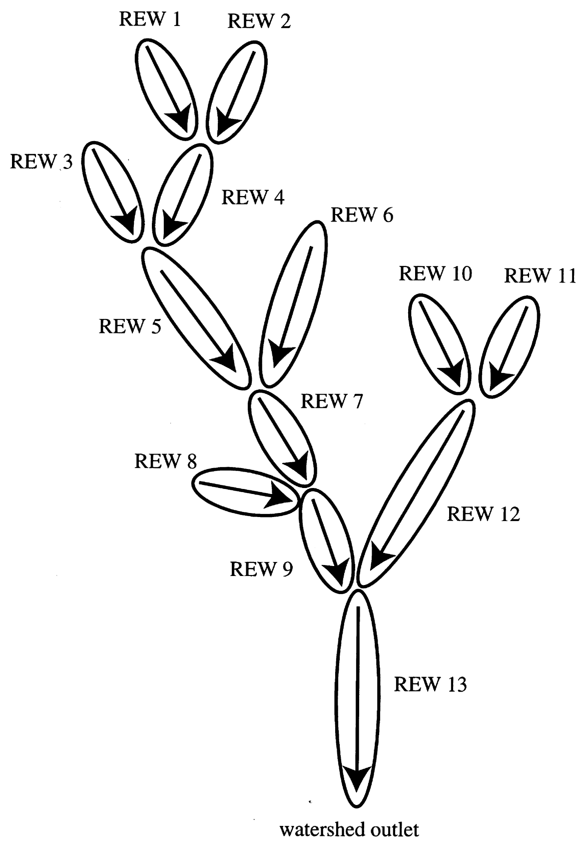

Fig. 2. Hierarchical arrangement of the 13 REWs from Fig. 1(c).

an agglomeration of M points. The points are mutually interconnected by plugging the outlet sections of two upstream REWs into the inlet of a downstream REW. In this fashion, the typical tree-like branching structure of the network is preserved. Fig. 2 shows an example of how REWs are assembled in the case of the watershed in Fig. 1(c), which has been subdivided into $M = 13$ sub-entities.

In the absence of surface erosion, the area of land covering the kth REW is considered as a time-invariant spatial domain and is denoted by S. Fig. 3 shows a 3-D view of a small watershed discretized into three REWs, two of them relative to first order streams, and one relative to a second order stream. The surface S is circumscribed by a curve labelled C^A and is considered coincident with the natural boundaries of the REW (i.e. ridges and divides). The rainfall reaching the ground within these boundaries is drained towards a common outlet located at the lowest point of C^A, or is transferred to a groundwater reservoir. Each REW communicates with neighbouring REWs through the main channel reach which crosses the boundary at the inlet and the outlet sections, and through mutual exchange of groundwater laterally. Next, a prismatic reference, volume V is associated with the REW, confined by a mantle surface A. The mantle is defined by the shape of the curve C^A and has an outward unit normal $\mathbf{N}$, which is at every point horizontal. On top the volume V is separated from the atmosphere by the surface S. At the bottom it is delimited either by the presence of impermeable strata or by some limit depth reaching into the groundwater reservoir. The limit depth can, for example, be chosen as a common datum for the ensemble of M REWs forming the watershed. The kth REW has a number of N_k neighbouring REWs and can have a part of its mantle surface A in common with the external boundary of the watershed. Therefore, the mantle surface A can be subdivided into a series of segments:

$$A = \sum_l A_l + A_{\text{ext}} \tag{2}$$

where A_l is the mantle segment forming the common boundary between the kth REW and its neighbouring REW l. The segment A_{ext} is the part of mantle, which the kth REW has in common with the external watershed boundary. For example, REW 1 in Fig. 1(c) has a mantle made up of four segments, one of which is in common with the external watershed boundary, $N_k = 3$ and l assumes the values 2, 3 and 4. We observe that A_{ext} is non-existent for REWs which have no mantle segment in common with the external boundary (e.g. REWs 4, 5 and 7 in Fig. 1(c)). The entire space outside the watershed is referred to as *external world*.

4 THE REW-SUBREGIONS

In previous sections, we emphasized that a watershed includes two basic components: the channel network and the hillslopes. Whereas observation and measurement of channel flow is relatively straightforward, there are a series of flow mechanisms occurring in the subsurface zone which are difficult to quantify. Subsurface flow together with other processes on the land surface (e.g. infiltration, evapotranspiration, depression storages, surface detention, overland flow), forms the hydrological cycle of a hillslope. Horton (see Refs. [25,28,26]) was amongst the first to try to quantify the hillslope hydrological cycle by analysing these processes on an individual basis. Horton explained the production of surface run-off by assuming that a rapidly decreasing infiltration capacity of the soil would lead to infiltration excess run-off (Hortonian overland flow) on the surface. This model has been improved through the observation by Hewlett and Hibbert[23] of saturation excess run-off (saturated overland flow) along the groundwater seepage faces in the lower parts of the hillslopes. Hewlett and Hibbert's findings have been further underpinned by extensive field investigations carried out by Dunne.[11]

The common description of hillslope hydrological processes (see e.g. Chorley[9]) assumes the presence of a saturated zone in the subsurface region, delimited by the water table. It is part of a regional groundwater which can have extensions reaching beyond the watershed boundaries while communicating with the channel network. The soil between the groundwater table and the land surface forms the unsaturated zone, where the soil matrix coexists with the water and the gaseous phase (air–vapour mixture). The subsurface

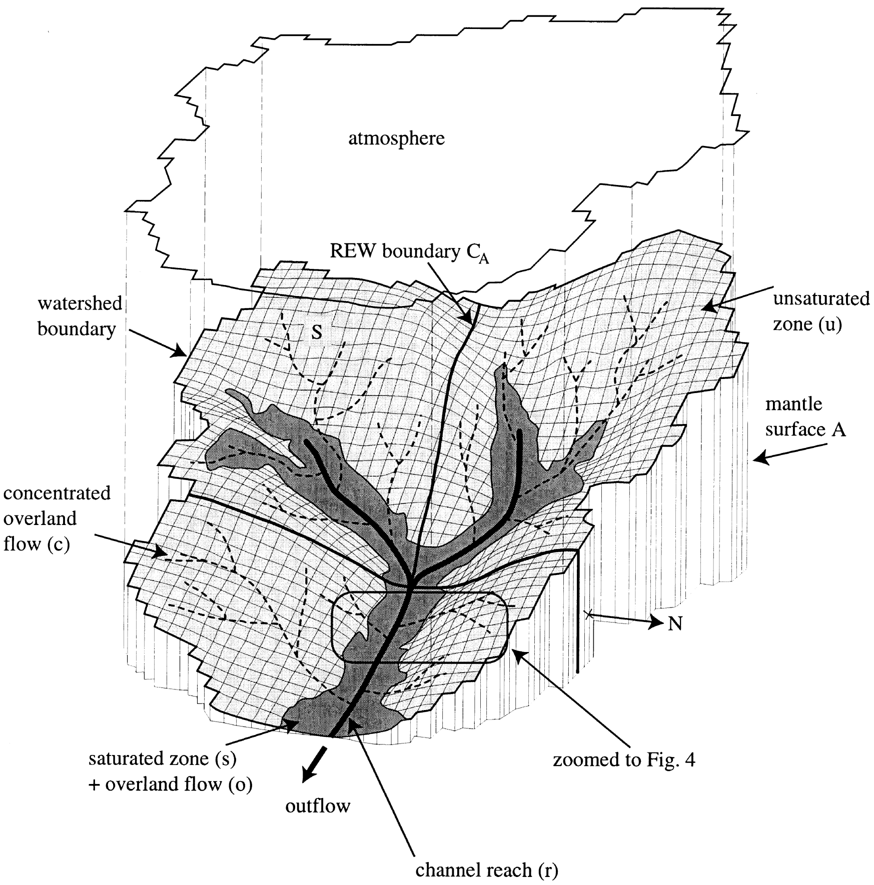

Fig. 3. Three-dimensional view of an ensemble of three REWs.

zone can be dissected by macropores and fractures, caused by discontinuities in the soil properties and by the presence of plant roots. In particular situations it is possible to observe the formation of a perched aquifer in the subsurface zone in the form of localized lenses of saturated soil. Often the water table of the perched aquifers are separated by less permeable strata from the groundwater reservoir. The water table of the groundwater reservoir or of the perched aquifers reaches the soil surface in the lower regions, at the foot of the hillslope. It generates saturated zones surrounding the channel. These zones, also called variable contributing area by Beven and Kirkby,[7] are subject to seasonal changes and can vary even at the time scale of a storm event. Rainfall reaching the ground within these saturated areas cannot infiltrate and joins the stream as saturated overland flow. In the remaining parts of the watershed, low infiltration capacities can generate Hortonian overland flow. In addition, early concentration of surface water generates a network of rills, gullies and ephemeral streams on top of the unsaturated land surface, which merge with the saturated overland flow in the zones surrounding the main channel.

Motivated by these field observations, and in order to describe various flow processes, the volume V occupied by the REW is divided into five subregions, for each of which we will derive balance equations for mass momentum, energy and entropy. The subregions are identified, based on different physical characteristics and on the various time scales typical for the flow within each zone. We emphasize that these subregions do not need to be mutually interconnected, and can also be composed of disconnected parts. The subregions will be identified with a prescript j, where j can assume the symbols u, s, o, r or c. The choice of these symbols is motivated by the names of the five subregions as described below:

The *u-subregion* is formed by the unsaturated zone. It includes those volumina of soil, water, and gas, confined at the top by the land surface and at the bottom towards the saturated zone by the water table. A typical situation is depicted in Fig. 4. Interactions of the water phase with the soil matrix and the gaseous phase at constant atmospheric pressure have also to be taken into consideration.

The *s-subregion* comprises the saturated zone and includes the volumina of soil and water underlying the unsaturated zone. In this case the water phase, in contrast to the unsaturated zone, coexists only with the solid phase. The physical upper boundary of this subregion is given by the water table. In the near-channel regions the water table reaches the soil surface, forming seepage faces, which cause saturation excess run-off. The upper boundary of the saturated zone is, in these areas, coincident with the land surface. The bottom boundary of the saturated zone is set either by a limit depth reaching into the groundwater

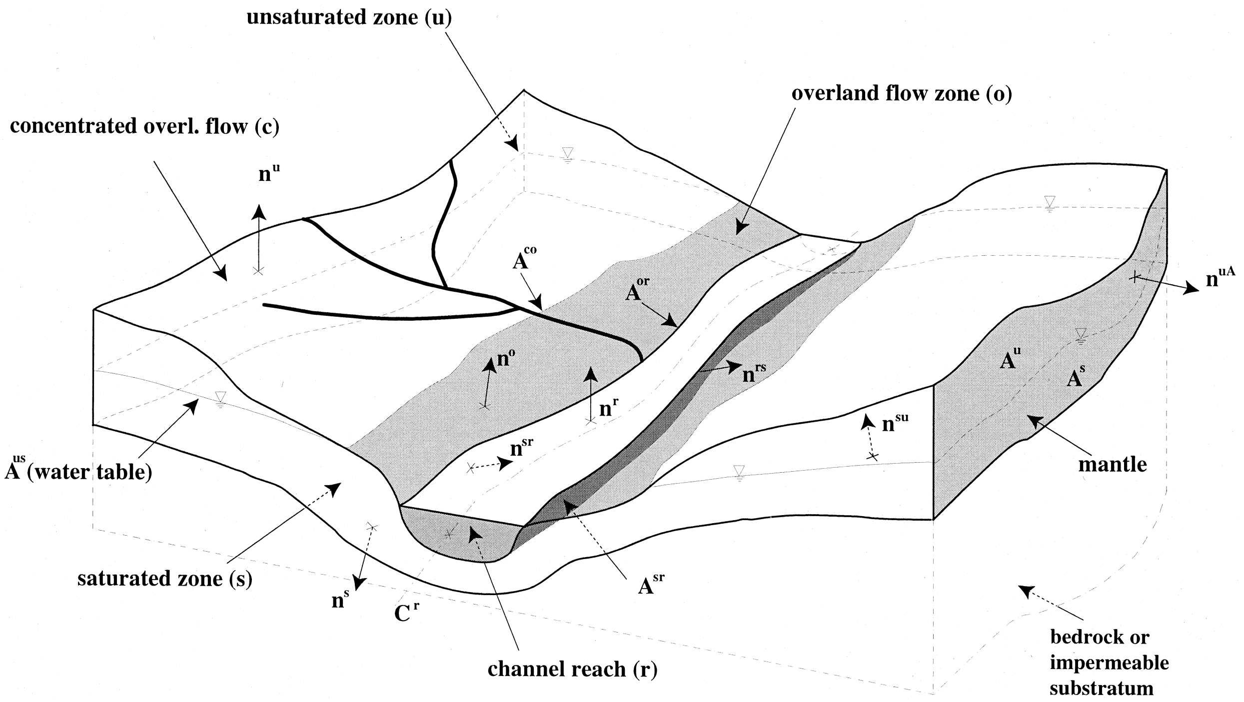

Fig. 4. Detailed view of the five subregions forming a REW.

reservoir or by the presence of impermeable strata. In the case of a bottom boundary formed by bedrock (see Fig. 4), the shape of the boundary is dictated by the natural topography of the substratum. In the case of a groundwater reservoir, the boundary can be drawn as a horizontal plane. Situations where the topography of the bedrock in combination with a horizontal plane determine the shape of the bottom boundary are also possible.

The *o-subregion* is the volume of saturated overland flow, forming on the seepage faces and within the sub-REW-scale network branches lying within the saturated portion of the land surface as depicted in Fig. 4. The extension of the o-subregion is clearly defined by the intersection curve of the water table with the land surface and by the contour curves forming the edges of the main channel reach. The saturation excess flow is fed by concentrated overland flow, return flow from the saturated zone and direct precipitation onto the saturated areas.

The *r-subregion* is the volume occupied by the main channel reach for a given REW. The channel reach is fed from the adjacent saturated overland flow zone (o-subregion) by lateral inflow and through direct rainfall from the atmosphere. Across the bed surface, the channel can exchange mass by either recharging the saturated zone or by filtration from the saturated zone towards the channel. Both phenomena depend on the regional flow regime within the saturated zone.

The *c-subregion* is the sub-REW-scale network of channels, rills, gullies, ephemeral streams and areas of Hortonian overland flow within the unsaturated portion of the land surface, collectively called concentrated overland flow. They form a volume of water, flowing towards the main channel and merging with the saturated overland flow. The introduction of this fifth zone is necessary in order to preserve the invariance of the REW with respect to spatial scaling and, therefore, to account for the self-similar nature of the system. The presence of the fifth subregion allows us to account in a lumped way for the entire sub-REW-scale network of channels and gullies as well as Hortonian overland flow.

The thermodynamic properties may be exchanged across inter-subregion boundaries (e.g. seepage areas, channel bed, channel edges) or inter-REW boundaries (mantle segments defined in eqn (2)) with neighbouring REWS. Furthermore, within the unsaturated and saturated zones, the phases exchange the properties across phase interfaces (i.e. the water–soil, water–gas and solid–gas interfaces). All these surfaces are assumed to be without inherent thermodynamic properties and, therefore, standard jump conditions apply between phases, subregions and REWs.

5 AVERAGING NOTATION AND DEFINITIONS

The derivations given here are based on the global balance laws written in terms of a generic thermodynamic property ψ at the microscale. For a continuum occupying an arbitrary volume $V*$, delimited by a boundary surface $A*$, the balance equation for ψ is stated as follows [12]:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{V*}\rho\psi \mathrm{d}V + \int_{A*}\mathbf{n}*\cdot[\rho(\mathbf{v}-\mathbf{w}*)\psi - i]\mathrm{d}A - \int_{V*}\rho f \mathrm{d}V = \int_{V*} G\mathrm{d}V \quad (3)$$

Table 2. Summary of the properties in the conservation equation

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

where $\mathbf{n}^*$ is the unit normal to A^* pointing outward, $\mathbf{v}$ is the velocity of the continuum, $\mathbf{w}^*$ is the velocity of A^*, $\mathbf{i}$ is a diffusive flux and ρ is the the mass density of the continuum. The quantities ψ, $\mathbf{i}$, f and G have to be chosen according to the type of thermodynamic property considered. For the equations of balance of mass, linear momentum, energy, and entropy, the appropriate microscopic properties are listed in Table 2. The property E is the microscopic internal energy per unit mass, $\mathbf{t}$ is the microscopic stress tensor, $\boldsymbol{g}$ is the gravity vector, $\mathbf{q}$ is the microscopic heat flux vector, h is the supply of internal energy from the outside world, η is the microscopic entropy per unit mass, $\mathbf{j}$ is the non-convective flux of entropy, b is the entropy supply from the external world and L is the entropy production within the continuum. We will refer to Table 2 throughout the whole paper for all the five subregions.

The following notational conventions will be introduced here for later use. The subregions are made up either by a single phase or constitute multi-phase systems with two (s-subregion) or three (u-subregion) coexisting phases. The REW-scale thermodynamic property intrinsic to a phase is denoted as where the superscript $j =$ u, s, c, o, r denotes the respective subregion and the Greek letter $\alpha =$ w, m, g indicates the respective phase.

A single phase is confined through boundary surfaces towards the outside world, the neighbouring subregions and the phases, which are present in the same subregion. The boundary surface, delimiting the j-subregion towards the external world on the mantle surface A, is denoted with A^{jA} the surfaces separating it from the atmosphere on top or from the underlying bedrock or the soil–groundwater system at the bottom are A^j_{top} and A^j_{bot}, and the surface forming the inter-subregion boundary between the i and the j-subregion is indicated with the symbol A^{ij} where the order of the superscripts is unimportant. Phase interfaces, on the other hand, are indicated by the symbol $S^j_{\alpha\beta}$, with $\alpha,\beta =$ w, m, g, where the superscript indicates the subregion and the Greek letters designate the two phases, which meet at the interface. Here also the order of α and β is unimportant.

Velocities of phases are indicated with the symbol $\mathbf{v}$. Velocities of boundary surfaces are denoted with $\mathbf{w}$. Thus the velocity of A^{jA} is denoted with $\mathbf{w}^{jA}$, and those of A^j_{top} A^j_{bot} and A^{ij} with w^j_{top}, w^j_{bot} and $\mathbf{w}^{ji}$, respectively. The velocity of phase interfaces is indicated with $\mathbf{w}^{\alpha\beta}$. Also in this case the order of the indices is unimportant.

Unit normal vectors to the boundary surfaces are indicated with $\mathbf{n}^{jA}$ for A^{jA}, $\mathbf{n}^j$ for A^j_{top} and A^j_{bot}, $\mathbf{n}^{ji}$ for A^{ji} and $\mathbf{n}^{\alpha\beta}$ for $S^j_{\alpha\beta}$, where the sequence of the indices is significant insofar as it indicates the direction in which the vector is pointing. The unit normal vector $\mathbf{n}^{jA}$ is always pointing outward with respect to the mantle surface A, $\mathbf{n}^{ji}$ is pointing from the j-subregion into the i-subregion, and $\mathbf{n}^{\alpha\beta}$ from the α-phase into the β-phase. The vector $\mathbf{n}^j$ points outward into the atmosphere or into the underlying layers.

In the same fashion, the sequence of the indices in the superscripts and subscripts is relevant for the REW-scale exchange terms, which will be defined in the respective appendices. So, for example, the term e^{ji}_{α} is the α-phase mass source term for the subregion indicated by the first superscript (j-subregion) through transfer from the subregion indicated by the second superscript (i-subregion). The term $e^j_{\alpha\beta}$ on the other hand, is the intra-subregion mass source term for the α-phase through mass released from the β-phase. The mass exchange across the mantle surface for the u- and the s-subregions, for example, is denoted with e^{jA}_{α}. As a consequence of eqn (2) the total mass flux can be written as a sum of fluxes across the segments forming the mantle:

$$e^{jA}_{\alpha} = \sum_{l} e^{jA}_{\alpha,l} + e^{jA}_{\alpha,\mathrm{ext}} \tag{4}$$

where the summation extends over the N_k surrounding REWs and $e^{jA}_{\alpha,\mathrm{ext}}$ is non-zero only if the REW has a mantle segment in common with the external watershed boundary. All other REW-scale exchange terms act also as source terms for the respective thermodynamic property.

In general, when we deal with the kth REW we omit the index k to keep the notation simple. If the ensemble of M REWs is considered, the terms relative to the kth REW are put between brackets, which will then carry a subscript k, e.g. $()_k$, $[]_k$, $\{\}_k$. Another possibility to indicate that a term is relative to the kth REW is given by a vertical bar carrying the subscript, e.g. $|_k$.

The various subregions are space filling and occupy volumes denoted with V^j. At the REW-scale, though, they appear as two-dimensional or one-dimensional domains. Therefore, a surface S^j is associated with the u-, s- and the o-subregions, whereas a total length C^{r} of the channel reach can be attributed to the r-subregion. The projections of the surface areas S^j onto the horizontal plane is denoted with Σ^j and the projection of the whole surface area S^j with Σ. The surface areas S^j and their projections Σ^j are allowed to expand or contract in time. The same is valid for the length C^{r} of the main channel reach. The following ratios are introduced here:

$$\omega^j = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\Sigma^j(\tau)\mathrm{d}\tau \;\; j = \mathrm{u, s, c, o} \tag{5}$$

are the time-averaged surface area fractions relative to the horizontal projections for the u-, s-, c- and the o-subregions. Next, average values are defined for the various properties involved in the balance equations. The averages are carried out over space and a characteristic time interval of length $2\Delta t$. For the unsaturated zone, saturated zone, and overland flow subregions, an average vertical depth y^j [L], is defined by:

$$y^j = \frac{1}{2\Delta t \omega^j \Sigma} \int_{t-\Delta t}^{t+\Delta t} \int_{V^j} \mathrm{d}V\mathrm{d}\tau; \; j = \mathrm{u, s, o, c} \tag{6}$$

where V^j denotes the space occupied by the j-subregion. The average mass density [M/L^3] of phase α of the j-subregion is defined by:

$$\langle\rho\rangle y^j_\alpha = \frac{1}{2\Delta t \epsilon^j_\alpha \omega^j \Sigma} \int_{t-\Delta t}^{t+\Delta t} \int_{V^j_\alpha} \rho \mathrm{d}V\mathrm{d}\tau; \; j = \mathrm{u, s, o, c} \tag{7}$$

where V^j_α and ϵ^j_α denote the space occupied by the α-phase of the j-subregion and its corresponding volume fraction, defined by

$$\epsilon^j_\alpha = \frac{1}{2\Delta t y^j \omega^j \Sigma} \int_{t-\Delta t}^{t+\Delta t} \int_{V^j} \gamma^j_\alpha \mathrm{d}V\mathrm{d}\tau; \; j = \mathrm{u, s} \tag{8}$$

It should be remembered that in the case of the overland flow and channel subregions, only water phase exists so that $\epsilon^j_\alpha = 1$. For this reason the average mass density carries only a superscript, i.e. $\langle\rho\rangle^j$, j = o, c. Next, we introduce the average porosity ϵ^j for the unsaturated zone (u-subregion). It is given by the sum of the volume fractions occupied by the water and the gas phases:

$$\epsilon^\mathrm{u} = \epsilon^\mathrm{u}_\mathrm{w} + \epsilon^\mathrm{u}_\mathrm{g} \tag{9}$$

whereas for the saturated s-subregion $\epsilon^\mathrm{s} = \epsilon^\mathrm{s}_\mathrm{w}$. In addition, a volume saturation function is introduced for the unsaturated zone:

$$s^\mathrm{u}_\alpha = \epsilon^\mathrm{u}_\alpha / \epsilon^\mathrm{u} \quad \alpha = \mathrm{w, g} \tag{10}$$

subject to the condition:

$$s^\mathrm{u}_\mathrm{w} + s^\mathrm{u}_\mathrm{g} = 1 \tag{11}$$

For the channel subregion, the average water mass density [M/L^3] is defined by

$$\langle\rho\rangle^\mathrm{r} = \frac{1}{2\Delta t m^\mathrm{r} \xi^\mathrm{r} \Sigma} \int_{t-\Delta t}^{t+\Delta t} \int_{V^\mathrm{r}} \rho \mathrm{d}V\mathrm{d}\tau \tag{12}$$

where m^r and ξ^r are the cross-sectional area [L^2] and an average length measure [L^{-1}] of the channel reach, respectively, given by:

$$m^\mathrm{r} = \frac{1}{2\Delta t \xi^\mathrm{r} \Sigma} \int_{t-\Delta t}^{t+\Delta t} \int_{V^\mathrm{r}} \mathrm{d}V\mathrm{d}\tau \tag{13}$$

and

$$\xi^\mathrm{r} = \frac{1}{2\Delta t \Sigma} \int_{t-\Delta t}^{t+\Delta t} C^\mathrm{r}(\tau)\mathrm{d}\tau \tag{14}$$

The length measure ξ^r is the time averaged length of the main channel reach per unit REW surface area projection and is defined as drainage density by Horton.[24,27] For the generic property ψ, expressed on a per unit mass basis, the average is defined through the expression

$$\bar{\psi}^j_\alpha = \frac{1}{2\Delta t \epsilon^j_\alpha y^j \langle\rho\rangle^j_\alpha \omega^j \Sigma} \int_{t-\Delta t}^{t+\Delta t} \int_{V_j} \rho\psi\gamma^j_\alpha \mathrm{d}V\mathrm{d}\tau; \; j = \mathrm{u, x, o, c} \tag{15}$$

where, once again, in the case of the c- and o-subregions only the water phase is present. This implies that $\epsilon^j_\alpha = 1$ and that the average quantity is denoted only with a superscript, i.e. $\bar{\psi}^j, j = \mathrm{o, c}$. For the channel reach, the average of the property ψ is given by:

$$\bar{\psi}^\mathrm{r} = \frac{1}{2\Delta t \langle\rho\rangle^\mathrm{r} m^\mathrm{r} \xi^\mathrm{r} \Sigma} \int_{t-\Delta t}^{t+\Delta t} \int_{V^\mathrm{r}} \rho\psi \mathrm{d}V\mathrm{d}\tau \tag{16}$$

Finally, we observe that the average of the microscopic property f, expressed on a per unit mass basis, is evaluated for the various subregions in analogy to eqns (15) and (16), whereas the average of the entropy production L is obtained in a way similar to eqns (7) and (12), respectively.

6 REW-SCALE BALANCE EQUATIONS

The formulation of global balance laws for mass, momentum, energy and entropy at the scale of the REW has been pursued in detail in the Appendices A, B, C, D, and E. In this section only the final results will be presented and the meaning of the various REW-scale terms in the equations will be explained. The groups of the four basic balance equations are different from subregion to subregion and will, therefore, be treated in separate sections. We recall that the mass, energy and entropy equations are scalar equations, whereas the momentum balance is a vectorial equation. Furthermore, the unsaturated zone (u-subregion) includes water, gas (air–vapour mixture) and soil matrix as constituent phases, whereas in the saturated zone the water phase coexists only with the soil matrix. These considerations require the derivation of separate balance equations for every single phase. In the study of watersheds only the water phase is crucial, for which the equations are reported here. We recall that the various equations listed below refer to the kth REW in an ensemble of M REWs.

6.1 Unsaturated zone (u-subregion)

6.1.1 Conservation of mass

The water mass balance equation for the unsaturated zone is derived from eqn (A19). It is reasonable to assume the complete absence of phase change phenomena between the solid phase and the remaining phases, within the aquifer (i.e. no absorption, no solid dissolution, i.e. $e^\mathrm{u}_\mathrm{sw} = e^\mathrm{u}_\mathrm{sg} = 0$). The possibility for mass exchange between water and gaseous phase within the soil pores has to be accounted for in order to describe soil water evaporation. The resultant balance equation for the water phase yields:

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho^\mathrm{u}_\mathrm{w} y^\mathrm{u} \epsilon^\mathrm{u} s^\mathrm{u}_\mathrm{w} \omega^\mathrm{u}) = \sum_l e^{\mathrm{u}A}_{\mathrm{w},l} + e^{\mathrm{u}A}_{\mathrm{w,ext}} + e^\mathrm{us}_\mathrm{w} + e^\mathrm{uc}_\mathrm{w} + e^\mathrm{u}_\mathrm{wg} \tag{17}$$

where $\rho^\mathrm{u}_\mathrm{w}$ is the average water density, y^u is the average vertical thickness of the unsaturated zone, ϵ^u is the average porosity of the soil matrix, s^u_w is the water phase saturation and ω^{u} is the horizontal fraction of watershed area covered by the unsaturated zone. The mass exchange terms represent, in order of appearance, the exchange towards the neighbouring REWs across the mantle segments, the exchange across the external watershed boundary (non-zero only for REWs which have one or more mantle segments in common with the external watershed boundary), the recharge to or the capillary rise from the saturated zone, the infiltration from the areas affected by concentrated overland flow (i.e rills, gullies or Hortonian overland flow), and the water phase evaporation or condensation within the soil pores, respectively.

6.1.2 Conservation of momentum

The next equation is given by the balance of forces acting on the water body within the unsaturated zone. As mentioned before, the equation is vectorial and is subsequently associated with a resultant direction. The momentum balance for the water phase is derived from eqn (A18) and is given in the general form by eqn (A20). Multiplication of the mass conservation eqn (A19) by the macroscopic velocity $\mathbf{v}_{\mathrm{w}}^{\mathrm{u}}$ and subsequent subtraction from the momentum balance (A20) yields:

$$(\rho_{\mathrm{w}}^{\mathrm{u}} y^{\mathrm{u}} \epsilon^{\mathrm{u}} s_{\mathrm{w}}^{\mathrm{u}} \omega^{\mathrm{u}}) \frac{\mathrm{d}}{\mathrm{d}t} v_{\mathrm{w}}^{\mathrm{u}} - \rho_{\mathrm{w}}^{\mathrm{u}} y^{\mathrm{u}} \epsilon^{\mathrm{u}} s_{\mathrm{w}}^{\mathrm{u}} g_{\mathrm{w}}^{\mathrm{u}} \omega^{\mathrm{u}} = \sum_l \mathbf{T}_{\mathrm{w},l}^{\mathrm{u}A} + \mathbf{T}_{\mathrm{w,ext}}^{\mathrm{u}A} + \mathbf{T}_{\mathrm{w}}^{\mathrm{us}} + \mathbf{T}_{\mathrm{w}}^{\mathrm{uc}} + \mathbf{T}_{\mathrm{wg}}^{\mathrm{u}} + \mathbf{T}_{\mathrm{wm}}^{\mathrm{u}} \tag{18}$$

The terms on the l.h.s are the inertial term and the water weight, respectively. The r.h.s. terms represent various forces: the total pressure forces acting on the mantle segments in common with neighbouring REWs and with the external watershed boundary, the forces exchanged with the atmosphere and the deep groundwater, the forces transmitted to the saturated zone across the water table, to the concentrated overland flow across the land surface, and, finally, the resultant forces exchanged with the gas phase and the soil matrix on the water–gas and water–solid interfaces, respectively.

6.1.3 Conservation of thermal energy

The REW-scale water phase conservation of thermal energy for the unsaturated zone is derived from the conservation of total energy (eqn (A32)) by subtracting the balance of mechanical energy (eqn (A33)). The result is:

$$(\rho_{\mathrm{w}}^{\mathrm{u}} y^{\mathrm{u}} \epsilon^{\mathrm{u}} s_{\mathrm{w}}^{\mathrm{u}} \omega^{\mathrm{u}}) \frac{\mathrm{d}}{\mathrm{d}t} E_{\mathrm{w}}^{\mathrm{u}} - \rho_{\mathrm{w}}^{\mathrm{u}} y^{\mathrm{u}} \epsilon^{\mathrm{u}} s_{\mathrm{w}}^{\mathrm{u}} h_{\mathrm{w}}^{\mathrm{u}} w^{\mathrm{u}} = \sum_l Q_{\mathrm{w},l}^{\mathrm{u}A} + Q_{\mathrm{w,ext}}^{\mathrm{u}A} + Q_{\mathrm{w}}^{\mathrm{us}} + Q_{\mathrm{w}}^{\mathrm{uc}} + Q_{\mathrm{wg}}^{\mathrm{u}} + Q_{\mathrm{wm}}^{\mathrm{u}} \tag{19}$$

where the terms on the l.h.s. are the energy storage due to change in internal energy and the external energy supply (i.e. solar radiation, geothermal energy sources). The terms on the r.h.s. are REW-scale heat exchange terms across the mantle segments, the exchanges with the saturated zone, the concentrated overland flow, the gaseous phase and the soil matrix, respectively.

6.1.4 Balance of entropy

The balance of entropy is given once again by multiplying the equation of mass conservation (eqn (A19)) by the REW-scale entropy and subtracting it subsequently from eqn (A34). The operation leads to the entropy equation in the following form:

$$(\rho_{\mathrm{w}}^{\mathrm{u}} y^{\mathrm{u}} \epsilon^{\mathrm{u}} s_{\mathrm{w}}^{\mathrm{u}} \omega^{\mathrm{u}}) \frac{\mathrm{d}}{\mathrm{d}t} \eta_{\mathrm{w}}^{\mathrm{u}} - \rho_{\mathrm{w}}^{\mathrm{u}} y^{\mathrm{u}} \epsilon^{\mathrm{u}} s_{\mathrm{w}}^{\mathrm{u}} \omega^{\mathrm{u}} = L_{\mathrm{w}}^{\mathrm{u}} \omega^{\mathrm{u}} + \sum_l F_{\mathrm{w},l}^{\mathrm{u}A} + F_{\mathrm{w,ext}}^{\mathrm{u}A} + F_{\mathrm{w}}^{\mathrm{us}} + F_{\mathrm{w}}^{\mathrm{uc}} + F_{\mathrm{wg}}^{\mathrm{u}} + F_{\mathrm{wm}}^{\mathrm{u}} \tag{20}$$

where the the terms on the l.h.s. represent the entropy storage and external supply, whereas the first term on the r.h.s. accounts for the internal production of entropy due to generation of heat by internal friction. The remaining REW-scale entropy exchange terms express the interaction with the surrounding REWs, subregions and phases in the same order as in the previous equations.

6.2 Saturated zone (s-subregion)

6.2.1 Conservation of mass

The balance of water for the saturated zone is derived from the general α-phase mass conservation (eqn (B14)) in Appendix B. The possibility of accounting for regional groundwater movement has to be included. This requires that the total mass exchange $e_{\mathrm{w}}^{\mathrm{s}A}$ between the saturated zones of two neighbouring REWs across the mantle surface A can be non-zero. There is no precipitation or solid dissolution between the soil matrix and the water assumed, i.e. $e_{\mathrm{ws}}^{\mathrm{s}} = 0$. The resultant conservation of mass is given by:

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho_{\mathrm{w}}^{\mathrm{s}} y^{\mathrm{s}} \epsilon^{\mathrm{s}} \omega^{\mathrm{s}}) = \sum_l e_{\mathrm{w},l}^{\mathrm{s}A} + e_{\mathrm{w,ext}}^{\mathrm{s}A} + e_{\mathrm{w}}^{\mathrm{s\,bot}} + e_{\mathrm{w}}^{\mathrm{su}} + e_{\mathrm{w}}^{\mathrm{so}} + e_{\mathrm{w}}^{\mathrm{sr}} \tag{21}$$

where y^{s} is the average vertical thickness of the saturated zone. The r.h.s. terms are given in order of sequence: the first term represents the mass exchange across the mantle segments forming the boundaries with neighbouring REWs, the second term is the flux across the mantle segments in common with the external watershed boundary (non-zero only for REWs which have part of the mantle in common with the external watershed boundary), the third term is the percolation to deeper groundwater zones, the fourth term is the flux across the water table (i.e. recharge or capillary rise), the fifth term is the flux towards the saturated overland flow zone on the seepage face and the last term is the mass exchanged with the channel reach across the bed surface (i.e. lateral channel inflow through seepage and groundwater recharge through channel losses).

6.2.2 Conservation of momentum

The balance of forces for the saturated zone water phase is derived from eqns (B13) and (B15), in complete analogy to what has been pursued for the unsaturated zone:

$$(\rho_w^s y^s \epsilon^s \omega^s)\frac{d}{dt}\mathbf{v}_w^s - \rho_w^s \boldsymbol{g}_w^s y^s \epsilon^s \omega^s = \sum_l \mathbf{T}_{w,l}^{sA} + \mathbf{T}_{w,\text{ext}}^{sA} + \mathbf{T}_w^{s\ \text{bot}} + \mathbf{T}_w^{su} + \mathbf{T}_w^{so} + \mathbf{T}_w^{sr} + \mathbf{T}_{ws}^{s} \quad (22)$$

The l.h.s. terms represent once again inertial force and weight of the water, whereas the r.h.s. terms are the ensemble of REW-scale forces, acting on the groundwater body, i.e. the forces exerted on the various mantle segments, the forces exchanged with the deep groundwater at the bottom, with the overland flow sheet on the seepage face, with the channel across the bed surface and with the soil matrix on the water–solid interfaces, respectively.

6.2.3 Conservation of thermal energy

The conservation of thermal energy is obtained from (B20), after subtraction of the mechanical energy:

$$(\rho_w^s y^s \epsilon^s \omega^s)\frac{d}{dt}E_w^s - \rho_w^s h_w^s y^s \epsilon^s \omega^s = \sum_l Q_{w,l}^{sA} + Q_{w,\text{ext}}^{sA} + Q_w^{s\ \text{bot}} + Q_w^{su} + Q_w^{so} + Q_w^{sr} + Q_{ws}^{s} \quad (23)$$

where the r.h.s. terms are the various heat exchanges of the water within the saturated zone with the neighbouring REWs, the external world, the surrounding subregions and the soil matrix.

6.2.4 Balance of entropy

This balance law is derived from eqn (B27) after subtraction of the mass balance multiplied by the REW-scale entropy. The result is:

$$(\rho_w^s y^s \epsilon^s \omega^s)\frac{d}{dt}\eta_w^s - \rho_w^s b_w^s y^s \epsilon^s \omega^s = L_w^s \omega^s + \sum_l F_{w,l}^{sA} + F_{w,\text{ext}}^{sA} + F_w^{s\ \text{bot}} + F_w^{su} + F_w^{so} + F_w^{sr} + F_{ws}^{s} \quad (24)$$

where the r.h.s. terms do not require further explanations.

6.3 Concentrated overland flow (c-subregion)

6.3.1 Conservation of mass

The concentrated overland flow region includes flow of water in the sub-REW-scale channel network (e.g. rills and gullies), ephemeral streams and Hortonian overland flow. It is modelled as a sheet of water covering the unsaturated land surface. It receives rainfall and communicates with the saturated overland flow around the main channel reach. The mass balance is derived in Appendix C from the general balance eqn (C9). The result is:

$$\frac{d}{dt}(\rho^c y^c \omega^c) = e^{c\ \text{top}} + e^{cu} + e^{co} \quad (25)$$

where y^c is the average vertical thickness of the flow region. The exchange terms on the r.h.s. are the input from the atmosphere (i.e. rainfall), the infiltration into the unsaturated zone and the total mass flux into the saturated overland flow region. If desirable, it is possible to represent the concentrated overland flow in terms of a drainage density and an average cross-sectional area, instead of a flow depth and an area fraction. This would require only small conceptual changes by casting the equations into a similar form as for the case of the channel reach (r-subregion).

6.3.2 Conservation of momentum

The total momentum of the concentrated overland flow is balanced by the gravity and the remaining forces acting on it. This is expressed by the following equation, which is derived from eqn (C11) after subtraction of the mass balance eqn (C10) multiplied by the average velocity of the c-subregion:

$$(\rho^c y^c \omega^c)\frac{d}{dt}\mathbf{v}^c - \rho^c y^c \boldsymbol{g}^c \omega^c = \mathbf{T}^{c\ \text{top}} + \mathbf{T}^{cu} + \mathbf{T}^{co} \quad (26)$$

where the three REW-scale forces on the r.h.s. are originated by viscous interaction with the atmosphere, through interaction with the unsaturated zone (i.e. pressure and drag force) and through exchange of momentum along the zones where the sub-REW-scale network merges with the saturated overland flow zone, respectively.

6.3.3 Conservation of thermal energy

The conservation of total energy is derived from the conservation of total energy (eqn (C14)) in the usual fashion through subtraction of the mechanical energy balance. The result is:

$$(\rho^c y^c \omega^c)\frac{d}{dt}E^c - \rho^c y^c h^c \omega^c = Q^{c\ \text{top}} + Q^{cu} + Q^{co} \quad (27)$$

where the r.h.s. terms are the REW-scale heat exchange terms between the concentrated overland flow water body and the surroundings.

6.3.4 Balance of entropy

Finally, the balance of energy obtained from eqn (C19) is:

$$(\rho^c y^c \omega^c)\frac{d}{dt}\eta^c - \rho^c y^c b^c \omega^c = L^c \omega^c + F^{c\ \text{top}} + F^{cu} + F^{co} \quad (28)$$

6.4 Saturated overland flow (o-subregion)

6.4.1 Conservation of mass

The saturated overland flow mass balance is derived in Appendix D from the generic REW-scale balance eqn (D8). The resulting equation is:

$$\frac{d}{dt}(\rho^o y^o \omega^o) = e^{o\ \text{top}} + e^{or} + e^{oc} + e^{os} \quad (29)$$

where y^o is the vertical average thickness of the water sheet. The r.h.s. terms represent, in order of appearance, the mass exchange with the atmosphere (i.e. rainfall and evaporation), the overland flow into the channel along the channel edges, the inflow from the concentrated overland flow regions uphill and the recharge of the flow sheet through seepage from the underlying saturated zone.

6.4.2 Conservation of momentum
The balance of forces is obtained from eqn (D10):

$$(\rho^{\mathrm{o}} y^{\mathrm{o}} \omega^{\mathrm{o}}) \frac{\mathrm{d}}{\mathrm{d}t} \mathbf{v}^{\mathrm{o}} - \rho^{\mathrm{o}} y^{\mathrm{o}} \boldsymbol{g}^{\mathrm{o}} \omega^{\mathrm{o}} = \mathbf{T}^{\mathrm{o\ top}} + \mathbf{T}^{\mathrm{or}} + \mathbf{T}^{\mathrm{oc}} + \mathbf{T}^{\mathrm{os}} \tag{30}$$

where the inertial term and the total weight are balanced by the following ensemble of resultant forces on the r.h.s.: the total force exchanged with the atmosphere on top, with the water in the channel along the channel edges (i.e. drag and pressure force), with the concentrated overland flow on the contact zones and the total force exchanged with the saturated zone (i.e. pressure and drag force transmitted to the soil matrix and the water in the saturated zone), respectively.

6.4.3 Conservation of thermal energy
The conservation law of thermal energy is derived in a straightforward manner form eqn (D13):

$$(\rho^{\mathrm{o}} y^{\mathrm{o}} \omega^{\mathrm{o}}) \frac{\mathrm{d}}{\mathrm{d}t} E^{\mathrm{o}} - \rho^{\mathrm{o}} y^{\mathrm{o}} h^{\mathrm{o}} \omega^{\mathrm{o}} = Q^{\mathrm{o\ top}} + Q^{\mathrm{or}} + Q^{\mathrm{oc}} + Q^{\mathrm{os}} \tag{31}$$

6.4.4 Balance of entropy
Finally, the balance of entropy is the result of manipulations of eqn (D18):

$$(\rho^{\mathrm{o}} y^{\mathrm{o}} \omega^{\mathrm{o}}) \frac{\mathrm{d}}{\mathrm{d}t} \eta^{\mathrm{o}} - \rho^{\mathrm{o}} y^{\mathrm{o}} b^{\mathrm{o}} \omega^{\mathrm{o}} = L^{\mathrm{o}} \omega^{\mathrm{o}} + F^{\mathrm{o\ top}} + F^{\mathrm{or}} + F^{\mathrm{oc}} + F^{\mathrm{os}} \tag{32}$$

6.5 Channel reach (r-subregion)

6.5.1 Conservation of mass
The REW-scale mass balance equation for the channel reach is derived in Appendix E:

$$\frac{\mathrm{d}}{\mathrm{d}t} (\rho^{\mathrm{r}} m^{\mathrm{r}} \xi^{\mathrm{r}}) = \sum_l e_l^{\mathrm{r}A} + e_{\mathrm{ext}}^{\mathrm{r}A} + e^{\mathrm{r\ top}} + e^{\mathrm{rs}} + e^{\mathrm{ro}} \tag{33}$$

where m^{r} is the average cross-sectional area of the reach and ξ^{r} is the *drainage density* defined in eqn (14). The r.h.s. terms are the various mass fluxes in and out of the channel. The first term is the sum of inflow and outflow at the inlet and outlet sections of the REW. In the case of source streams there will be only an outflow section. In the case of higher order streams, there will be two inflows (from each of the two reaches converging at the REW inlet) and one outflow. The second term is the mass exchange of the channel reach across the external watershed boundary. This term is non-zero only for the REW situated at the outlet, e.g. REW 13 in Fig. 1(c). The third term is the mass exchange between the channel free surface and the atmosphere (i.e. rainfall and open water evaporation). The fourth term is the mass exchange with the saturated zone across the channel bed and the last term is the lateral inflow into the channel from the overland flow region.

6.5.2 Conservation of momentum
The momentum balance is derived from eqn (E16):

$$(\rho^{\mathrm{r}} m^{\mathrm{r}} \xi^{\mathrm{r}}) \frac{\mathrm{d}}{\mathrm{d}t} \mathbf{v}^{\mathrm{r}} - \rho^{\mathrm{r}} m^{\mathrm{r}} \boldsymbol{g}^{\mathrm{r}} \xi^{\mathrm{r}} = \sum_l \mathbf{T}_l^{\mathrm{r}A} + \mathbf{T}^{\mathrm{r\ top}} + \mathbf{T}^{\mathrm{rs}} + \mathbf{T}^{\mathrm{ro}} \tag{34}$$

It expresses the balance of forces between the inertial force, the weight of the water stored in the channel and the forces acting on the surroundings. These are, in order of appearance, the total force acting on the end sections of the channel by interaction with the upstream and downstream reaches, the force exchanged across the external watershed boundary (non-zero only for the REW situated at the watershed outlet), the force exerted by the atmosphere on the free surface (i.e. wind stress), the force due to interaction with the channel bed (i.e. pressure and drag force) and the total drag force exerted by the channel water on the overland flow sheet along the channel edges.

6.5.3 Conservation of thermal energy
The balance of thermal energy is derived from eqn (E20)

$$(\rho^{\mathrm{r}} m^{\mathrm{r}} \xi^{\mathrm{r}}) \frac{\mathrm{d}}{\mathrm{d}t} E^{\mathrm{r}} - \rho^{\mathrm{r}} m^{\mathrm{r}} h^{\mathrm{r}} \xi^{\mathrm{r}} = \sum_l Q_l^{\mathrm{r}A} + Q_{\mathrm{ext}}^{\mathrm{r}A} + Q^{\mathrm{r\ top}} + Q^{\mathrm{rs}} + Q^{\mathrm{ro}} \tag{35}$$

where the interpretation of the heat exchange terms is straightforward.

6.5.4 Balance of entropy
This final equation is obtained by manipulation of eqn (E26):

$$(\rho^{\mathrm{r}} m^{\mathrm{r}} \xi^{\mathrm{r}}) \frac{\mathrm{d}}{\mathrm{d}t} \eta^{\mathrm{r}} - \rho^{\mathrm{r}} m^{\mathrm{r}} b^{\mathrm{r}} \xi^{\mathrm{r}} = L^{\mathrm{r}} \xi^{\mathrm{r}} + \sum_l F_l^{\mathrm{r}A} + F_{\mathrm{ext}}^{\mathrm{r}A} + F^{\mathrm{r\ top}} + F^{\mathrm{rs}} + F^{\mathrm{ro}} \tag{36}$$

7 RESTRICTIONS ON THE EXCHANGE TERMS FOR THE THERMODYNAMIC PROPERTIES

The previously defined subregions include one or more phases. The flow in the channel network and in the overland flow region is a one-phase flow, whereas for the subsurface flow regions the coexistence of two or three phases has to be considered. The thermodynamic properties are exchanged between the different phases within the same subregion, between different subregions and among REWs.

Phases are separated by phase interfaces, subregions by inter-subregion boundary surfaces (e.g. the channel bed surface or the saturated land surface). REWs are separated from each other by the mantle surface *A*. These boundaries are assumed to have no inherent thermodynamic properties, i.e. they are not able to store any of the properties or to sustain stress. Under these circumstances the conservation equations for mass, momentum, energy and entropy become, along these curves and surfaces, standard jump conditions for the conservation laws, as initially derived by Eringen[12]

Table 3. Inter-phase jump conditions for momentum, energy and entropy for the *u* and *s*-subregion

Subregion	Property	Boundary	Jump condition
u	Mass	S^{u}_{wg}	$e^{u}_{wg} + e^{u}_{gw} = 0$
u	Momentum	S^{u}_{mg}	$\mathbf{T}^{u}_{mg} + \mathbf{T}^{u}_{gm} = 0$
		S^{u}_{wg}	$(e^{u}_{wg}\cdot\mathbf{v}^{u}_{w} + \mathbf{T}^{u}_{wg}) + (e^{u}_{gw}\cdot\mathbf{v}^{u}_{g} + \mathbf{T}^{u}_{gw}) = 0$
		S^{u}_{wm}	$\mathbf{T}^{u}_{wm} + \mathbf{T}^{u}_{mw} = 0$
s		S^{s}_{wm}	$\mathbf{T}^{s}_{wm} + \mathbf{T}^{s}_{mw} = 0$
u	Energy	S^{u}_{mg}	$Q^{u}_{mg} + Q^{u}_{gm} = 0$
		S^{u}_{wg}	$\{e^{u}_{wg}[E^{u}_{w} + (v^{u2}_{w})/2] + \mathbf{T}^{u}_{wg}\cdot\mathbf{v}^{u}_{w} + Q^{u}_{wg}\} + \{e^{u}_{gw}[E^{u}_{g} + (v^{u2}_{g})/2] + \mathbf{T}^{u}_{gw}\cdot\mathbf{v}^{u}_{g} + Q^{u}_{gw} = 0$
		S^{u}_{wm}	$(\mathbf{T}^{u}_{wm}\cdot\mathbf{v}^{u} + Q^{u}_{wm}) + Q^{u}_{mw} = 0$
s		S^{s}_{wm}	$(\mathbf{T}^{s}_{wm}\cdot\mathbf{v}^{s} + Q^{s}_{wm}) + Q^{s}_{mw} = 0$
u	Entropy	S^{u}_{mg}	$F^{u}_{mg} + F^{u}_{mg} \geq 0$
		S^{u}_{wg}	$(e^{u}_{wg} + F^{u}_{wg}) + (e^{u}_{wg}\eta^{u}_{g} + F^{u}_{gw}) \geq 0$
		S^{u}_{wm}	$F^{u}_{wm} + F^{u}_{wm} \geq 0$
s		S^{s}_{wm}	$F^{s}_{wm} + F^{s}_{mw} \geq 0$

and further generalized by Hassanizadeh and Gray.[17,18] In the present case the following assumptions are made:

(1) The solid matrix is inert, i.e. there is no phase change or absorption between the soil matrix and the remaining phases and, therefore, $e^{u}_{mw} = e^{u}_{wm} = e^{u}_{mg} = e^{u}_{gm} = e^{s}_{mw} = e^{s}_{mw} = 0$.
(2) There are no sediment transport phenomena considered (i.e. no surface or channel erosion) and, hence, the mass exchange terms between the solid phase of the u- and s-subregions with the two overland flow regions and the channel are zero: $e^{so}_{m} = e^{sr}_{m} = e^{uc}_{m} = 0$. There are no mass exchanges of gas or solid phase across the mantle: $e^{uA}_{g} = e^{uA}_{m} = e^{sA}_{m} = 0$.
(3) The solid matrix is a rigid medium, i.e. $\mathbf{v}^{u}_{m} = \mathbf{v}^{s}_{m} = 0$, and the gaseous phase has negligible motion, i.e. $\mathbf{v}^{u}_{g} = 0$.

In assembling the subregions to REWs and the REWs to the entire watershed, it has to be noted that the water phase can exchange momentum, energy and entropy with the remaining phases (soil matrix, gas) within the same subregion and that the c-, o- and r-subregions, comprising only the water phase, interact with the water and the solid phase of the adjacent u- and s-subregions. Appropriate jump conditions between different phases, subregions and REWs have, therefore, to be imposed.

Assumptions 1 and 2 allow the introduction of the following notational simplifications: the mass exchange terms between subregions are non-zero only for the water phase. Therefore, the symbols e^{us}_{w}, e^{su}_{w}, e^{uc}_{w}, e^{so}_{w}, e^{sr}_{w}, $e^{sA}_{w,l}$, $e^{uA}_{w,l}$, $e^{uA}_{w,ext}$ and $e^{sA}_{w,ext}$ are substituted by e^{us}, e^{su}, e^{uc}, e^{so}, e^{sr}, e^{sA}_{l}, e^{uA}_{l}, e^{uA}_{ext} and e^{sA}_{ext}, respectively. Following Assumption 3, only the velocities of the water phase are considered in the unsaturated and the saturated zones. We replace the symbols $\mathbf{v}^{u}_{w}$ and $\mathbf{v}^{s}_{w}$ for the water with $\mathbf{v}^{u}$ and $\mathbf{v}^{s}$, respectively. The jump conditions are summarized in three tables: Table 3 contains the inter-phase jump conditions for mass, momentum, energy and entropy for the u- and the s-subregion within the *k*th REW, Table 4 contains the respective jump conditions between the five subregions within a REW and Table 5 summarizes the jump conditions between the *k*th REW and its *l*th neighbouring REW ($l = 1,\ldots,N_k$). These jump conditions will be employed for the manipulation of the second law of thermodynamics, pursued in Section 8.

8 THE SECOND LAW OF THERMODYNAMICS

In order to complete the series of balance laws for a REW, the second law of thermodynamics has to be included. It will be useful for the derivation of constitutive relationships. The second law of thermodynamics states that the rate of entropy production has to be non-negative for the physical system under consideration. In the present study the physical system of interest is the entire watershed, which is made up by an agglomeration of *M* REWs. Every REW is an ensemble of five subregions. As a consequence the second law of thermodynamics has to be written for all *M* REWs together:

$$L = \sum_{k=1}^{M}\left(\sum_{\alpha=m,w,g}\int_{V^{u}} L\gamma^{u}_{\alpha}\mathrm{d}V\right)_{k} + \sum_{k=1}^{M}\left(\sum_{\alpha=m,w}\int_{V^{s}} L\gamma^{s}_{\alpha}\mathrm{d}V\right)_{k} + \sum_{k=1}^{M}\left(\int_{V^{c}} L\mathrm{d}V\right)_{k} + \sum_{k=1}^{M}\left(\int_{V^{o}} L\mathrm{d}V\right)_{k} + \sum_{k=1}^{M}\left(\int_{V^{r}} L\mathrm{d}V\right)k \geq 0 \tag{37}$$

Introduction of REW-scale quantities defined in Section 5

Table 4. Inter-subregion jump conditions for mass momentum and energy and entropy

Property	Boundary	Jump condition
Mass	A^{us}	$e^{\mathrm{us}} + e^{\mathrm{su}} = 0$
	A^{uc}	$e^{\mathrm{uc}} + e^{\mathrm{cu}} = 0$
	A^{so}	$e^{\mathrm{so}} + e^{\mathrm{os}} = 0$
	A^{sc}	$e^{\mathrm{sr}} + e^{\mathrm{rs}} = 0$
	A^{co}	$e^{\mathrm{co}} + e^{\mathrm{oc}} = 0$
	A^{or}	$e^{\mathrm{or}} + e^{\mathrm{ro}} = 0$
Momentum	A^{us}	$\mathbf{T}_{\mathrm{m}}^{\mathrm{us}} + \mathbf{T}_{\mathrm{m}}^{\mathrm{su}} = 0$
		$(e^{\mathrm{us}}\cdot\mathbf{v}^{\mathrm{u}} + \mathbf{T}_{\mathrm{w}}^{\mathrm{us}}) + (e^{\mathrm{su}}\cdot\mathbf{v}^{\mathrm{u}} + \mathbf{T}_{\mathrm{w}}^{\mathrm{us}}) + (e^{\mathrm{su}}\cdot\mathbf{v}^{\mathrm{s}} + \mathbf{T}_{\mathrm{w}}^{\mathrm{su}}) = 0$
	A^{uc}	$(e^{\mathrm{uc}}\cdot\mathbf{v}^{\mathrm{u}} + \mathbf{T}_{\mathrm{w}}^{\mathrm{uc}} + \mathbf{T}_{\mathrm{m}}^{\mathrm{uc}} + \mathbf{T}_{g}^{\mathrm{uc}}) + (e^{\mathrm{cu}}\cdot\mathbf{v}^{c} + \mathbf{T}^{\mathrm{cu}}) = 0$
	A^{so}	$(e^{\mathrm{so}}\cdot\mathbf{v}^{\mathrm{s}} + \mathbf{T}_{\mathrm{w}}^{\mathrm{so}} + \mathbf{T}_{\mathrm{m}}^{\mathrm{so}}) + (e^{os}\cdot\mathbf{v}^{\mathrm{o}} + \mathbf{T}^{\mathrm{os}}) = 0$
	A^{sr}	$(e^{\mathrm{sr}}\cdot\mathbf{v}^{\mathrm{s}} + \mathbf{T}_{\mathrm{w}}^{\mathrm{sr}} + \mathbf{T}_{\mathrm{m}}^{\mathrm{sr}}) + (e^{rs}\cdot\mathbf{v}^{\mathrm{r}} + \mathbf{T}^{\mathrm{rs}}) = 0$
	A^{co}	$(e^{\mathrm{co}}\cdot\mathbf{v}^{c} + \mathbf{T}^{\mathrm{co}}) + (e^{\mathrm{oc}}\cdot\mathbf{v}^{\mathrm{o}} + \mathbf{T}^{\mathrm{oc}}) = 0$
	A^{or}	$(e^{\vee}\cdot\mathbf{v}^{\mathrm{o}} + \mathbf{T}^{\vee}) + (e^{\mathrm{ro}}\cdot\mathbf{v}^{\mathrm{r}} + \mathbf{T}^{\mathrm{ro}}) = 0$
Energy	A^{us}	$Q_{\mathrm{m}}^{\mathrm{us}} + Q_{\mathrm{m}}^{\mathrm{su}} = 0$
		$\{e^{\mathrm{us}}[E^{\mathrm{u}} + (v^{\mathrm{u}2})/2] + \mathbf{T}_{\mathrm{w}}^{\mathrm{us}}\cdot\mathbf{v}^{\mathrm{u}} + Q_{\mathrm{w}}^{\mathrm{us}}\} + \{e^{\mathrm{su}}[E^{\mathrm{s}} + (v^{\mathrm{s}2})/2] + \mathbf{T}_{\mathrm{w}}^{\mathrm{su}}\cdot\mathbf{v}^{\mathrm{s}} + Q_{\mathrm{w}}^{\mathrm{su}}\} = 0$
	A^{uc}	$\{e^{\mathrm{uc}}[E^{\mathrm{u}} + (v^{\mathrm{u}2})/2] + \mathbf{T}_{\mathrm{w}}^{\mathrm{uc}}\cdot\mathbf{v}^{\mathrm{u}} + Q_{\mathrm{w}}^{\mathrm{uc}} + Q_{\mathrm{m}}^{\mathrm{uc}} + Q_{\mathrm{g}}^{\mathrm{uc}}\} + \{e^{\mathrm{cu}}[E^{c} + (v^{\mathrm{c}2})/2] + \mathbf{T}^{\mathrm{cu}}\cdot\mathbf{v}^{c} + Q^{\mathrm{cu}}\} = 0$
	A^{so}	$\{e^{\mathrm{so}}[E^{\mathrm{s}} + (v^{\mathrm{s}2})/2] + \mathbf{T}_{\mathrm{w}}^{\mathrm{so}}\cdot\mathbf{v}^{\mathrm{s}} + Q_{\mathrm{w}}^{\mathrm{so}} + Q_{\mathrm{m}}^{\mathrm{so}}\} + \{e^{\mathrm{os}}[E^{\mathrm{o}} + (v^{\mathrm{o}2})/2] + \mathbf{T}^{\mathrm{os}}\cdot\mathbf{v}^{\mathrm{o}} + Q^{\mathrm{os}}\} = 0$
	A^{sr}	$\{e^{\mathrm{sr}}[E^{\mathrm{s}} + (v^{\mathrm{s}2})/2] + \mathbf{T}_{\mathrm{w}}^{\mathrm{sr}}\cdot\mathbf{v}^{\mathrm{s}} + Q_{\mathrm{w}}^{\mathrm{sr}} + Q_{\mathrm{m}}^{\mathrm{sr}}\} + \{e^{\mathrm{rs}}[E^{\mathrm{r}} + (v^{\mathrm{r}2})/2] + \mathbf{T}^{\mathrm{rs}}\cdot\mathbf{v}^{\mathrm{r}} + Q^{\mathrm{rs}}\} = 0$
	A^{co}	$\{e^{\mathrm{co}}[E^{c} + (v^{\mathrm{c}2})/2] + \mathbf{T}^{\mathrm{co}}\cdot\mathbf{v}^{c} + Q^{\mathrm{co}}\} + \{e^{\mathrm{oc}}[E^{\mathrm{o}} + (v^{\mathrm{o}2})/2] + \mathbf{T}^{\mathrm{oc}}\cdot\mathbf{v}^{\mathrm{o}} + Q^{\mathrm{oc}}\} = 0$
	A^{or}	$\{e^{\mathrm{or}}[E^{\mathrm{o}} + (v^{\mathrm{o}2})/2] + \mathbf{T}^{\mathrm{or}}\cdot\mathbf{v}^{\mathrm{o}} + Q^{\mathrm{or}}\} + \{e^{\mathrm{ro}}[E^{\mathrm{r}} + (v^{\mathrm{r}2})/2] + \mathbf{T}^{\mathrm{ro}}\cdot\mathbf{v}^{\mathrm{r}} + Q^{\mathrm{ro}}\} = 0$
Entropy	A^{us}	$F_{\mathrm{m}}^{\mathrm{us}} + F_{\mathrm{m}}^{\mathrm{su}} \geq 0$
		$(e^{\mathrm{us}}\eta^{\mathrm{u}} + F_{\mathrm{w}}^{\mathrm{us}}) + (e^{\mathrm{su}}\eta^{\mathrm{s}} + F_{\mathrm{w}}^{\mathrm{su}}) \geq 0$
	A^{uc}	$(e^{\mathrm{uc}}\eta^{\mathrm{u}} + F_{\mathrm{w}}^{\mathrm{uc}}) + (F_{\mathrm{m}}^{\mathrm{uc}} + F_{\mathrm{g}}^{\mathrm{uc}}) + (e^{\mathrm{cu}}\eta^{c} + F^{\mathrm{cu}}) \geq 0$
	A^{so}	$(e^{\mathrm{so}}\eta^{\mathrm{s}} + F_{\mathrm{w}}^{\mathrm{so}}) + F_{\mathrm{m}}^{\mathrm{so}} + (e^{\mathrm{os}}\eta^{\mathrm{o}} + F^{\mathrm{os}}) \geq 0$
	A^{sr}	$(e^{\mathrm{sr}}\eta^{\mathrm{s}} + F_{\mathrm{w}}^{\mathrm{sr}}) + F_{\mathrm{m}}^{\mathrm{sr}} + (e^{\mathrm{rs}}\eta^{\mathrm{r}} + F^{\mathrm{rs}}) \geq 0$
	A^{co}	$(e^{\mathrm{co}}\eta^{c} + F^{\mathrm{co}}) + (e^{\mathrm{co}}\eta^{\mathrm{o}} + F^{\mathrm{oc}}) \geq 0$
	A^{or}	$(e^{\mathrm{or}}\eta^{\mathrm{o}} + F^{\mathrm{or}}) + (e^{\mathrm{ro}}\eta^{\mathrm{r}} + F^{\mathrm{ro}}) \geq 0$

leads to:

$$L = \sum_{k=1}^{M}\left(\sum_{\alpha=\mathrm{m,w,g}} L_{\alpha}^{\mathrm{u}}\omega^{\mathrm{u}}\Sigma\right)_{k} + \sum_{k=1}^{M}\left(\sum_{\alpha=\mathrm{m,w}} L_{\alpha}^{\mathrm{s}}\omega^{\mathrm{s}}\Sigma\right)_{k} + \sum_{k=1}^{M}(L^{\mathrm{c}}\omega^{\mathrm{c}}\Sigma)_{k} + \sum_{k=1}^{M}(L^{\mathrm{o}}\omega^{\mathrm{o}}\Sigma)_{k} + \sum_{k=1}^{M}(L^{\mathrm{r}}\xi^{\mathrm{r}}\Sigma)_{k} \geq 0 \tag{38}$$

This inequality can be rewritten after eliminating L_{α}^{u}, L_{α}^{s}, L^{c}, L^{o} and L^{r} with the use of eqns (A34), (B27), (C19), (D18) and (E26) and employing the equations of mass conservation. After exploiting the inter-phase jump conditions of Table 3 and dividing by the surface area projection Σ we obtain:

$$\begin{aligned}
&\sum_{k=1}^{M}\left\{\sum_{\alpha=\mathrm{m,w,g}}\left[(\rho_{\alpha}^{\mathrm{u}}y^{\mathrm{u}}\epsilon_{\alpha}^{\mathrm{u}}\omega^{\mathrm{u}})\frac{\mathrm{d}}{\mathrm{d}t}\eta_{\alpha}^{\mathrm{u}} - F_{\alpha}^{\mathrm{u}A} - \rho_{\alpha}^{\mathrm{u}}b_{\alpha}^{\mathrm{u}}y^{\mathrm{u}}\epsilon_{\alpha}^{\mathrm{u}}\omega^{\mathrm{u}} - F_{\alpha}^{\mathrm{us}} - F_{\alpha}^{\mathrm{uc}} - F_{\alpha\beta}^{\mathrm{u}}\right]\right\}_{k} \\
&+ \sum_{k=1}^{M}\left\{\sum_{\alpha=\mathrm{m,w}}\left[(\rho_{\alpha}^{\mathrm{s}}y^{\mathrm{s}}\epsilon_{\alpha}^{\mathrm{s}}\omega^{\mathrm{s}})\frac{\mathrm{d}}{\mathrm{d}t}\eta_{\alpha}^{\mathrm{s}} - F_{\alpha}^{\mathrm{s}A} - \rho_{\alpha}^{\mathrm{s}}b_{\alpha}^{\mathrm{s}}y^{\mathrm{s}}\epsilon_{\alpha}^{\mathrm{s}}\omega^{\mathrm{s}} - F_{\alpha}^{\mathrm{s\ bot}} - F_{\alpha}^{\mathrm{su}} - F_{\alpha}^{\mathrm{so}} - F_{\alpha}^{\mathrm{sr}} - F_{\alpha\beta}^{\mathrm{s}}\right]\right\}_{k} \\
&+ \sum_{k=1}^{M}\left[(\rho^{\mathrm{c}}y^{\mathrm{c}}\omega^{\mathrm{c}})\frac{\mathrm{d}}{\mathrm{d}t}\eta^{\mathrm{c}} - \rho^{\mathrm{c}}y^{\mathrm{c}}b^{\mathrm{c}}\omega^{\mathrm{c}} - F^{\mathrm{c\ top}} - F^{\mathrm{cu}} - F^{\mathrm{co}}\right]_{k} \\
&+ \sum_{k=1}^{M}\left[(\rho^{\mathrm{o}}y^{\mathrm{o}}\omega^{\mathrm{o}})\frac{\mathrm{d}}{\mathrm{d}t}\eta^{\mathrm{o}} - \rho^{\mathrm{o}}y^{\mathrm{o}}b^{\mathrm{o}}\omega^{\mathrm{o}} - F^{\mathrm{o\ top}} - F^{\mathrm{oc}} - F^{\mathrm{or}} - F^{\mathrm{os}}\right]_{k} \\
&+ \sum_{k=1}^{M}\left[(\rho^{\mathrm{r}}y^{\mathrm{r}}\xi^{\mathrm{r}})\frac{\mathrm{d}}{\mathrm{d}t}\eta^{\mathrm{r}} - F^{\mathrm{r}A}\rho^{\mathrm{r}}m^{\mathrm{r}}b^{\mathrm{r}}\xi^{\mathrm{r}} - F^{\mathrm{r\ top}} - F^{\mathrm{rs}} - F^{\mathrm{ro}}\right]_{k} \\
&\geq 0
\end{aligned} \tag{39}$$

Eqn (39) can be expressed in terms of the entropies and

Table 5. Jump conditions between the *k*th REW and the neighbouring REWs across the mantle segments

Property	Boundary	Jump condition
Mass	$A_l^{\mathrm{u}A}$	$e_l^{\mathrm{u}A}\|_k + e_k^{\mathrm{u}A}\|_l = 0$
	$A_l^{\mathrm{s}A}$	$e_l^{\mathrm{s}A}\|_k + e_k^{\mathrm{s}A}\|_l = 0$
Momentum	$A_l^{\mathrm{u}A}$	$\mathbf{T}^{\mathrm{u}A}_{\mathrm{m},l}\|_k + \mathbf{T}^{\mathrm{u}A}_{\mathrm{m},k}\|_l = 0$
		$\mathbf{T}^{\mathrm{u}A}_{\mathrm{g},l}\|_k + \mathbf{T}^{\mathrm{u}A}_{\mathrm{g},k}\|_l = 0$
		$(e_l^{\mathrm{u}A}\cdot\mathbf{v}^{\mathrm{u}} + \mathbf{T}^{\mathrm{u}A}_{\mathrm{w},l})_k + (e_k^{\mathrm{u}A}\cdot\mathbf{v}^{\mathrm{u}} + \mathbf{T}^{\mathrm{u}A}_{\mathrm{w},k})_l = 0$
	$A_l^{\mathrm{s}A}$	$\mathbf{T}^{\mathrm{u}A}_{\mathrm{m},l}\|_k + \mathbf{T}^{\mathrm{s}A}_{\mathrm{m},k}\|_l = 0$
		$(e_l^{\mathrm{s}A}\cdot\mathbf{v}^{\mathrm{s}} + \mathbf{T}^{\mathrm{s}A}_{\mathrm{w},l})_k + (e_k^{\mathrm{s}A}\cdot\mathbf{v}^{\mathrm{s}} + \mathbf{T}^{\mathrm{s}A}_{\mathrm{w},k})_l = 0$
Energy		$Q^{\mathrm{u}A}_{\mathrm{m},l}\|_k + Q^{\mathrm{u}A}_{\mathrm{m},k}\|_l = 0$
		$Q^{\mathrm{u}A}_{\mathrm{g},l}\|_k + Q^{\mathrm{g}A}_{\mathrm{w},k}\|_l = 0$
		$\{e_l^{\mathrm{u}A}[E^{\mathrm{u}} + (v^{\mathrm{u}2})/2] + \mathbf{T}^{\mathrm{u}A}_{\mathrm{w},l}\cdot\mathbf{v}^{\mathrm{u}} + Q^{\mathrm{u}A}_{\mathrm{w},l}\}_k +$
		$\{e_k^{\mathrm{u}A}[E^{\mathrm{u}} + (v^{\mathrm{u}2})/2] + \mathbf{T}^{\mathrm{u}A}_{\mathrm{w},k}\cdot\mathbf{v}^{\mathrm{u}} + Q^{\mathrm{u}A}_{\mathrm{w},k}\}_l = 0$
	$A_l^{\mathrm{s}A}$	$Q^{\mathrm{s}A}_{\mathrm{m},l}\|_k + Q^{\mathrm{s}A}_{\mathrm{m},k}\|_l = 0$
		$\{e_l^{\mathrm{s}A}[E^{\mathrm{s}} + (v^{\mathrm{s}2})/2] + \mathbf{T}^{\mathrm{s}A}_{\mathrm{w},l}\cdot\mathbf{v}^{\mathrm{s}} + Q^{\mathrm{s}A}_{\mathrm{w},l}\}_k +$
		$\{e_k^{\mathrm{s}A}[E^{\mathrm{s}} + (v^{\mathrm{s}2})/2] + \mathbf{T}^{\mathrm{s}A}_{\mathrm{w},k}\cdot\mathbf{v}^{\mathrm{s}} + Q^{\mathrm{s}A}_{\mathrm{w},k}\}_l = 0$
Entropy	$A_l^{\mathrm{u}A}$	$F^{\mathrm{u}A}_{\mathrm{m},l}\|_k + F^{\mathrm{u}A}_{\mathrm{m},k}\|_l \geq 0$
		$F^{\mathrm{u}A}_{\mathrm{g},l}\|_k + F^{\mathrm{u}A}_{\mathrm{g},k}\|_l \geq 0$
		$(e_l^{\mathrm{u}A}\cdot\eta^{\mathrm{u}} + F^{\mathrm{u}A}_{\mathrm{w},l})_k + (e_k^{\mathrm{u}A}\cdot\eta^{\mathrm{u}} + F^{\mathrm{u}A}_{\mathrm{w},k})_l \geq 0$
	$A_l^{\mathrm{s}A}$	$F^{\mathrm{s}A}_{\mathrm{m},l}\|_k + F^{\mathrm{s}A}_{\mathrm{m},k}\|_l \geq 0$
		$(e_l^{\mathrm{s}A}\cdot\eta^{\mathrm{s}} + F^{\mathrm{s}A}_{\mathrm{w},l})_k + (e_k^{\mathrm{s}A}\cdot\eta^{\mathrm{s}} + F^{\mathrm{s}A}_{\mathrm{w},k})_l \geq 0$

internal energies expressed on a per unit REW area basis

$$\hat{\eta}^j_\alpha = \rho^j_\alpha \epsilon^j_\alpha y^j \omega^j \eta^j_\alpha \quad j = \mathrm{u,s} \tag{40}$$

$$\hat{\eta}_j = \rho^j y^j \omega^j \eta^j \quad j = \mathrm{c,o,r} \tag{41}$$

$$\hat{E}^j_\alpha = \rho^j_\alpha \epsilon^j_\alpha y^j \omega^j E^j_\alpha \quad j = \mathrm{u,s} \tag{42}$$

$$\hat{E}_j = \rho^j y^j \omega^j E^j \quad j = \mathrm{c,o,r} \tag{43}$$

At this stage one more assumption is made:

(4) The temperatures of all phases within the u- and the s-subregion are equal to a common temperature θ^{u} and θ^{s}, respectively. The temperatures of the same subregions are equal among all M REWs making up the watershed, i.e. $\theta^j|_k = \theta^j|_l$; $j =$ u,s,c,o,r; $k,l = 1\ldots M$.

This assumption allows for further notational simplifications: $\theta^{\mathrm{u}}_{\mathrm{m}} = \theta^{\mathrm{u}}_{\mathrm{w}} = \theta^{\mathrm{u}}_{\mathrm{g}} = \theta^{\mathrm{u}}$ and $\theta^{\mathrm{s}}_{\mathrm{m}} = \theta^{\mathrm{s}}_{\mathrm{w}} = \theta^{\mathrm{s}}$.

The entropy inequality in the form of eqn (39) can now be restated by formulating the entropy in terms of the internal energy and the entropy on a per unit area basis, by exploiting the balance equations of thermal energy and by employing the jump conditions summarized in Tables 4 and 5. After some algebraic manipulations one obtains:

$$\begin{aligned}
L = &- \frac{1}{\theta^{\mathrm{u}}} \sum_{k=1}^{M} \left(\frac{\mathrm{d}\hat{E}^{\mathrm{u}}_{\mathrm{m}}}{\mathrm{d}t} - \theta^{\mathrm{u}} \frac{\mathrm{d}\hat{\eta}^{\mathrm{u}}_{\mathrm{m}}}{\mathrm{d}t} \right)_k \\
&- \frac{1}{\theta^{\mathrm{u}}} \sum_{k=1}^{M} \left(\frac{\mathrm{d}\hat{E}^{\mathrm{u}}_{\mathrm{w}}}{\mathrm{d}t} - \theta^{\mathrm{u}} \frac{\mathrm{d}\hat{\eta}^{\mathrm{u}}_{\mathrm{w}}}{\mathrm{d}t} \right)_k \\
&- \frac{1}{\theta^{\mathrm{u}}} \sum_{k=1}^{M} \left(\frac{\mathrm{d}\hat{E}^{\mathrm{u}}_{\mathrm{g}}}{\mathrm{d}t} - \theta^{\mathrm{u}} \frac{\mathrm{d}\hat{\eta}^{\mathrm{u}}_{\mathrm{g}}}{\mathrm{d}t} \right)_k \\
&- \frac{1}{\theta^{\mathrm{s}}} \sum_{k=1}^{M} \left(\frac{\mathrm{d}\hat{E}^{\mathrm{s}}_{\mathrm{m}}}{\mathrm{d}t} - \theta^{\mathrm{s}} \frac{\mathrm{d}\hat{\eta}^{\mathrm{s}}_{\mathrm{m}}}{\mathrm{d}t} \right)_k \\
&- \frac{1}{\theta^{\mathrm{s}}} \sum_{k=1}^{M} \left(\frac{\mathrm{d}\hat{E}^{\mathrm{s}}_{\mathrm{w}}}{\mathrm{d}t} - \theta^{\mathrm{s}} \frac{\mathrm{d}\hat{\eta}^{\mathrm{s}}_{\mathrm{w}}}{\mathrm{d}t} \right)_k \\
&- \frac{1}{\theta^{\mathrm{c}}} \sum_{k=1}^{M} \left(\frac{\mathrm{d}\hat{E}^{\mathrm{c}}}{\mathrm{d}t} - \theta^{\mathrm{c}} \frac{\mathrm{d}\hat{\eta}^{\mathrm{c}}}{\mathrm{d}t} \right)_k \\
&- \frac{1}{\theta^{\mathrm{o}}} \sum_{k=1}^{M} \left(\frac{\mathrm{d}\hat{E}^{\mathrm{o}}}{\mathrm{d}t} - \theta^{\mathrm{o}} \frac{\mathrm{d}\hat{\eta}^{\mathrm{o}}}{\mathrm{d}t} \right)_k \\
&- \frac{1}{\theta^{\mathrm{r}}} \sum_{k=1}^{M} \left(\frac{\mathrm{d}\hat{E}^{\mathrm{r}}}{\mathrm{d}t} - \theta^{\mathrm{r}} \frac{\mathrm{d}\hat{\eta}^{\mathrm{r}}}{\mathrm{d}t} \right)_k \\
&- \sum_{k=1}^{M} \left[\sum_{\alpha=\mathrm{m,w,g}} \rho^{\mathrm{u}}_\alpha y^{\mathrm{u}} \epsilon^{\mathrm{u}}_\alpha \omega^{\mathrm{u}} \left(b^{\mathrm{u}}_\alpha - \frac{h^{\mathrm{u}}_\alpha}{\theta^{\mathrm{u}}} \right) \right]_k \\
&- \sum_{k=1}^{M} \left[\sum_{\alpha=\mathrm{m,w,g}} \left(F^{\mathrm{u}A}_{\alpha,\mathrm{ext}} - \frac{Q^{\mathrm{u}A}_{\alpha,\mathrm{ext}}}{\theta^{\mathrm{u}}} \right) \right]_k
\end{aligned}$$

$$
\begin{aligned}
&- \sum_{k=1}^{M}\left[\sum_{\alpha=\mathrm{m,w}} \rho^{\mathrm{s}}_{\alpha} y^{\mathrm{s}} \epsilon^{\mathrm{s}}_{\alpha} \omega^{\mathrm{s}} \left(b^{\mathrm{s}}_{\alpha} - \frac{h^{\mathrm{s}}_{\alpha}}{\theta^{\mathrm{s}}}\right)\right]_k \\
&- \sum_{k=1}^{M}\left[\sum_{\alpha=\mathrm{m,w}} \left(F^{\mathrm{s\ bot}}_{\alpha} - \frac{Q^{\mathrm{s\ bot}}_{\alpha}}{\theta^{\mathrm{s}}}\right)\right]_k \\
&- \sum_{k=1}^{M}\left[\sum_{\alpha=\mathrm{m,w}} \left(F^{\mathrm{s}A}_{\alpha,\mathrm{ext}} - \frac{Q^{\mathrm{s}A}_{\alpha,\mathrm{ext}}}{\theta^{\mathrm{s}}}\right)\right]_k \\
&- \sum_{k=1}^{M}\left[\rho^{\mathrm{c}} y^{\mathrm{c}} \omega^{\mathrm{c}} \left(b^{\mathrm{c}} - \frac{h^{\mathrm{c}}}{\theta^{\mathrm{c}}}\right)\right]_k - \sum_{k=1}^{M}\left(F^{\mathrm{c\ top}} - \frac{Q^{\mathrm{c\ top}}}{\theta^{\mathrm{c}}}\right)_k \\
&- \sum_{k=1}^{M}\left[\rho^{\mathrm{o}} y^{\mathrm{o}} \omega^{\mathrm{o}} \left(b^{\mathrm{o}} - \frac{h^{\mathrm{o}}}{\theta^{\mathrm{o}}}\right)\right]_k - \sum_{k=1}^{M}\left(F^{\mathrm{o\ top}} - \frac{Q^{\mathrm{o\ top}}}{\theta^{\mathrm{o}}}\right)_k \\
&- \sum_{k=1}^{M}\left[\rho^{\mathrm{r}} m^{\mathrm{r}} \xi^{\mathrm{r}} \left(b^{\mathrm{r}} - \frac{h^{\mathrm{r}}}{\theta^{\mathrm{r}}}\right)\right]_k - \sum_{k=1}^{M}\left(F^{\mathrm{r\ top}} - \frac{Q^{\mathrm{r\ top}}}{\theta^{\mathrm{r}}}\right)_k \\
&- \sum_{k=1}^{M}\left(F^{\mathrm{r}A}_{\mathrm{ext}} - \frac{Q^{\mathrm{r}A}_{\mathrm{ext}}}{\theta^{\mathrm{r}}}\right)_k \\
&- \frac{1}{\theta^{\mathrm{u}}}\sum_{k=1}^{M}\left\{\left[\mathbf{T}^{\mathrm{us}}_{\mathrm{w}} + \mathbf{T}^{\mathrm{uc}}_{\mathrm{w}} + \mathbf{T}^{\mathrm{u}}_{\mathrm{wm}} + \mathbf{T}^{\mathrm{u}}_{\mathrm{wg}} + \mathbf{T}^{\mathrm{u}A}_{\mathrm{w}}\right.\right. \\
&\left.\left. + \frac{1}{2}(e^{\mathrm{uc}} + e^{\mathrm{us}} + e^{\mathrm{u}}_{\mathrm{wg}} + \sum_{l} e^{\mathrm{u}A}_{l})\mathbf{v}^{\mathrm{u},R}\right]\cdot\mathbf{v}^{\mathrm{u},R}\right\}_k \\
&- \frac{1}{\theta^{\mathrm{s}}}\sum_{k=1}^{M}\left\{\left[\mathbf{T}^{\mathrm{so}}_{\mathrm{w}} + \mathbf{T}^{\mathrm{sr}}_{\mathrm{w}} + \mathbf{T}^{\mathrm{su}}_{\mathrm{w}} + \mathbf{T}^{\mathrm{s}}_{\mathrm{wm}} + \mathbf{T}^{\mathrm{sA}}_{\mathrm{w}}\right.\right. \\
&\left.\left. + \frac{1}{2}(e^{\mathrm{sr}} + e^{\mathrm{so}} + e^{\mathrm{su}} + \sum_{l} e^{\mathrm{s}A}_{l})\mathbf{v}^{\mathrm{s},R}\right]\cdot\mathbf{v}^{\mathrm{s},R}\right\}_k \\
&- \frac{1}{\theta^{\mathrm{c}}}\sum_{k=1}^{M}\left\{\left[\mathbf{T}^{\mathrm{co}} + \mathbf{T}^{\mathrm{cu}} + \frac{1}{2}(e^{\mathrm{cu}} + e^{\mathrm{co}})\mathbf{v}^{\mathrm{c},R}\right]\cdot\mathbf{v}^{\mathrm{c},R}\right\}_k \\
&- \frac{1}{\theta^{\mathrm{o}}}\sum_{k=1}^{M}\left\{\left[\mathbf{T}^{\mathrm{or}} + \mathbf{T}^{\mathrm{oc}} + \mathbf{T}^{\mathrm{os}} + \frac{1}{2}(e^{\mathrm{oc}} + e^{\mathrm{or}} + e^{\mathrm{os}})\mathbf{v}^{\mathrm{o},R}\right]\right. \\
&\left.\cdot\mathbf{v}^{\mathrm{o},R}\right\}_k - \frac{1}{\theta^{\mathrm{r}}}\sum_{k=1}^{M} \\
&\times\left\{\left[\mathbf{T}^{\mathrm{ro}} + \mathbf{T}^{\mathrm{rs}} + \mathbf{T}^{\mathrm{r}A} + \frac{1}{2}(e^{\mathrm{ro}} + e^{\mathrm{rs}} + \sum_{l} e^{\mathrm{r}A}_{l})\mathbf{v}^{\mathrm{r},R}\right]\cdot\mathbf{v}^{\mathrm{r},R}\right\}_k \\
&- \frac{1}{\theta^{\mathrm{u}}}\sum_{k=1}^{M}\sum_{l}[(E^{\mathrm{u}}_{\mathrm{w}} - \theta^{\mathrm{u}}\eta^{\mathrm{u}}_{\mathrm{w}})_k - (E^{\mathrm{u}}_{\mathrm{w}} - \theta^{\mathrm{u}}\eta^{\mathrm{u}}_{\mathrm{w}})_l]e^{\mathrm{u}A}_{l}|_k \\
&- \frac{1}{\theta^{\mathrm{s}}}\sum_{k=1}^{M}\sum_{l}[(E^{\mathrm{s}}_{\mathrm{w}} - \theta^{\mathrm{s}}\eta^{\mathrm{s}}_{\mathrm{w}})_k - (E^{\mathrm{s}}_{\mathrm{w}} - \theta^{\mathrm{s}}\eta^{\mathrm{s}}_{\mathrm{w}})_l]e^{\mathrm{s}A}_{l}|_k \\
&- \frac{1}{\theta^{\mathrm{r}}}\sum_{k=1}^{M}\sum_{l}[(E^{\mathrm{r}} - \theta^{\mathrm{r}}\eta^{\mathrm{r}})_k - (E^{\mathrm{r}} - \theta^{\mathrm{r}}\eta^{\mathrm{r}})_l]e^{\mathrm{r}A}_{l}|_k \\
&+ \frac{1}{\theta^{\mathrm{u}}}\sum_{k=1}^{M}[(E^{\mathrm{u}}_{\mathrm{w}} - \theta^{\mathrm{u}}\eta^{\mathrm{u}}_{\mathrm{w}})e^{\mathrm{u}A}_{\mathrm{ext}}]_k \\
&+ \frac{1}{\theta^{\mathrm{s}}}\sum_{k=1}^{M}[(E^{\mathrm{s}}_{\mathrm{w}} - \theta^{\mathrm{s}}\eta^{\mathrm{s}}_{\mathrm{w}})e^{\mathrm{s}A}_{\mathrm{ext}}]_k + \frac{1}{\theta^{\mathrm{c}}}\sum_{k=1}^{M}[(E^{\mathrm{c}} - \theta^{\mathrm{c}}\eta^{\mathrm{c}})e^{\mathrm{c\ top}}]_k \\
&+ \frac{1}{\theta^{\mathrm{o}}}\sum_{k=1}^{M}[(E^{\mathrm{o}} - \theta^{\mathrm{o}}\eta^{\mathrm{o}})e^{\mathrm{o\ top}}]_k \\
&+ \frac{1}{\theta^{\mathrm{r}}}\sum_{k=1}^{M}[(E^{\mathrm{r}} - \theta^{\mathrm{r}}\eta^{\mathrm{r}})e^{\mathrm{r}A}_{\mathrm{ext}}]_k + \frac{1}{\theta^{\mathrm{r}}}\sum_{k=1}^{M}[(E^{\mathrm{r}} - \theta^{\mathrm{r}}\eta^{\mathrm{r}})e^{\mathrm{r\ top}}]_k \\
&- \frac{\theta^{\mathrm{u,s}}}{\theta^{\mathrm{u}}\theta^{\mathrm{s}}}\sum_{k=1}^{M}(Q^{\mathrm{us}}_{\mathrm{w}} + e^{\mathrm{us}}E^{\mathrm{u}}_{\mathrm{w}}))_k - \frac{\theta^{\mathrm{o,r}}}{\theta^{\mathrm{o}}\theta^{\mathrm{r}}}\sum_{k=1}^{M}(Q^{\mathrm{or}} + e^{\mathrm{or}}E^{\mathrm{o}})_k \\
&- \frac{\theta^{\mathrm{u,c}}}{\theta^{\mathrm{u}}\theta^{\mathrm{c}}}\sum_{k=1}^{M}(Q^{\mathrm{uc}}_{\mathrm{w}} + Q^{\mathrm{uc}}_{\mathrm{m}} + Q^{\mathrm{uc}}_{\mathrm{g}} + e^{\mathrm{uc}}E^{\mathrm{u}}_{\mathrm{w}})_k \\
&- \frac{\theta^{\mathrm{c,o}}}{\theta^{\mathrm{c}}\theta^{\mathrm{o}}}\sum_{k=1}^{M}(Q^{\mathrm{co}} + e^{\mathrm{co}}E^{\mathrm{c}})_k - \frac{\theta^{\mathrm{s,o}}}{\theta^{\mathrm{s}}\theta^{\mathrm{o}}}\sum_{k=1}^{M}(Q^{\mathrm{so}}_{\mathrm{w}} + Q^{\mathrm{so}}_{\mathrm{m}} + e^{\mathrm{so}}E^{\mathrm{s}}_{\mathrm{w}})_k \\
&- \frac{\theta^{\mathrm{s,r}}}{\theta^{\mathrm{s}}\theta^{\mathrm{r}}}\sum_{k=1}^{M}(Q^{\mathrm{sr}}_{\mathrm{w}} + Q^{\mathrm{sr}}_{\mathrm{m}} + e^{\mathrm{sr}}E^{\mathrm{s}}_{\mathrm{w}})_k \geq 0 \qquad (44)
\end{aligned}
$$

where:

$$\mathbf{v}^{j,R}_{\alpha} = \mathbf{v}^{j}_{\alpha} - \mathbf{v}^{\mathrm{R}}; \quad j = \mathrm{u,s} \ \ \alpha = \mathrm{m,w,g} \qquad (45)$$

and

$$\mathbf{v}^{j,R} = \mathbf{v}^{j} - \mathbf{v}^{\mathrm{R}}; \ j = \mathrm{c,o,r} \quad \alpha = \mathrm{m,w,g} \qquad (46)$$

are the velocities of the various phases with respect to a reference velocity $\mathbf{v}^R$ whereas

$$\theta^{j,i} = \theta^{j} - \theta^{i}; \ j,i = \mathrm{u,s,c,o,r} \qquad (47)$$

is the temperature difference between the *j*- and the *i*-subregion. In subsequent steps, constitutive relationships will be assumed for the external entropy supplies and the entropy exchanges between the various phases and the surroundings (i.e. atmosphere, soil–groundwater system and the external world) for all subregions and REWs. The inequality (eqn (44)) can be exploited as a constraint on the form of constitutive relationships. This procedure will be presented in detail in a future paper and will be applied to derive a REW-scale theory of water flow.

9 CONCLUSIONS

An averaging procedure has been developed and applied here to formulate a unifying framework for the study of watershed thermodynamics. The watershed is discretized into elementary entities, representative elementary watersheds (REW) by preserving the basic structure of the channel network. The REW is a new concept introduced here for the first time. Each REW is in fact a sub-watershed. Its size may vary from that of the entire watershed to the smallest identifiable sub-watershed; that depends on spatial and temporal resolution of the data available, the type of application, and the time scale of the hydrologic phenomenon to be studied. Each REW is subdivided into five subregions. The subdivision is motivated by hydrological field evidence and identifies flow regions based on geometry and hydrodynamic regime.

REW-scale conservation equations for mass, momentum, energy and entropy have been derived for the ensemble of phases in the unsaturated and the saturated zones and for the water phase in the sub-regions concerned with overland flow and channel flow. The equations are expressed in terms of variables at the scale of the REW. The interactions of a given phase with the remaining phases within a subregion, with the adjacent subregions, and with the neighbouring REWs are accounted for through exchange terms of mass, momentum, energy and entropy at the same scale. Additional averaging of the balance equations in time allows to filter out fluctuations of the dynamic variables at time scales smaller than the scale typical for the specific process under study. The equations, furthermore, depend only on time and represent the REW as being lumped into a single point. The spatial structure of the various subsurface flow zones, overland regions and the channel are represented by average quantities such as surface area fractions and drainage density which are watershed-scale parameters measurable in the field.

The system of equations has a redundant number of variables for which constitutive relationships are necessary. The second law of thermodynamics will be needed as a constraint on any proposed set of constitutive equations. The second law has been derived here by combining the ensemble of phases, subregions and REWs for the whole watershed together. The exploitation of the second law will be the subject of a subsequent paper. The formulation of generic balance equations, of the type presented in this paper, has never been attempted before in watershed hydrology. Also, the fact that equations of momentum and energy balance will be explicitly used in the derivation of constitutive relationships is new. The procedure developed here is invariant with respect to spatial scales and is flexible for the study of hydrological processes evolving over different temporal scales.

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APPENDIX A. CONSERVATION EQUATIONS FOR THE UNSATURATED ZONE (U-SUBREGION)

In the u-subregion the flow is delimited on top by the land surface. It communicates with the saturated s-subregion across the water table, as shown in Fig. 4, and is bounded laterally by the mantle with a horizontal normal. The u-subregion exchanges the thermodynamic property ψ across the water table with the saturated zone (s-subregion) and interacts laterally with the neighbouring REWs and the external world through the mantle. At the top it communicates with the rills, gullies and Hortonian overland flow areas forming the c-subregion. In the present case the global balance laws, written in terms of microscopic quantities, are applied directly to the whole u-subregion. The system is here considered in the most general sense as a three-phase system due to the coexistence of a liquid phase w (water), a solid phase m (soil matrix) and a gaseous phase g (air–vapour mixture within the soil pores).

The balance law will be stated for all three phases, here labelled as α-phases with $\alpha = \mathrm{w, m, g}$. The integration over a phase is performed by making use of phase distribution functions γ_α^j, for $j = \mathrm{u, s}$, as proposed by Gray and Lee.[14] These functions are defined such that they assume the value of 1 within the g-subregion α-phase and are 0 elsewhere. This approach allows the transfer of the integration limits into the integrand and, therefore, to integrate over less complex geometries. The use of a phase distribution function is not needed for the c-, o- and r-subregions because only the water phase is present there.

With reference to Fig. 4, the balance law for an α-phase thermodynamic property within the u-subregion is written as follows:

$$\begin{aligned} &\frac{\mathrm{d}}{\mathrm{d}t}\int_{V^\mathrm{u}}\rho\psi\gamma_\alpha^\mathrm{u}\mathrm{d}V + \int_{A^{\mathrm{u}A}}\mathbf{n}^{\mathrm{u}A}\cdot[\rho(\mathbf{v}-\mathbf{w}^{\mathrm{u}A})\psi-\mathbf{i}]\gamma_\alpha^\mathrm{u}\mathrm{d}A \\ &\quad + \int_{A^\mathrm{uc}} n^\mathrm{uc}\cdot[\rho(\mathbf{v}-\mathbf{w}^\mathrm{uc})\psi-\mathbf{i}]\gamma_\alpha^\mathrm{u}\mathrm{d}A \\ &\quad + \int_{A^\mathrm{us}} n^\mathrm{us}\cdot[\rho(\mathbf{v}-\mathbf{w}^\mathrm{us})\psi-\mathbf{i}]\gamma_\alpha^\mathrm{u}\mathrm{d}A \\ &\quad + \sum_{\beta\neq\alpha}\int_{S_{\alpha\beta}^\mathrm{u}} n^{\alpha\beta}\cdot[\rho(\mathbf{v}-\mathbf{w}^{\alpha\beta})\psi-\mathbf{i}]\gamma_\alpha^\mathrm{u}\mathrm{d}S + \int_V \rho f\gamma_\alpha^\mathrm{u}\mathrm{d}V \\ &= \int_{V^\mathrm{u}} G\gamma_\alpha^\mathrm{u}\mathrm{d}V;\ \ \alpha = \mathrm{m,w,g} \end{aligned} \tag{A1}$$

where the inter-subregion boundary surfaces $A^{\mathrm{u}A}$ and $A^{\mathrm{u}j}$, the phase interfaces $S_{\alpha\beta}^\mathrm{u}$, the unit normal vectors $\mathbf{n}^{\mathrm{u}A}$ and $\mathbf{n}^{\mathrm{u}j}$ and the velocities $\mathbf{v}_\alpha^\mathrm{u}$, $\mathbf{w}^{\mathrm{u}A}$, and $\mathbf{w}^{\mathrm{u}j}$ and $\mathbf{w}^{\alpha\beta}$ have been defined in Section 5. The inter-subregion boundary A^us is formed by the water table and A^uc by the part of land surface affected by concentrated overland flow. The summation $\sum_{\beta\neq\alpha}$ extends over all phases different from the α-phase. Eqn (A1) is successively averaged in time by integrating each term separately over the interval $(t - \Delta t, t + \Delta t)$ and dividing by $2\Delta t$. According to a well-known theorem (see Whitaker[34], pp. 192–193), the order of time integration and time differentiation may be changed so that the first term in eqn (A1) becomes:

$$\begin{aligned} &\frac{1}{2\Delta t}\frac{\mathrm{d}}{\mathrm{d}t}\int_{t-\Delta t}^{t+\Delta t}\int_{V^\mathrm{u}}\rho\psi\gamma_\alpha^\mathrm{s}\mathrm{d}V\mathrm{d}\tau \\ &\quad = \frac{1}{2\Delta t}\frac{\mathrm{d}}{\mathrm{d}t}\int_{t-\Delta t}^{t+\Delta t}\int_{V^\mathrm{u}}\rho\psi\gamma_\alpha^\mathrm{u}\mathrm{d}V\mathrm{d}\tau \end{aligned} \tag{A2}$$

Now, applying the definition of average quantities Section (5)–(8) and (15), introduced in Section 5, one obtains:

$$\frac{1}{2\Delta t}\frac{\mathrm{d}}{\mathrm{d}t}\int_{t-\Delta t}^{t+\Delta t}\int_{V^\mathrm{u}}\rho\psi\gamma_\alpha^\mathrm{u}\mathrm{d}V\mathrm{d}\tau = \frac{\mathrm{d}}{\mathrm{d}t}(\epsilon_\alpha^\mathrm{u} y^\mathrm{u}\omega^\mathrm{u} < \rho >_\alpha^\mathrm{u} \bar{\psi}_\alpha^\mathrm{u}\Sigma) \tag{A3}$$

Next, a series of REW-scale exchange terms can be defined for the u-subregion:

$$e_\alpha^{\mathrm{u}A} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{\mathrm{u}A}}\mathbf{n}^{\mathrm{u}A}\cdot[\rho(\mathbf{w}^{\mathrm{u}A}-\mathbf{v})]\gamma_\alpha^\mathrm{u}\mathrm{d}A\mathrm{d}\tau;\quad \alpha = \mathrm{m,w,g} \tag{A4}$$

is the REW-scale mass exchange of the u-subregion α-phase across the mantle A, while

$$I_\alpha^{uA} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{uA}} \mathbf{n}^{uA}\cdot[\mathbf{i} - \rho(\mathbf{v} - \mathbf{w}^{uA})\tilde{\psi}_\alpha^u]\gamma_\alpha^u \mathrm{d}A\mathrm{d}\tau$$
$$\alpha = \mathrm{m, w, g} \quad (A5)$$

is the non-convective exchange of the property ψ of the α-phase across A. The quantity $\tilde{\psi}_\alpha^u$ is the deviation of ψ from its space and time average value:

$$\tilde{\psi}_\alpha^u = \psi - \bar{\psi}_\alpha^u \quad (A6)$$

We observe that the exchange terms defined through eqns (A4) and (A5) can be rewritten as a sum of exchanges across the various segments forming the mantle, as shown in eqn (2). As a result we can state the following equalities:

$$e_\alpha^{uA} = \sum_l e_{\alpha,l}^{uA} + e_{\alpha,\mathrm{ext}}^{uA} \quad (A7)$$

$$I_\alpha^{uA} = \sum_l I_{\alpha,l}^{uA} + I_{\alpha,\mathrm{ext}}^{uA} \quad (A8)$$

where the sum extends over the N_k mantle segments which the REW has in common with neighbouring REWS. The second term on the r.h.s. is non-zero only for those REWs, which have one or more mantle segments in common with the external boundary of the watershed. It is implicit for all the other balance equations of the unsaturated zone that the exchanges across the mantle can be separated into the components relative to each segment. Following on, the quantities defined as:

$$e_\alpha^{uj} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{uj}} \mathbf{n}^{uj}\cdot[\rho(\mathbf{w}^{uj} - \mathbf{v})]\gamma_\alpha^u \mathrm{d}A\mathrm{d}\tau;$$
$$j = \mathrm{s, c} \quad \alpha = \mathrm{m, w, g} \quad (A9)$$

are the mass exchange terms of the u-subregion α-phase with the saturated zone across the water table A^{us}, and with the concentrated overland flow across the areas of land surface A^{uc}, whereas

$$I_\alpha^{uj} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{us}} \mathbf{n}^{uj}\cdot[\mathbf{i} - \rho(\mathbf{v} - \mathbf{w}^{uj})\tilde{\psi}_\alpha^u]\gamma_\alpha^u \mathrm{d}A\mathrm{d}\tau$$
$$j = \mathrm{s, c} \quad \alpha = \mathrm{m, w, g} \quad (A10)$$

are the non-convective interactions between the u-subregion α-phase, the underlying saturated zone and the concentrated overland flow, respectively. In a similar fashion

$$e_{\alpha\beta}^{u} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{S_{\alpha\beta}^{u}} \mathbf{n}^{\alpha\beta}\cdot[\rho(\mathbf{w}^{\alpha\beta} - \mathbf{v})]\gamma_\alpha^u \mathrm{d}S\mathrm{d}\tau;$$
$$\alpha, \beta = \mathrm{m, w, g} \quad (A11)$$

is the mass exchange term between the α-phase and the remaining phases. The term defined as:

$$I_{\alpha\beta}^{uj} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{S_{\alpha\beta}^{us}} n^{\alpha\beta}\cdot[\mathbf{i} - \rho(\mathbf{v} - \mathbf{w}^{\alpha\beta})\tilde{\psi}_\alpha^u]\gamma_\alpha^u \mathrm{d}S\mathrm{d}\tau$$
$$\alpha, \beta = \mathrm{m, w, g} \quad (A12)$$

is the non-convective exchange of property ψ between the α-phase and the other phases, accounting for the inter-phase exchanges of momentum, energy and entropy. Substitution of the exchange terms into the previously time-averaged eqn (A1) and use of the average quantities eqns (5)–(8) and (15), yields the generic balance law for the u-subregion α-phase:

$$\frac{\mathrm{d}}{\mathrm{d}t}(\langle\rho\rangle_\alpha^u y^u \epsilon_\alpha^u \bar{\psi}_\alpha^u \omega^u \Sigma) - (e_\alpha^{uA}\bar{\psi}_\alpha^u + I_\alpha^{uA})\Sigma - \langle\rho\rangle_\alpha^u y^u \epsilon_\alpha^u \bar{f}_\alpha^u \omega^u \Sigma$$
$$= \langle G\rangle_\alpha^u \omega^u \Sigma + (e_\alpha^{us}\bar{\psi}_\alpha^u + I_\alpha^{us})\Sigma + (e_\alpha^{uc}\bar{\psi}_\alpha^u + I_\alpha^{uc})\Sigma$$
$$+ \sum_{\beta\neq\alpha}(e_{\alpha\beta}^u \psi_\alpha^u + I_{\alpha\beta}^u)\Sigma; \alpha = \mathrm{m, w, g} \quad (A13)$$

In the interest of brevity the averaging symbols are omitted unless otherwise confusion arises. Thus, the following REW-scale quantities are defined:

$$\langle\rho\rangle_\alpha^u = \rho_\alpha^u \quad (A14)$$

$$\bar{\psi}_\alpha^u = \psi_\alpha^u \quad (A15)$$

$$\bar{f}_\alpha^u = f_\alpha^u \quad (A16)$$

$$\langle G\rangle_\alpha^u = G_\alpha^u \quad (A17)$$

eqn (A14) can be recast after division by the total projected surface area Σ in the form:

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho_\alpha^u \psi_\alpha^u y^u \epsilon_\alpha^u \omega^u) - (e_\alpha^{uA}\psi_\alpha^u + I_\alpha^{uA}) - \rho_\alpha^u f_\alpha^u y^u \epsilon_\alpha^u \omega^u$$
$$= G_\alpha^u \omega^u + (e_\alpha^{us}\psi_\alpha^u + I_\alpha^{us}) + (e_\alpha^{uc}\psi_\alpha^u + I_\alpha^{uc})$$
$$+ \sum_{\beta\neq\alpha}(e_{\alpha\beta}^u \psi_\alpha^u + I_{\alpha\beta}^u); \alpha = \mathrm{m, w, g}$$

For the water, the general conservation equation can be rewritten in terms of the water saturation s_w^u and the average porosity ϵ^u, defined by eqn (9):

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho_\alpha^u \psi_w^u y^u s_w^u \epsilon^u \omega^u) - (e_w^{uA}\psi_w^u + I_w^{uA}) - \rho_\alpha^u f_w^u y^u s_w^u \epsilon^u \omega^u = \quad (A18)$$
$$G_w^u \omega^u + (e_w^{us}\psi_w^u + I_w^{us}) + (e_w^{uc}\psi_w^u + I_w^{uc})$$
$$+ \sum_{\beta=\mathrm{s,g}}(e_{w\beta}^u \psi_w^u + I_{w\beta}^u)$$

In the subsequent paragraphs the α-phase conservation equations for mass, momentum, energy and entropy will be derived for the u-subregion.

Appendix A.1. Conservation of mass

For the α-phase mass conservation within the u-subregion the microscale properties have to be defined according to Table 2 such that $\psi = 1$, $\mathbf{i} = 0$, $f = 0$ and $G = 0$. Subsequently, eqn (A18) is reduced to the general form of the mass balance for the u-subregion α-phase:

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho_\alpha^u y^u \epsilon_\alpha^u \omega^u) = e_\alpha^{uA} + e_\alpha^{us} + e_\alpha^{uc} + e_{\alpha\beta}^u \quad (A19)$$

The terms on the r.h.s. account for the mass exchange of the α-phase with the neighbouring REWs and the external world across the mantle, with the adjacent s- and c-subregions, and with the remaining phases within the u-subregion.

Appendix A.2. Conservation of momentum

The REW-scale α-phase equation for conservation of momentum is derived by selecting the microscale properties from Table 2 such that $\psi = \mathbf{v}$, $\mathbf{i} = \mathbf{t}$, $f = \boldsymbol{g}$ and $G = 0$. Substitution into eqn (A18) yields:

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho_\alpha^{\mathrm{u}}\mathbf{v}_\alpha^{\mathrm{u}}y^{\mathrm{u}}\epsilon_\alpha^{\mathrm{u}}\omega^{\mathrm{u}}) - (e_\alpha^{\mathrm{u}A}\mathbf{v}_\alpha^{\mathrm{u}} + \mathbf{T}_\alpha^{\mathrm{u}A}) - \rho_\alpha^{\mathrm{u}}y^{\mathrm{u}}\epsilon_\alpha^{\mathrm{u}}\boldsymbol{g}_\alpha^{\mathrm{u}}\omega^{\mathrm{u}} = (e_\alpha^{\mathrm{us}}\mathbf{v}_\alpha^{\mathrm{u}} + \mathbf{T}_\alpha^{\mathrm{us}}) + (e_\alpha^{\mathrm{uc}}\mathbf{v}_\alpha^{\mathrm{u}} + \mathbf{T}_\alpha^{\mathrm{uc}}) + \sum_{\beta\neq\alpha}(e_{\alpha\beta}^{\mathrm{u}}\mathbf{v}_\alpha^{\mathrm{u}} + \mathbf{T}_{\alpha\beta}^{\mathrm{u}}) \tag{A20}$$

where:

$$\mathbf{T}_\alpha^{\mathrm{u}A} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{\mathrm{u}A}}\mathbf{n}^{\mathrm{u}A}\cdot[\mathbf{t} - \rho(\mathbf{v}^- \mathbf{w}^{\mathrm{u}A})\tilde{\mathbf{v}}_\alpha^{\mathrm{u}}]\gamma_\alpha^{\mathrm{u}}\mathrm{d}A\mathrm{d}\tau \tag{A21}$$

is the REW-scale momentum exchange of the u-subregion α-phase with the neighbouring REWs and the external world across the mantle A and

$$\mathbf{T}_\alpha^{\mathrm{u}j} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{\mathrm{u}j}}\mathbf{n}^{\mathrm{u}j}\cdot[\mathbf{t} - \rho(\mathbf{v}_- \mathbf{w}^{\mathrm{u}j})\tilde{\mathbf{v}}_\alpha^{\mathrm{u}}]\gamma_\alpha^{\mathrm{u}}\mathrm{d}A\mathrm{d}\tau; \quad j = \mathrm{s, c} \tag{A22}$$

are the momentum exchange terms with the s-subregion across A^{us} and with the c-subregion through A^{uc}, respectively. Furthermore,

$$\mathbf{T}_{\alpha\beta}^{\mathrm{u}} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{S_{\alpha\beta}^{\mathrm{u}}}\mathbf{n}^{\alpha\beta}\cdot[\mathbf{t} - \rho(\mathbf{v} - \mathbf{w}^{\alpha\beta})\tilde{\mathbf{v}}_\alpha^{\mathrm{u}}]\gamma_\alpha^{\mathrm{u}}\mathrm{d}S\mathrm{d}\tau; \quad \alpha,\beta = \mathrm{m, w, g} \tag{A23}$$

is the momentum exchange between the α-phase and the remaining phases filling the u-subregion. Multiplication of the mass conservation eqn (A19) by the average velocity $\mathbf{v}_\alpha^{\mathrm{u}}$ and subsequent subtraction from eqn (A20) gives the momentum balance in the following form:

$$(\rho_\alpha^{\mathrm{u}}y^{\mathrm{u}}\epsilon_\alpha^{\mathrm{u}}\omega^{\mathrm{u}})\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{v}_\alpha^{\mathrm{u}} - \mathbf{T}_\alpha^{\mathrm{u}A} - \rho_\alpha^{\mathrm{u}}y^{\mathrm{u}}\epsilon_\alpha^{\mathrm{u}}\boldsymbol{g}_\alpha^{\mathrm{u}}\omega^{\mathrm{u}} = \mathbf{T}_\alpha^{\mathrm{us}} + \mathbf{T}_\alpha^{\mathrm{uc}} + \sum_{\beta\neq\alpha}\mathbf{T}_{\alpha\beta}^{\mathrm{u}} \tag{A24}$$

Appendix A.3. Conservation of energy

The REW-scale α-phase equation for conservation of energy for the u-subregion is derived by defining the microscale properties after Table 2, such that $\psi = E + v^2/2$, $\mathbf{i} = (\mathbf{t}\cdot\mathbf{v} + \mathbf{q})$, $f = (\boldsymbol{g}\cdot\mathbf{v} + h)$ and $G = 0$. Substitution of these quantities into eqn (A18) leads to:

$$\frac{\mathrm{d}}{\mathrm{d}t}\{\rho_\alpha^{\mathrm{u}}y^{\mathrm{u}}\epsilon_\alpha^{\mathrm{u}}[E_\alpha^{\mathrm{u}} + (\mathbf{v}_\alpha^{\mathrm{u}})^2/2]\omega^{\mathrm{u}}\} - \{e_\alpha^{\mathrm{u}A}[E_\alpha^{\mathrm{u}} + (\mathbf{v}_\alpha^{\mathrm{u}})^2/2] + \mathbf{T}_\alpha^{\mathrm{u}A}\cdot\mathbf{v}_\alpha^{\mathrm{u}} + Q_\alpha^{\mathrm{u}A}\} - \rho_\alpha^{\mathrm{u}}y^{\mathrm{u}}\epsilon_\alpha^{\mathrm{u}}(\boldsymbol{g}_\alpha^{\mathrm{u}}\cdot\mathbf{v}_\alpha^{\mathrm{u}} + h_\alpha^{\mathrm{u}})\omega^{\mathrm{u}}$$
$$= \{e_\alpha^{\mathrm{us}}[E_\alpha^{\mathrm{u}} + (\mathbf{v}_\alpha^{\mathrm{u}})^2/2] + \mathbf{T}_\alpha^{\mathrm{us}}\cdot\mathbf{v}_\alpha^{\mathrm{u}} + Q_\alpha^{\mathrm{us}}\} + \{e_\alpha^{\mathrm{uc}}[E_\alpha^{\mathrm{u}} + (\mathbf{v}_\alpha^{\mathrm{u}})^2/2] + \mathbf{T}_\alpha^{\mathrm{uc}}\cdot\mathbf{v}_\alpha^{\mathrm{u}} + Q_\alpha^{\mathrm{uc}}\} + \sum_{\beta\neq\alpha}\{e_{\alpha\beta}^{\mathrm{u}}[E_\alpha^{\mathrm{u}} + (\mathbf{v}_\alpha^{\mathrm{u}})^2/2] + \mathbf{T}_{\alpha\beta}^{\mathrm{u}}\cdot\mathbf{v}_\alpha^{\mathrm{u}} + Q_{\alpha\beta}^{\mathrm{u}}\} \tag{A25}$$

where:

$$E_\alpha^{\mathrm{u}} = \bar{E}_\alpha^{\mathrm{u}} + \overline{(\tilde{v}_\alpha^{\mathrm{u}})^{2^{\mathrm{u}}}}/2 \tag{A26}$$

$$h_\alpha^{\mathrm{u}} = \bar{h}_\alpha^{\mathrm{u}} + \overline{\tilde{\boldsymbol{g}}_\alpha^{\mathrm{u}}\cdot\tilde{\mathbf{v}}_\alpha^{\mathrm{u}}\mathrm{u}} \tag{A27}$$

are the REW-scale internal energy and the total heat supply from the external world, respectively. The r.h.s. terms of the last two equations are composed of the average of microscopic values plus a term attributable to sub-REW-scale fluctuations. The definitions of $\tilde{\mathbf{v}}_\alpha^{\mathrm{u}}$ and $\tilde{\boldsymbol{g}}_\alpha^{\mathrm{u}}$ are given similarly to eqn (A6). In the case of eqn (A26) the second term on the r.h.s. is given by averaged sub-REW scale deviations of kinetic energy and for eqn (A27) by deviations of velocity and gravity. Further, note the following definitions:

$$Q_\alpha^{\mathrm{u}A} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{\mathrm{u}A}}\mathbf{n}^{\mathrm{u}A}\cdot\{\mathbf{q} + \mathbf{t}\cdot\tilde{\mathbf{v}}_\alpha^{\mathrm{u}} - \rho(\mathbf{v} - \mathbf{w}^{\mathrm{u}A}) \times [\tilde{E}_\alpha^{\mathrm{u}} + (\tilde{v}_\alpha^{\mathrm{u}})^2/2]\}\gamma_\alpha^{\mathrm{u}}\mathrm{d}A\mathrm{d}\tau \tag{A28}$$

is the energy exchange of the u-subregion α-phase across the mantle. Next, the terms defined as

$$Q_\alpha^{\mathrm{u}j} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{\mathrm{u}j}}\mathbf{n}^{\mathrm{u}j}\cdot\{\mathbf{q} + \mathbf{t}\cdot\tilde{\mathbf{v}}_\alpha^{\mathrm{u}} - \rho(\mathbf{v} - \mathbf{w}^{\mathrm{u}j}) \times [\tilde{E}_\alpha^{\mathrm{u}} + (\tilde{v}_\alpha^{\mathrm{u}})^2/2]\}\gamma_\alpha^{\mathrm{u}}\mathrm{d}A\mathrm{d}\tau; \; j = \mathrm{s, c} \tag{A29}$$

are the energy exchanges with the s-subregion and the c-subregion, respectively, while

$$Q_{\alpha\beta}^{\mathrm{u}} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{S_{\alpha\beta}^{\mathrm{u}j}}\mathbf{n}^{\alpha\beta}\cdot\{\mathbf{q} + \mathbf{t}\cdot\tilde{\mathbf{v}}_\alpha^{\mathrm{u}} - \rho(\mathbf{v} - \mathbf{w}^{\alpha\beta}) \times [\tilde{E}_\alpha^{\mathrm{u}} + (\tilde{v}_\alpha^{\mathrm{u}})^2/2]\}\gamma_\alpha^{\mathrm{u}}\mathrm{d}S\mathrm{d}\tau; \; \alpha,\beta = \mathrm{m, w, g} \tag{A30}$$

is the energy exchange between the α-phase and the remaining phases. The quantity

$$\tilde{E}_\alpha^{\mathrm{u}} = E_\alpha + (\bar{E}_\alpha^{\mathrm{u}} + \overline{(\tilde{v}_\alpha^{\mathrm{u}})^{2^{\mathrm{u}}}})/2 = E_\alpha - E_\alpha^{\mathrm{u}} \tag{A31}$$

is the deviation of the α-phase internal energy from its average value. Subtraction of the equation for conservation of mass (eqn (A19)), multiplied by $E_\alpha^{\mathrm{u}} + (v_\alpha^{\mathrm{u}})^2/2$, from eqn (A25) yields:

$$(\rho_\alpha^{\mathrm{u}}y^{\mathrm{u}}\epsilon_\alpha^{\mathrm{u}}\omega^{\mathrm{u}})\frac{\mathrm{d}}{\mathrm{d}t}[E_\alpha^{\mathrm{u}} + (v_\alpha^{\mathrm{u}})^2/2] - (\mathbf{T}_\alpha^{\mathrm{u}A}\cdot\mathbf{v}_\alpha^{\mathrm{u}} + Q_\alpha^{\mathrm{u}A}) - \rho_\alpha^{\mathrm{u}}y^{\mathrm{u}}\epsilon_\alpha^{\mathrm{u}}(\boldsymbol{g}_\alpha^{\mathrm{u}}\cdot\mathbf{v}_\alpha^{\mathrm{u}} + h_\alpha^{\mathrm{u}})\omega^{\mathrm{u}} = (\mathbf{T}_\alpha^{\mathrm{us}}\cdot\mathbf{v}_\alpha^{\mathrm{u}} + Q_\alpha^{\mathrm{us}}) + (\mathbf{T}_\alpha^{\mathrm{uc}}\cdot\mathbf{v}_\alpha^{\mathrm{u}} + Q_\alpha^{\mathrm{uc}}) + \sum_{\beta\neq\alpha}(\mathbf{T}_{\alpha\beta}^{\mathrm{u}}\cdot\mathbf{v}_\alpha^{\mathrm{u}} + Q_{\alpha\beta}^{\mathrm{u}}) \tag{A32}$$

The mechanical energy balance equation is obtained by forming the inner product of the velocity $\mathbf{v}_\alpha^{\mathrm{u}}$ with the momentum balance eqn (A24):

$$(\rho_\alpha^{\mathrm{u}} y^{\mathrm{u}} \epsilon_\alpha^{\mathrm{u}} \omega^{\mathrm{u}}) \frac{\mathrm{d}}{\mathrm{d}t}[(v_\alpha^{\mathrm{u}})^2/2] - \mathbf{T}_\alpha^{\mathrm{u}A} \cdot \mathbf{v}_\alpha^{\mathrm{u}} - \rho_\alpha^{\mathrm{u}} y^{\mathrm{u}} \epsilon_\alpha^{\mathrm{u}} (\boldsymbol{g}_\alpha^{\mathrm{u}} \cdot \mathbf{v}_\alpha^{\mathrm{u}}) \omega^u = \mathbf{T}_\alpha^{\mathrm{us}} \cdot \mathbf{v}_\alpha^{\mathrm{u}} + \mathbf{T}_\alpha^{\mathrm{uc}} \cdot \mathbf{v}_\alpha^{\mathrm{u}} + \sum_{\beta \neq \alpha} \mathbf{T}_{\alpha\beta}^{\mathrm{u}} \cdot \mathbf{v}_\alpha^{\mathrm{u}} \tag{A33}$$

Appendix A.4. Balance of entropy

The balance of entropy for the u-subregion α-phase is obtained by defining the microscale properties following Table 2 as $\psi = \eta$, $\mathbf{i} = \mathbf{j}$, $f = b$ and $G = L$. The resulting equation is:

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho_\alpha^{\mathrm{u}} y^{\mathrm{u}} \epsilon_\alpha^{\mathrm{u}} \omega^{\mathrm{u}}) - F_\alpha^{\mathrm{u}A} - \rho_\alpha^{\mathrm{u}} y^{\mathrm{u}} \epsilon_\alpha^{\mathrm{u}} b_\alpha^{\mathrm{u}} \omega^{\mathrm{u}} = L_\alpha^{\mathrm{u}} \omega^{\mathrm{u}} + (e_\alpha^{\mathrm{us}} \eta_\alpha^{\mathrm{u}} + F_\alpha^{\mathrm{us}}) + (e_\alpha^{\mathrm{uc}} \eta_\alpha^{\mathrm{u}} + F_\alpha^{\mathrm{uc}}) + \sum_{\beta \neq \alpha} F_{\alpha\beta}^{\mathrm{u}} \tag{A34}$$

where:

$$\eta_\alpha^{\mathrm{u}} = \bar{\eta}_\alpha^{\mathrm{u}} \tag{A35}$$

$$b_\alpha^{\mathrm{u}} = \bar{b}_\alpha^{\mathrm{u}} \tag{A36}$$

$$L_\alpha^{\mathrm{u}} = \langle L \rangle_\alpha^{\mathrm{u}} \tag{A37}$$

are the average entropy and the REW-scale terms of entropy supply and internal generation of entropy, respectively, while

$$F_\alpha^{\mathrm{u}A} = \frac{1}{2\Delta t \Sigma} \int_{t-\Delta t}^{t+\Delta t} \int_{A^{\mathrm{u}A}} \mathbf{n}^{\mathrm{u}A} \cdot [\mathbf{j} - \rho(\mathbf{v} - \mathbf{w}^{\mathrm{u}A}) \tilde{\eta}_\alpha^{\mathrm{u}}] \gamma_\alpha^{\mathrm{u}} \mathrm{d}A \mathrm{d}\tau \tag{A38}$$

is the entropy exchange across the mantle A, and

$$F_\alpha^{\mathrm{u}j} = \frac{1}{2\Delta t \Sigma} \int_{t-\Delta t}^{t+\Delta t} \int_{A^{\mathrm{u}j}} \mathbf{n}^{\mathrm{u}j} \cdot [\mathbf{j} - \rho(\mathbf{v} - \mathbf{w}^{\mathrm{u}j}) \tilde{\eta}_\alpha^{\mathrm{u}}] \gamma_\alpha^{\mathrm{u}} \mathrm{d}A \mathrm{d}\tau \quad j = \mathrm{s, c} \tag{A39}$$

are the entropy fluxes into the s- and c-subregions, respectively. Finally,

$$F_{\alpha\beta}^{\mathrm{u}} = \frac{1}{2\Delta t \Sigma} \int_{t-\Delta t}^{t+\Delta t} \int_{S_{\alpha\beta}^{\mathrm{u}}} \mathbf{n}^{\alpha\beta} \cdot [\mathbf{j} - \rho(\mathbf{v} - \mathbf{w}^{\alpha\beta}) \tilde{\eta}_\alpha^{\mathrm{u}}] \gamma_\alpha^{\mathrm{u}} \mathrm{d}S \mathrm{d}\tau \quad \alpha, \beta = \mathrm{m, w, g} \tag{A40}$$

account for the REW-scale intra-subregion entropy exchange between the α-phase and the remaining phases.

APPENDIX B. CONSERVATION EQUATIONS FOR THE SATURATED ZONE (S-SUBREGION)

The saturated zone (s-subregion) comprises the subsurface region, which is saturated with water, as depicted in Fig. 4. The s-subregion exchanges water with the overlying subregions: the unsaturated zone, the saturated overland flow and the main channel reach. At the bottom, the saturated zone can be confined either by impermeable strata or can interact with the deep groundwater reservoir. The contact surface between the s-subregion and the channel is defined by the channel bed, which is carved into the soil, while the contact surface with the o-subregion is coincident with the saturated land surface. Interaction with the neighbouring REWs or the external world across the mantle surface A is also possible, as evident from Figs 3 and 4.

The saturated zone constitutes a two-phase system due to the coexistence of water and soil matrix. The general balance law for a thermodynamic property for the s-subregion α-phase is written as follows:

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_{V^{\mathrm{s}}} \rho \psi \gamma_\alpha^{\mathrm{s}} \mathrm{d}V + \int_{A^{\mathrm{s}A}} \mathbf{n}^{\mathrm{s}A} \cdot [\rho(\mathbf{v} - \mathbf{w}^{\mathrm{s}A})\psi - \mathbf{i}] \gamma_\alpha^{\mathrm{s}} \mathrm{d}A \mathrm{d}\tau + \int_{A^{\mathrm{us}}} \mathbf{n}^{\mathrm{su}} \cdot [\rho(\mathbf{v} - \mathbf{w}^{\mathrm{us}})\psi - \mathbf{i}] \gamma_\alpha^{\mathrm{s}} \mathrm{d}A \mathrm{d}\tau + \sum_{j=\mathrm{o,r}} \int_{A^{\mathrm{s}j}} \mathbf{n}^{\mathrm{s}j} \cdot [\rho(\mathbf{v} - \mathbf{w}^{\mathrm{s}j})\psi - \mathbf{i}] \gamma_\alpha^{\mathrm{s}} \mathrm{d}A \mathrm{d}\tau + \int_{A_{\mathrm{bot}}^{\mathrm{s}}} \mathbf{n}^{\mathrm{s}} \cdot [\rho(\mathbf{v} - \mathbf{w}_{\mathrm{bot}}^{\mathrm{s}})\psi - \mathbf{i}] \gamma_\alpha^{\mathrm{s}} \mathrm{d}A \mathrm{d}\tau + \int_{S_{\alpha\beta}^{\mathrm{s}}} \mathbf{n}^{\alpha\beta} \cdot [\rho(\mathbf{v} - \mathbf{w}^{\alpha\beta})\psi - \mathbf{i}] \gamma_\alpha^{\mathrm{s}} \mathrm{d}S - \int_{V^{\mathrm{s}}} \rho f \gamma_\alpha^{\mathrm{s}} \mathrm{d}V = \int_{V^{\mathrm{s}}} G \gamma_\alpha^{\mathrm{s}} \mathrm{d}V; \quad \alpha = \mathrm{m, w} \tag{B1}$$

where the contact surface A^{so} (seepage face) is formed by the saturated land surface, in immediate contact with the sheet of water forming the overland flow, and A^{sr} is defined by the channel bed. Following a time averaging procedure similar to that outlined for the u-subregion, the first term becomes:

$$\frac{1}{2\Delta t} \frac{\mathrm{d}}{\mathrm{d}t} \int_{t-\Delta t}^{t+\Delta t} \int_{V^{\mathrm{s}}} \rho \psi \gamma_\alpha^{\mathrm{s}} \mathrm{d}V \mathrm{d}\tau = \frac{\mathrm{d}}{\mathrm{d}t}(\epsilon_\alpha^{\mathrm{s}} y^{\mathrm{s}} \omega^{\mathrm{s}} \langle \rho \rangle_\alpha^{\mathrm{s}} \bar{\psi}_\alpha^{\mathrm{s}} \Sigma) \tag{B2}$$

Furthermore, the following REW-scale exchange terms can be defined:

$$e_\alpha^{\mathrm{s}A} = \frac{1}{2\Delta t \Sigma} \int_{t-\Delta t}^{t+\Delta t} \int_{A^{\mathrm{s}A}} \mathbf{n}^{\mathrm{s}A} \cdot [\rho(\mathbf{w}^{\mathrm{s}A} - \mathbf{v})] \gamma_\alpha^{\mathrm{s}} \mathrm{d}A \mathrm{d}\tau; \quad \alpha = \mathrm{m, w} \tag{B3}$$

and

$$I_\alpha^{\mathrm{s}A} = \frac{1}{2\Delta t \Sigma} \int_{t-\Delta t}^{t+\Delta t} \int_{A^{\mathrm{s}A}} \mathbf{n}^{\mathrm{s}A} \cdot [\mathbf{i} - \rho(\mathbf{v} - \mathbf{w}^{\mathrm{s}A}) \tilde{\psi}_\alpha^{\mathrm{s}}] \gamma_\alpha^{\mathrm{s}} \mathrm{d}A \mathrm{d}\tau \quad \alpha = \mathrm{m, w} \tag{B4}$$

are the REW-scale mass exchange and the non-convective interaction of the α-phase across the mantle surface A, where the deviation quantity $\tilde{\psi}_\alpha^{\mathrm{s}}$ is defined in analogy to eqn (A6). Similar to what we observed for the u-subregion, the eqns (B3) and (B4) can be written as a sum of components relative to each segment forming part of the mantle (see eqn (2)):

$$e_\alpha^{uA} = \sum_l e_{\alpha,l}^{uA} + e_{\alpha,\text{ext}}^{uA} \tag{B5}$$

$$I_\alpha^{uA} = \sum_l I_{\alpha,l}^{uA} + I_{\alpha,\text{ext}}^{uA} \tag{B6}$$

where the second term on the r.h.s. is non-zero only for REWs which have part of the mantle in common with the external watershed boundary. For all the following balance equations the exchange across the mantle is implicitly understood as a sum of more components. Next,

$$e_\alpha^{sj} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{sj}} \mathbf{n}^{sj}\cdot[\rho(\mathbf{w}^{sj}-\mathbf{v})]\gamma_\alpha^{u}\mathrm{d}A\mathrm{d}\tau; \quad j = \mathrm{u,o,r} \quad \alpha = \mathrm{m,w} \tag{B7}$$

and

$$I_\alpha^{sj} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{sj}} \mathbf{n}^{sj}\cdot[\mathbf{i}-\rho(\mathbf{v}-\mathbf{w}^{sj})\tilde{\psi}_\alpha^{s}]\gamma_\alpha^{s}\mathrm{d}A\mathrm{d}\tau \quad j = \mathrm{u,o,r} \quad \alpha = \mathrm{m,w} \tag{B8}$$

are the mass exchange and the non-convective interaction of the s-subregion α-phase with the unsaturated zone, with the overland flow region and the channel, for solid and water phases, respectively. In a similar fashion we define

$$e_\alpha^{s\,\text{bot}} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A_{\text{bot}}^{s}} \mathbf{n}^{s}\cdot[\rho(\mathbf{w}_{\text{bot}}^{s}-\mathbf{v})]\gamma_\alpha^{s}\mathrm{d}A\mathrm{d}\tau; \quad \alpha = \mathrm{m,w} \tag{B9}$$

as the mass exchange term, and

$$I_\alpha^{s\,\text{bot}} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A_{\text{bot}}^{s}} \mathbf{n}^{s}\cdot[\mathbf{i}-\rho(\mathbf{v}-\mathbf{w}_{\text{bot}}^{s})\tilde{\psi}_\alpha^{s}]\gamma_\alpha^{s}\mathrm{d}A\mathrm{d}\tau \quad \alpha = \mathrm{m,w} \tag{B10}$$

as the non-convective exchange of ψ between water and solid phase of the saturated zone, the deep groundwater or the underlying impermeable strata. Finally,

$$e_{\alpha\beta}^{s} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{S_{\alpha\beta}^{s}} \mathbf{n}^{\alpha\beta}\cdot[\rho(\mathbf{w}^{\alpha\beta}-\mathbf{v})]\gamma_\alpha^{s}\mathrm{d}S; \quad \alpha,\beta = \mathrm{m,w} \tag{B11}$$

is the mass exchange between the α-phase and the β-phase, while

$$I_{\alpha\beta}^{s} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{S_{\alpha\beta}^{s}} \mathbf{n}^{\alpha\beta}\cdot[\mathbf{i}-\rho(\mathbf{v}-\mathbf{w}^{\alpha\beta})\tilde{\psi}_\alpha^{s}]\gamma_\alpha^{s}\mathrm{d}S\mathrm{d}\tau \quad \alpha,\beta = \mathrm{m,w} \tag{B12}$$

is the non-convective exchange of ψ between the two phases. Substitution of the exchange terms into the eqn (B1), after it has been averaged in time, introduction of average quantities given by eqns (5)–(8) and (15), and, finally, definition of REW-scale quantities based on the averages, lead to the generic α-phase balance equation:

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho_\alpha^{s}\psi_\alpha^{s}y^{s}\epsilon_\alpha^{s}\omega^{s}) - (e_\alpha^{sA}+I_\alpha^{sA}) - \rho f_\alpha^{s}y^{s}\epsilon_\alpha^{s}\omega^{s} = G_\alpha^{s}\omega^{s} + (e_\alpha^{s\,\text{bot}}\psi_\alpha^{s} + I_\alpha^{s\,\text{bot}}) + \sum_{j=\mathrm{u,o,r}}(e_\alpha^{sj}\psi_\alpha^{s}+I_\alpha^{sj}) + (e_{\alpha\beta}^{s}\psi_{w}^{s}+I_{\alpha\beta}^{s}); \quad \alpha = \mathrm{s,w} \tag{B13}$$

In the following paragraphs the conservation equations for mass, momentum, energy and entropy will be stated. The concepts so far are straightforward extensions of what has been shown for the u-subregion and, therefore, details will be omitted.

Conservation of mass

The mass conservation for for the s-subregion α-phase is obtained from eqn (B13), analogous to what has been pursued for the u-subregion. The result is:

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho_\alpha^{s}y^{s}\epsilon_\alpha^{s}\omega^{s}) = e_\alpha^{sA} + e_\alpha^{s\,\text{bot}} + \sum_{j=\mathrm{u,o,r}} e_\alpha^{sj}; \quad \alpha,\beta = \mathrm{m,w} \tag{B14}$$

The terms on the r.h.s. represent the mass exchange of the α-phase with the neighbouring REWs and the external world across A, the exchanges with the deep groundwater reservoir as well as the neighbouring u-, o- and r-subregions, respectively.

Conservation of momentum

The REW-scale equation for conservation of momentum is once again obtained from eqn (B13) by introducing the appropriate microscopic properties from Table 2 into eqn (B1):

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho_\alpha^{s}\mathbf{v}_\alpha^{s}y^{s}\epsilon_\alpha^{s}\omega^{s}) - (e_\alpha^{sA}\mathbf{v}_\alpha^{s}+\mathbf{T}_\alpha^{sA}) - \rho_\alpha^{s}\boldsymbol{g}_\alpha^{s}y^{s}\epsilon_\alpha^{s}\omega^{s} = (e_\alpha^{s\,\text{bot}}\mathbf{v}_\alpha^{s}+\mathbf{T}_\alpha^{s\,\text{bot}}) + \sum_{j=\mathrm{u,o,r}}(e_\alpha^{sj}\mathbf{v}_\alpha^{s}+\mathbf{T}_\alpha^{sj}) + (e_{\alpha\beta}^{s}\mathbf{v}_\alpha^{s}+\mathbf{T}_{\alpha\beta}^{s}) \tag{B15}$$

where:

$$\mathbf{T}_\alpha^{sA} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{sA}} \mathbf{n}^{sA}\cdot[\mathbf{t}-\rho(\mathbf{v}-\mathbf{w}^{sA})\tilde{\mathbf{v}}_\alpha^{s}]\gamma_\alpha^{s}\mathrm{d}A\mathrm{d}\tau \tag{B16}$$

is the momentum exchange between the s-subregion α-phase and neighbouring REWs as well as the external world across the mantle, and

$$\mathbf{T}_\alpha^{s\,\text{bot}} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A_{\text{bot}}^{s}} \mathbf{n}^{s}\cdot[\mathbf{t}-\rho(\mathbf{v}-\mathbf{w}_{\text{bot}}^{s})\tilde{\mathbf{v}}_\alpha^{s}]\gamma_\alpha^{s}\mathrm{d}A\mathrm{d}\tau \tag{B17}$$

is the momentum exchange between the s-subregion and the underlying impermeable strata or the deeper groundwater. Furthermore,

$$\mathbf{T}_\alpha^{sj} = \frac{1}{2\Delta t \Sigma} \int_{t-\Delta t}^{t+\Delta t} \int_{A^{uj}} \mathbf{n}^{sj} \cdot [\mathbf{t} - \rho(\mathbf{v} - \mathbf{w}^{sj})\tilde{\mathbf{v}}_\alpha^s] \gamma_\alpha^s \mathrm{d}A \mathrm{d}\tau; \quad j = \mathrm{u, o, r} \tag{B18}$$

are the momentum exchange terms between the s-subregion, the u-subregion, the overland flow region and the channel reach, and

$$\mathbf{T}_{\alpha\beta}^s = \frac{1}{2\Delta t \Sigma} \int_{t-\Delta t}^{t+\Delta t} \int_{S_{\alpha\beta}^s} \mathbf{n}^{\alpha\beta} \cdot [\mathbf{t} - \rho(\mathbf{v} - \mathbf{w}^{\alpha\beta})\tilde{\mathbf{v}}_\alpha^s] \gamma_\alpha^s \mathrm{d}S \mathrm{d}\tau; \quad \alpha, \beta = \mathrm{m, w} \tag{B19}$$

accounts for the momentum exchange of the s-subregion α-phase with the β-phase across the intra-subregion phase boundaries.

Conservation of energy

The α-phase equation for conservation of energy is stated in analogy to what has been pursued for the u-subregion as follows:

$$\frac{\mathrm{d}}{\mathrm{d}t}\{\rho_\alpha^s [E_\alpha^s + (\mathbf{v}_\alpha^s)^2/2] y^s \epsilon_\alpha^s \omega^s\} - \{e_\alpha^{sA}[E_\alpha^s + (\mathbf{v}_\alpha^s)^2/2] + \mathbf{T}_\alpha^{sA} \cdot \mathbf{v}_\alpha^s + Q_\alpha^{sA}\} - \tag{B20}$$

$$\rho_\alpha^s (\boldsymbol{g}_\alpha^s \cdot \mathbf{v}_\alpha^s + h_\alpha^s) y^s \epsilon_\alpha^s \omega^s = \{e_\alpha^{s\,\mathrm{bot}}[E_\alpha^s + (\mathbf{v}_\alpha^s)^2/2] + \mathbf{T}_\alpha^{s\,\mathrm{bot}} \cdot \mathbf{v}_\alpha^s + Q_\alpha^{s\,\mathrm{bot}}\} + \sum_{j=\mathrm{a,o,r}} \{e_\alpha^{sj}[E_\alpha^s + (\mathbf{v}_\alpha^s)^2/2] + \mathbf{T}_\alpha^{sj} \cdot \mathbf{v}_\alpha^s + Q_\alpha^{sj}\} + \{e_{\alpha\beta}^s[E_\alpha^s + (\mathbf{v}_\alpha^s)^2/2] + \mathbf{T}_{\alpha\beta}^s \cdot \mathbf{v}_\alpha^s + Q_{\alpha\beta}^s\}$$

where the REW-scale internal energy and external energy supply are given by

$$E_\alpha^s = \bar{E}_\alpha^s + \overline{(\tilde{v}_\alpha^s)^2}^s/2 \tag{B21}$$

$$h_\alpha^s = \bar{h}_\alpha^s + \overline{\tilde{\boldsymbol{g}}_\alpha^s \cdot \tilde{\mathbf{v}}_\alpha^s}^s \tag{B22}$$

Next, the REW-scale energy exchange terms are introduced:

$$Q_\alpha^{sA} = \frac{1}{2\Delta t \Sigma} \int_{t-\Delta t}^{t+\Delta t} \int_{A^{sA}} \mathbf{n}^{sA} \cdot \{\mathbf{q} + \mathbf{t} \cdot \tilde{\mathbf{v}}_\alpha^s - \rho(\mathbf{v} - \mathbf{w}^{sA}) \times [\tilde{E}_\alpha^s + (\tilde{v}_\alpha^s)^2/2]\} \gamma_\alpha^s \mathrm{d}A \mathrm{d}\tau \tag{B23}$$

is the energy transfer from the s-subregion α-phase towards the neighbouring REWs and the external world across the mantle, while

$$Q_\alpha^{s\,\mathrm{bot}} = \frac{1}{2\Delta t \Sigma} \int_{t-\Delta t}^{t+\Delta t} \int_{A_{\mathrm{bot}}^s} \mathbf{n}^s \cdot \{\mathbf{q} + \mathbf{t} \cdot \tilde{\mathbf{v}}_\alpha^s - \rho(\mathbf{v} - \mathbf{w}_{\mathrm{bot}}^s) \times [\tilde{E}_\alpha^s + (\tilde{v}_\alpha^s)^2/2]\} \gamma_\alpha^s \mathrm{d}A \mathrm{d}\tau \tag{B24}$$

is the energy transfer from the s-subregion towards the underlying deep groundwater or the impermeable strata. Furthermore, the term defined as

$$Q_\alpha^{sj} = \frac{1}{2\Delta t \Sigma} \int_{t-\Delta t}^{t+\Delta t} \int_{A^{sj}} \mathbf{n}^{sj} \cdot \{\mathbf{q} + \mathbf{t} \cdot \tilde{\mathbf{v}}_\alpha^s - \rho(\mathbf{v} - \mathbf{w}^{sj}) \times [\tilde{E}_\alpha^s + (\tilde{v}_\alpha^s)^2/2]\} \gamma_\alpha^s \mathrm{d}A \mathrm{d}\tau; \; j = \mathrm{u, o, r} \tag{B25}$$

is the energy transfer from the s-subregion α-phase into the u-subregion, the overland flow region and the channel reach, and finally,

$$Q_{\alpha\beta}^s = \frac{1}{2\Delta t \Sigma} \int_{t-\Delta t}^{t+\Delta t} \int_{S_{\alpha\beta}^s} \mathbf{n}^{\alpha\beta} \cdot \{\mathbf{q} + \mathbf{t} \cdot \tilde{\mathbf{v}}_\alpha^s - \rho(\mathbf{v} - \mathbf{w}^{\alpha\beta}) \times [\tilde{E}_\alpha^s + (\tilde{v}_\alpha^s)^2/2]\} \gamma_\alpha^s \mathrm{d}S \mathrm{d}\tau; \; \alpha, \beta = \mathrm{m, w} \tag{B26}$$

accounts for the energy exchange of the s-subregion α-phase with the β-phase across the intra-subregion phase boundary.

Balance of entropy

The balance equation for the s-subregion α-phase entropy is:

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho_\alpha^s y^s \epsilon_\alpha^s \eta_\alpha^s \omega^s) - (e_\alpha^{sA} \eta_\alpha^s + F_\alpha^{sA}) - \rho_\alpha^s b_\alpha^s y^s \epsilon_\alpha^s \omega^s = L_\alpha^s \omega^s + (e_\alpha^{s\,\mathrm{bot}} \eta_\alpha^s + F_\alpha^{s\,\mathrm{bot}}) + \sum_{j=\mathrm{u,o,r}} (e_\alpha^{sj} \eta_\alpha^s + F_\alpha^{sj}) + (e_{\alpha\beta}^s \eta_\alpha^s + F_{\alpha\beta}^s) \tag{B27}$$

where:

$$\eta_\alpha^s = \bar{\eta}_\alpha^s \tag{B28}$$

$$b_\alpha^s = \bar{b}_\alpha^s \tag{B29}$$

$$L_\alpha^s = \langle L \rangle_\alpha^s \tag{B30}$$

are the REW-scale entropy, entropy supply and internal generation of entropy, respectively, while

$$F_\alpha^{sA} = \frac{1}{2\Delta t \Sigma} \int_{t-\Delta t}^{t+\Delta t} \int_{A^{sA}} \mathbf{n}^{sA} \cdot [\mathbf{j} - \rho(\mathbf{v} - \mathbf{w}^{sA})\tilde{\eta}_\alpha^s] \gamma_\alpha^s \mathrm{d}A \mathrm{d}\tau \tag{B31}$$

is the entropy exchange from the s-subregion α-phase across the mantle. Next,

$$F_\alpha^{s\,\mathrm{bot}} = \frac{1}{2\Delta t \Sigma} \int_{t-\Delta t}^{t+\Delta t} \int_{A_{\mathrm{bot}}^s} \mathbf{n}^s \cdot [\mathbf{j} - \rho(\mathbf{v} - \mathbf{w}_{\mathrm{bot}}^s)\tilde{\eta}_\alpha^s] \gamma_\alpha^s \mathrm{d}A \mathrm{d}\tau \tag{B32}$$

is the entropy exchange between the s-subregion α-phase and the underlying deep groundwater or the impermeable layers, while

$$F_\alpha^{sj} = \frac{1}{2\Delta t \Sigma} \int_{t-\Delta t}^{t+\Delta t} \int_{A^{sj}} \mathbf{n}^{sj} \cdot [\mathbf{j} - \rho(\mathbf{v} - \mathbf{w}^{sj})\tilde{\eta}_\alpha^s] \gamma_\alpha^s \mathrm{d}A \mathrm{d}\tau \quad j = \mathrm{u, o, r} \tag{B33}$$

is the entropy exchange between the s-subregion α-phase and the u-subregion, the overland flow region and the channel reach. Finally,

$$F^{\mathrm{s}}_{\alpha\beta} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{S^{\mathrm{s}}_{\alpha\beta}} \mathbf{n}^{\alpha\beta}\cdot[\mathbf{j} - \rho(\mathbf{v} - \mathbf{w}^{\alpha\beta})\tilde{\eta}^{\mathrm{s}}_{\alpha}]\gamma^{\mathrm{s}}_{\alpha}\mathrm{d}S\mathrm{d}\tau; \quad \alpha,\beta = \mathrm{m},\mathrm{w} \qquad \text{(B34)}$$

accounts for the entropy exchange of the s-subregion α-phase with the β-phase across the intrasubregion phase boundaries.

APPENDIX C. CONSERVATION EQUATIONS FOR THE REGION OF CONCENTRATED OVERLAND FLOW (C-SUBREGION)

The subregion here identified as concentrated overland flow zone, comprises all the flow occurring on the unsaturated portion of the land surface. It includes Hortonian overland flow and flow in rills and gullies. Furthermore, the c-subregion comprises the sub-REW scale channel network within the unsaturated land surface. This allows to account for the self-similar structure of the channel network, which implies that, whatever the scale of observation, there is always a treelike branching network present at smaller scales. The flow within the c-subregion is supposed to include only the water phase. The presence of sediment transport phenomena is *a priori* excluded. The framework presented here, however, does not necessarily require this assumption, which is merely a simplifying expedient. Sediment transport can be included by introducing a solid phase in the c-, o- and r-subregions in an appropriate fashion.

The c-subregion will be described as a sheet of water which communicates with the atmosphere on top, the unsaturated zone at the bottom, and with the saturated overland flow sheet along the intersection line of the water table with the land surface. The global balance law for the c-subregion can be stated, in analogy to what has been pursued previously:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{V^{\mathrm{c}}}\rho\psi\mathrm{d}V &+ \int_{A^{\mathrm{cu}}}\mathbf{n}^{\mathrm{cu}}\cdot[\rho(\mathbf{v}-\mathbf{w}^{\mathrm{c}j})\psi \\ &+ \int_{A^{\mathrm{co}}}\mathbf{n}^{\mathrm{co}}\cdot[\rho(\mathbf{v}-\mathbf{w}^{\mathrm{co}})\psi - \mathbf{i}]\mathrm{d}A\mathrm{d}\tau \\ &+ \int_{A^{\mathrm{c}}_{\mathrm{top}}}\mathbf{n}^{\mathrm{c}}\cdot[\rho(\mathbf{v}-\mathbf{w}^{\mathrm{c}}_{\mathrm{top}})\psi - \mathbf{i}]\mathrm{d}A\mathrm{d}\tau - \int_{V^{\mathrm{c}}}\rho f\mathrm{d}V \\ &= \int_{V^{\mathrm{c}}}G\mathrm{d}V \end{aligned} \qquad \text{(C1)}$$

where A^{co} is the sum of cross-sectional areas where the concentrated overland flow merges with the saturated overland flow sheet (see Fig. 4). After applying a similar time-averaging procedure to eqn (C1) as outlined in eqn (A2) for the u-subregion, and employing the average quantities (eqns (5)–(7) and (15)), the first term becomes:

$$\frac{1}{2\Delta t}\frac{\mathrm{d}}{\mathrm{d}t}\int_{t-\Delta t}^{t+\Delta t}\int_{V^{\mathrm{c}}}\rho\psi\mathrm{d}V\mathrm{d}\tau = \frac{\mathrm{d}}{\mathrm{d}t}(y^{\mathrm{c}}\omega^{\mathrm{c}}\langle a\rangle^{\mathrm{c}}\bar{\psi}^{\mathrm{c}}\Sigma) \qquad \text{(C2)}$$

Next, appropriate REW-scale exchange terms for the property ψ have to be defined:

$$e^{\mathrm{c}j} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{\mathrm{c}j}}\mathbf{n}^{\mathrm{c}j}\cdot[\rho(\mathbf{w}^{\mathrm{c}j}-\mathbf{v})]\mathrm{d}A\mathrm{d}\tau; \; j = \mathrm{u},\mathrm{o} \qquad \text{(C3)}$$

are the mass exchange, and

$$I^{\mathrm{c}j} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{\mathrm{c}j}}\mathbf{n}^{\mathrm{c}j}\cdot[\mathbf{i} - \rho(\mathbf{v}-\mathbf{w}^{\mathrm{c}j})\tilde{\psi}^{\mathrm{c}}]\mathrm{d}A\mathrm{d}\tau; \; j = \mathrm{u},\mathrm{o} \qquad \text{(C4)}$$

are the non-convective fluxes between the c-subregion, the unsaturated zone across the area A^{cu} and the region of saturated overland flow. The deviation $\tilde{\psi}^{\mathrm{c}}$ from the space and time average of the property ψ is defined as:

$$\tilde{\psi}^{\mathrm{c}} = \psi - \tilde{\psi}^{\mathrm{c}} \qquad \text{(C5)}$$

Subsequently,

$$e^{\mathrm{c\ top}} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{\mathrm{c}}_{\mathrm{top}}}\mathbf{n}^{\mathrm{c}}\cdot[\rho(\mathbf{w}^{\mathrm{c}}_{\mathrm{top}}-\mathbf{v})]\mathrm{d}A\mathrm{d}\tau \qquad \text{(C6)}$$

is the mass exchange between the c-subregion and the atmosphere on top. The non-convective flux is consistently defined as:

$$I^{\mathrm{c\ top}} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{\mathrm{c}}_{\mathrm{top}}}\mathbf{n}^{\mathrm{c}}\cdot[\mathbf{i} - \rho(\mathbf{v}-\mathbf{w}^{\mathrm{c}}_{\mathrm{top}})\tilde{\psi}^{\mathrm{c}}]\mathrm{d}A\mathrm{d}\tau \qquad \text{(C7)}$$

Substitution of the previously defined quantities into the time-averaged general balance law (eqn (C1)), introduction of the averages defined through eqns (5)–(7) and (15) and division by the surface area projection Σ yields:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}(\langle\rho\rangle^{\mathrm{c}}y^{\mathrm{c}}\bar{\psi}^{\mathrm{c}}\omega^{\mathrm{c}}) - \langle\rho\rangle^{\mathrm{c}}y^{\mathrm{c}}\bar{f}^{\mathrm{c}}\omega^{\mathrm{c}} &= \langle G\rangle^{\mathrm{c}}\omega^{\mathrm{c}} + (e^{\mathrm{c\ top}}\bar{\psi}^{\mathrm{c}} + I^{\mathrm{c\ top}}) \\ &+ (e^{\mathrm{cu}}\bar{\psi}^{\mathrm{c}} + I^{\mathrm{cu}}) + (e^{\mathrm{co}}\bar{\psi}^{\mathrm{o}} + I^{\mathrm{co}})\end{aligned} \qquad \text{(C8)}$$

The equation can, once again, be rewritten after definition of REW-scale quantities in terms of averages:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}(\rho^{\mathrm{c}}y^{\mathrm{c}}\psi^{\mathrm{c}}\omega^{\mathrm{c}}) - \rho^{\mathrm{c}}y^{\mathrm{c}}f^{\mathrm{c}}\omega^{\mathrm{c}} &= G^{\mathrm{c}}\omega^{\mathrm{c}} + (e^{\mathrm{c\ top}}\psi^{\mathrm{c}} + I^{\mathrm{c\ top}}) \\ &+ (e^{\mathrm{cu}}\psi^{\mathrm{c}} + I^{\mathrm{cu}}) + (e^{\mathrm{co}}\psi^{\mathrm{c}} + I^{\mathrm{co}})\end{aligned} \qquad \text{(C9)}$$

Conservation of mass

The REW-scale mass balance for the c-subregion is obtained by introducing the appropriate microscopic quantities from Table 2 into the balance eqn (C1). The resulting mass balance assumes the following expression:

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho^{c}y^{c}\omega^{c}) = e^{c\ top} + e^{cu} + e^{co} \tag{C10}$$

The terms on the r.h.s. account for the exchange of mass of the c-subregion with the atmosphere, with the underlying u-subregion and with the saturated overland flow region.

Conservation of momentum

The REW-scale equation for conservation of momentum for the c-subregion is derived b introducing the microscopic quantities according to Table 2 into eqn (C1):

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho^{c}y^{c}\mathbf{v}^{c}\omega^{c}) - \rho^{c}y^{c}\boldsymbol{g}^{c}\omega^{c} = (e^{c\ top}\mathbf{v}^{c} + \mathbf{T}^{c\ top}) + (e^{co}\mathbf{v}^{c} + \mathbf{T}^{co}) + (e^{cu}\mathbf{v}^{c} + \mathbf{T}^{cu}) \tag{C11}$$

where:

$$\mathbf{T}^{c\ top} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{c}_{top}} \mathbf{n}^{c}\cdot[\mathbf{t} - \rho(\mathbf{v} - \mathbf{w}^{c}_{top})\tilde{\mathbf{v}}^{c}]\mathrm{d}A\mathrm{d}\tau \tag{C12}$$

is the REW-scale momentum exchange term between the c-subregion and the atmosphere, and

$$\mathbf{T}^{cj} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{cj}} \mathbf{n}^{cj}\cdot[\mathbf{t} - \rho(\mathbf{v} - \mathbf{w}^{cj})\tilde{\mathbf{v}}^{c}]\mathrm{d}A\mathrm{d}\tau;\ j = \mathrm{u,o} \tag{C13}$$

is the momentum transfer to the u- and o-subregions.

Conservation of energy

The equation for conservation of energy is derived by defining the microscopic quantities according to Table 2. The resulting equation is

$$\frac{\mathrm{d}}{\mathrm{d}t}\{\rho^{c}y^{c}[E^{c} + (v^{c})^{2}/2]\omega^{c}\} - \rho^{c}y^{c}(\boldsymbol{g}^{c}\cdot\mathbf{v}^{c} + h^{c})\omega^{c} = \tag{C14}$$

$$\{e^{c\ top}[E^{c} + (v^{c})^{2}/2] + \mathbf{T}^{c\ top}\cdot\mathbf{v}^{c} + Q^{c\ top}\} + \{e^{cu}[E^{c} + (v^{c})^{2}/2] + \mathbf{T}^{cu}\cdot\mathbf{v}^{c} + Q^{cu}\} + \{e^{co}[E^{c} + (v^{c})^{2}/2] + \mathbf{T}^{co}\cdot\mathbf{v}^{c} + Q^{co}\}$$

where:

$$E^{c} = \bar{E}^{c} + \overline{(\tilde{v}^{c})^{2}}^{c}/2 \tag{C15}$$

$$h^{c} = \bar{h}^{c} + \overline{\tilde{\boldsymbol{g}}^{c}\cdot\tilde{\mathbf{v}}^{c}\mathrm{c}} \tag{C16}$$

are the REW-scale internal energy and the total heat supply from the external world, respectively. Furthermore,

$$Q^{c\ top} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{c}} \mathbf{n}^{c}\cdot\{\mathbf{q} + \mathbf{t}\cdot\tilde{\mathbf{v}}^{c} - \rho(\mathbf{v} - \mathbf{w}^{c}_{top}) \times [\tilde{E}^{c} + (\tilde{v}^{c})^{2}/2]\}\mathrm{d}A\mathrm{d}\tau \tag{C17}$$

is the exchange of energy with the atmosphere, and

$$Q^{cj} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{cj}} \mathbf{n}^{cj}\cdot\{\mathbf{q} + \mathbf{t}\cdot\tilde{\mathbf{v}}^{c} - \rho(\mathbf{v} - \mathbf{w}^{cj}) \times [\tilde{E}^{c} + (\tilde{v}^{c})^{2}/2]\}\mathrm{d}A\mathrm{d}\tau;\ j = \mathrm{u,o} \tag{C18}$$

accounts for the energy transfer to the underlying unsaturated zone and the saturated overland flow region.

Balance of entropy

The REW-scale balance of entropy for the c-subregion is obtained by defining the microscopic quantities as given in Table 2. The equation resulting from eqn (C1) is:

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho^{c}y^{c}\eta^{c}\omega^{c}) - \rho^{c}y^{c}b^{c}\omega^{c} = L^{c}\omega^{c} + (e^{c\ top}\eta^{c} + F^{c\ top}) + (e^{cu}\eta^{c} + F^{cu}) + (e^{co}\eta^{c} + F^{co}) \tag{C19}$$

where:

$$\eta^{c} = \bar{\eta}^{c} \tag{C20}$$

$$b^{c} = \bar{b}^{c} \tag{C21}$$

$$L^{c} = \langle L\rangle^{c} \tag{C22}$$

are the entropy, and the REW-scale terms of entropy supply and internal generation of entropy, respectively, while

$$F^{c\ top} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{c}} \mathbf{n}^{c\ top}\cdot[\mathbf{j} - \rho(\mathbf{v} - \mathbf{w}^{c}_{top})\tilde{\eta}^{c}]\mathrm{d}A\mathrm{d}\tau \tag{C23}$$

is the term of entropy exchange between the c-subregion and the atmosphere, and

$$F^{cj} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{cj}} \mathbf{n}^{cj}\cdot[\mathbf{j} - \rho(\mathbf{v} - \mathbf{w}^{cj})\tilde{\eta}^{c}]\mathrm{d}A\mathrm{d}\tau;\ j = \mathrm{u,o} \tag{C24}$$

account for the entropy exchange between the c-subregion and the underlying u-subregion and the overland flow region, respectively.

APPENDIX D. CONSERVATION EQUATIONS FOR THE REGION OF SATURATED OVERLAND FLOW (O-SUBREGION)

The flow characterizing the the o-subregion is occurring on the land surface, along the seepage faces of the saturated zone (s-subregion). it also includes the sub-REW-scale channel network flow within the saturated portion of the land surface. The saturated zone is composed of the water and the solid phases. The exchange of the property ψ of the o-subregion with both phases of the underlying aquifer has, therefore, to be considered. The o-subregion can further exchange ψ with the main channel reach along the channel edge and with the the c-subregion from the uphill regions, as shown in Fig. 4. There is no interaction with the unsaturated zone (u-subregion). Also here, presence of sediment transport is excluded. The generic balance law for the o-subregion can be stated in analogy to what has been pursued previously:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{V^{\mathrm{o}}}\rho\psi\mathrm{d}V+\int_{A^{\mathrm{o}}_{\mathrm{top}}}\mathbf{n}^{\mathrm{o}}\cdot[\rho(\mathbf{v}-\mathbf{w}^{\mathrm{o}}_{\mathrm{top}})\psi-\mathbf{j}]\mathrm{d}A\mathrm{d}\tau$$
$$+\int_{A^{\mathrm{so}}}\mathbf{n}^{\mathrm{os}}\cdot[\rho(\mathbf{v}-\mathbf{w}^{\mathrm{os}})\psi-\mathbf{j}]\mathrm{d}A\mathrm{d}\tau$$
$$+\int_{A^{\mathrm{co}}}\mathbf{n}^{\mathrm{oc}}\cdot[\rho(\mathbf{v}-\mathbf{w}^{\mathrm{co}})\psi-\mathbf{j}]\mathrm{d}A\mathrm{d}\tau$$
$$+\int_{A^{\mathrm{or}}}\mathbf{n}^{\mathrm{or}}\cdot[\rho(\mathbf{v}-\mathbf{w}^{\mathrm{or}})\psi-\mathbf{j}]\mathrm{d}A\mathrm{d}\tau-\int_{V^{\mathrm{o}}}\rho f\mathrm{d}V$$
$$=\int_{V^{\mathrm{o}}}G\mathrm{d}V \qquad \text{(D1)}$$

where A^{or} is the total cross-sectional area of the overland flow water sheet at the inflows along the channel edges. After application of an analogous procedure as pursued for the unsaturated zone (see eqn (A2)), and by employing the average quantities defined in Appendix E, the first term of eqn (D1) becomes:

$$\frac{1}{2\Delta t}\frac{\mathrm{d}}{\mathrm{d}t}\int_{t-\Delta t}^{t+\Delta t}\int_{V^{\mathrm{o}}}\rho\psi\mathrm{d}V\mathrm{d}\tau=\frac{\mathrm{d}}{\mathrm{d}t}(y^{\mathrm{o}}\omega^{\mathrm{o}}\langle\rho\rangle^{\mathrm{o}}\bar{\psi}^{\mathrm{o}}\Sigma) \qquad \text{(D2)}$$

Next, we introduce appropriate REW-scale exchange terms for the property ψ:

$$e^{\mathrm{o\ top}}=\frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{\mathrm{o}}_{\mathrm{top}}}\mathbf{n}^{\mathrm{o}}\cdot[\rho(\mathbf{w}^{\mathrm{o}}_{\mathrm{top}}-\mathbf{v})]\mathrm{d}A\mathrm{d}\tau \qquad \text{(D3)}$$

is the exchange between the o-subregion and the atmosphere on top, and

$$I^{\mathrm{o\ top}}=\frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{\mathrm{o}}_{\mathrm{top}}}\mathbf{n}^{\mathrm{o}}\cdot[\mathbf{j}-\rho(\mathbf{v}-\mathbf{w}^{\mathrm{o}}_{\mathrm{top}})\tilde{\psi}^{\mathrm{o}}]\mathrm{d}A\mathrm{d}\tau \qquad \text{(D4)}$$

is the respective non-convective flux term, where the deviation quantity $\tilde{\psi}^{\mathrm{o}}$ is defined in analogy to eqn (C5). Furthermore,

$$e^{\mathrm{o}j}=\frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{\mathrm{o}j}}\mathbf{n}^{\mathrm{o}j}\cdot[\rho(\mathbf{w}^{\mathrm{o}j}-\mathbf{v})]\mathrm{d}A\mathrm{d}\tau;\ j=\mathrm{s,c,r} \qquad \text{(D5)}$$

are the mass exchange terms between the o-subregion and the underlying s-subregion across the seepage face A^{os}, with the c-subregion from uphill, and the channel reach through lateral inflow. The non-convective fluxes are defined as:

$$I^{\mathrm{o}j}=\frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{\mathrm{o}j}}\mathbf{n}^{\mathrm{o}j}\cdot[\mathbf{j}-\rho(\mathbf{v}-\mathbf{w}^{\mathrm{o}j})\tilde{\psi}^{\mathrm{o}}]\mathrm{d}A\mathrm{d}\tau\ \ j=\mathrm{s,c,r} \qquad \text{(D6)}$$

Substitution of the previously defined quantities into eqn (D1) after it has been averaged in time, introduction of the average quantities eqns (5)–(7) and (15), and division by the surface area projection Σ yields:

$$\frac{\mathrm{d}}{\mathrm{d}t}(\langle\rho\rangle^{\mathrm{o}}y^{\mathrm{o}}\bar{\psi}^{\mathrm{r}}\omega^{\mathrm{o}})-\langle\rho\rangle^{\mathrm{o}}y^{\mathrm{o}}\bar{f}^{\mathrm{o}}\omega^{\mathrm{o}}=\langle G\rangle^{\mathrm{o}}\omega^{\mathrm{o}}+(e^{\mathrm{o\ top}}\bar{\psi}^{\mathrm{o}}I^{\mathrm{o\ top}})$$
$$+(e^{\mathrm{os}}\bar{\psi}^{\mathrm{o}}+I^{\mathrm{os}})+(e^{\mathrm{oc}}\bar{\psi}^{\mathrm{o}}+I^{\mathrm{oc}})+(e^{\mathrm{or}}\bar{\psi}^{\mathrm{o}}+I^{\mathrm{or}}) \qquad \text{(D7)}$$

The equation can be restated in terms of appropriate REW-scale quantities:

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho^{\mathrm{o}}y^{\mathrm{o}}\psi^{\mathrm{o}}\omega^{\mathrm{o}})-\rho^{\mathrm{o}}y^{\mathrm{o}}f^{\mathrm{o}}\omega^{\mathrm{o}}=G^{\mathrm{o}}\omega^{\mathrm{o}}+(e^{\mathrm{o\ top}}\psi^{\mathrm{o}}+I^{\mathrm{o\ top}})$$
$$+(e^{\mathrm{os}}\psi^{\mathrm{o}}+I^{\mathrm{os}})+(e^{\mathrm{oc}}\psi^{\mathrm{o}}+I^{\mathrm{oc}})+(e^{\mathrm{or}}\psi^{\mathrm{o}}+I^{\mathrm{or}}) \qquad \text{(D8)}$$

Conservation of mass

The REW-scale mass balance for the o-subregion is obtained by introducing the corresponding microscopic quantities from Table 2 into the balance eqn (D1). The resulting mass balance eqn (D8) assumes the following expression:

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho^{\mathrm{o}}y^{\mathrm{o}}\omega^{\mathrm{o}})=e^{\mathrm{o\ top}}+e^{\mathrm{os}}+e^{\mathrm{oc}}+e^{\mathrm{or}} \qquad \text{(D9)}$$

The terms on the r.h.s. account for the exchange of mass of the o-subregion with the atmosphere, with the s- and c-subregions, and with the channel reach through lateral inflow.

Conservation of momentum

The REW-scale equation for conservation of momentum for the o-subregion is derived by introducing the microscopic quantities according to Table 2 into eqn (D1). The equation resulting from eqn (D2) is:

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho^{\mathrm{o}}y^{\mathrm{o}}\mathbf{v}^{\mathrm{o}}\omega^{\mathrm{o}})-\rho^{\mathrm{o}}y^{\mathrm{o}}\boldsymbol{g}^{\mathrm{o}}\omega^{\mathrm{o}}=(e^{\mathrm{o\ top}}\mathbf{v}^{\mathrm{o}}+\mathbf{T}^{\mathrm{o\ top}})$$
$$+(e^{\mathrm{os}}\mathbf{v}^{\mathrm{o}}+\mathbf{T}^{\mathrm{os}})+(e^{\mathrm{oc}}\mathbf{v}^{\mathrm{o}}+\mathbf{T}^{\mathrm{oc}})+(e^{\mathrm{or}}v^{\mathrm{o}}+\mathbf{T}^{\mathrm{or}}) \qquad \text{(D10)}$$

where:

$$\mathbf{T}^{\mathrm{o\ top}}=\frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{\mathrm{o}}_{\mathrm{top}}}\mathbf{n}^{\mathrm{o}}\cdot[\mathbf{t}-\rho(\mathbf{v}-\mathbf{w}^{\mathrm{o}}_{\mathrm{top}})\tilde{\mathbf{v}}^{\mathrm{o}}]\mathrm{d}A\mathrm{d}\tau \qquad \text{(D11)}$$

is the momentum exchange term between the o-subregion and the atmosphere, while

$$\mathbf{T}^{\mathrm{o}j}=\frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{\mathrm{o}j}}\mathbf{n}^{\mathrm{o}j}\cdot[\mathbf{t}-\rho(\mathbf{v}-\mathbf{w}^{\mathrm{o}j})\tilde{\mathbf{v}}^{\mathrm{o}}]\mathrm{d}A\mathrm{d}\tau;$$
$$j=\mathrm{s,c,r} \qquad \text{(D12)}$$

are the momentum transfer terms to the s-subregion, the c-subregion and the channel reach, respectively.

Conservation of energy

The equation for conservation of energy is derived by defining the microscopic quantities according to Table 2.

The resulting equation is

$$\frac{\mathrm{d}}{\mathrm{d}t}\{\rho^{o}y^{o}[E^{o}+(v^{o})^{2}/2]\omega^{o}\}-\rho^{o}y^{o}(\boldsymbol{g}^{o}\cdot\mathbf{v}^{o}+h^{o})\omega^{o}$$
$$=\{e^{o\ top}[E^{o}+(v^{o})^{2}/2]+\mathbf{T}^{o\ top}\cdot\mathbf{v}^{o}+Q^{o\ top}\}$$
$$+\{e^{os}[E^{o}+(v^{o})^{2}/2]+\mathbf{T}^{os}\cdot\mathbf{v}^{o}+Q^{os}\}$$
$$+\{e^{oc}[E^{o}+(v^{o})^{2}/2]+\mathbf{T}^{oc}\cdot\mathbf{v}^{o}+Q^{oc}\}$$
$$+\{e^{or}[E^{o}+(v^{o})^{2}/2]+\mathbf{T}^{or}\cdot\mathbf{v}^{o}+Q^{or}\} \quad (D13)$$

where:

$$E^{o}=\bar{E}^{o}+\overline{(\tilde{v}^{o})^{2}}^{o}/2 \quad (D14)$$

$$h^{o}=\bar{h}^{o}+\overline{\tilde{\boldsymbol{g}}^{o}\cdot\tilde{\mathbf{v}}^{o}}^{o} \quad (D15)$$

are the average internal energy and the total heat supply from the external world, respectively,

$$Q^{o\ top}=\frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{o}}\mathbf{n}^{o}\cdot\{\mathbf{q}+\mathbf{t}\cdot\tilde{\mathbf{v}}^{o}-\rho(\mathbf{v}-\mathbf{w}^{o}_{top})\times[\tilde{E}^{o}+(\tilde{v}^{o})^{2}/2]\}\mathrm{d}A\mathrm{d}\tau \quad (D16)$$

is the energy exchange with the atmosphere, and

$$Q^{oj}=\frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{oj}}\mathbf{n}^{oj}\cdot\{\mathbf{q}+\mathbf{t}\cdot\tilde{\mathbf{v}}^{o}-\rho(\mathbf{v}-\mathbf{w}^{oj})\times[\tilde{E}^{o}+(\tilde{v}^{o})^{2}/2]\}\mathrm{d}A\mathrm{d}\tau;\ j=\mathrm{s,c,r} \quad (D17)$$

are the energy transfer terms to the underlying saturated zone, the concentrated overland flow and the channel reach.

Balance of entropy

The REW-scale balance of entropy for the o-subregion is obtained by defining the microscopic quantities as given in Table 2. The equation resulting from eqn (D1) is:

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho^{o}y^{o}\eta^{o}\omega^{o})-\rho^{o}y^{o}b^{o}\omega^{o}=L^{o}\omega^{o}+(e^{o\ top}\eta^{o}+F^{o\ top})$$
$$+(e^{os}\eta^{o}+F^{os})+(e^{oc}\eta^{o}+F^{oc})+(e^{or}\eta^{o}+F^{or}) \quad (D18)$$

where:

$$\eta^{o}=\bar{\eta}^{o} \quad (D19)$$

$$b^{o}=\bar{b}^{o} \quad (D20)$$

$$L^{o}=\langle L\rangle^{o} \quad (D21)$$

are the REW-scale entropy and the terms of entropy supply and internal generation of entropy, respectively, while

$$F^{o\ top}=\frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{o}}\mathbf{n}^{o\ top}\cdot[\mathbf{j}-\rho(\mathbf{v}-\mathbf{w}^{o}_{top})\tilde{\eta}^{o}]\mathrm{d}A\mathrm{d}\tau \quad (D22)$$

is the term of entropy exchange between the o-subregion and the atmosphere, and

$$F^{oj}=\frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{oj}}\mathbf{n}^{oj}\cdot[\mathbf{j}-\rho(\mathbf{v}-\mathbf{w}^{oj})\tilde{\eta}^{o}]\mathrm{d}A\mathrm{d}\tau$$
$$j=\mathrm{s,c,r} \quad (D23)$$

are the entropy exchange terms between the o-subregion, the underlying s-subregion, the c-subregion from the uphill regions, and the channel reach.

APPENDIX E. CONSERVATION EQUATIONS FOR THE CHANNEL REACH (R-SUBREGION)

The main channel reach of the REW exchanges ψ with the atmosphere on the channel free surface, with the underlying saturated zone (s-subregion) across the channel bed, with the overland run-off areas (o-subregion) along the edges of the channel, with the neighbouring REWs and the external world across the mantle A at the REW outlet and inlet. We recall that, in the case of REWs associated with *first order streams*, there is only an outlet and no inlet. The geometric properties inherent to the channel at a cross-section are the width of the free surface, the wetted perimeter, and the cross-sectional area m (equivalent to a volume per unit length $[L^3/L]$) normal to the spatial curve C^r forming the axis of the channel. The volume V^r associated with the channel reach is slender and can be approximated through the integration

$$V^{r}=\int_{C^{r}}m\mathrm{d}C \quad (E1)$$

where $\mathrm{d}C$ is an infinitesimal segment of the curve C^r. By making this approximation, the effects of volume distortion due to curvature of the channel have been neglected. The respective terms have been derived in a rigorous manner by Gray et al.,[15] to which the reader is referred for more detailed explanation. The general conservation equation for a generic property ψ within the volume V^r is stated as:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{V^{r}}\rho\psi\mathrm{d}V+\int_{A^{rA}}\mathbf{n}^{rA}\cdot[\rho(\mathbf{v}-\mathbf{w}^{rA})\psi-\mathbf{i}]\mathrm{d}A\mathrm{d}\tau+ \quad (E2)$$
$$\int_{A^{r}_{top}}\mathbf{n}^{r}\cdot[\rho(\mathbf{v}-\mathbf{w}^{r}_{top})\psi-\mathbf{i}]\mathrm{d}A\mathrm{d}\tau$$
$$+\int_{A^{sr}}\mathbf{n}^{rs}\cdot[\rho(\mathbf{v}-\mathbf{w}^{sr})\psi-\mathbf{i}]\mathrm{d}A\mathrm{d}\tau+$$
$$\int_{A^{or}}\mathbf{n}^{ro}\cdot[\rho(\mathbf{v}-\mathbf{w}^{or})\psi-\mathbf{i}]\mathrm{d}A\mathrm{d}\tau-\int_{V^{r}}\rho f\mathrm{d}V=\int_{V^{r}}G\mathrm{d}V$$

where A^{rA} is the total cross-sectional area defined by the intersection of the channel with the mantle A at the outlet and inlet, and A^{r}_{top} is the channel free surface. After application of the top time-averaging theorem (eqn (A2)), as shown for the case of the unsaturated zone, and use of the average quantities eqns (12)–(14) and (16), defined in

Appendix 5, the first term of eqn (E2) becomes:

$$\frac{1}{2\Delta t}\frac{\mathrm{d}}{\mathrm{d}t}\int_{t-\Delta t}^{t+\Delta t}\int_{V^{\mathrm{r}}}\rho\psi\mathrm{d}V\mathrm{d}\tau = \frac{\mathrm{d}}{\mathrm{d}t}(m^{\mathrm{r}}\xi^{\mathrm{r}}\langle\rho\rangle^{\mathrm{r}}\bar{\psi}^{\mathrm{r}}\Sigma) \quad \text{(E3)}$$

The following exchange terms between the channel reach and its surroundings are subsequently defined:

$$e^{\mathrm{r}A} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{\mathrm{r}A}}\mathbf{n}^{\mathrm{r}A}\cdot[\rho(\mathbf{w}^{\mathrm{r}A}-\mathbf{v})]\mathrm{d}A\mathrm{d}\tau \quad \text{(E4)}$$

is the mass exchange of the channel reach across the mantle at the outlet and inlet, and

$$I^{\mathrm{r}A} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{\mathrm{r}A}}\mathbf{n}^{\mathrm{r}A}\cdot[\mathbf{i}-\rho(\mathbf{v}-\mathbf{w}^{\mathrm{r}A})\tilde{\psi}^{\mathrm{r}}]\mathrm{d}A\mathrm{d}\tau \quad \text{(E5)}$$

is the non-convective interaction of the channel across A, where, once again, the deviation $\tilde{\psi}^{\mathrm{r}}$ from the time and space average is defined as:

$$\tilde{\psi}^{\mathrm{r}} = \psi - \bar{\psi}^{\mathrm{r}} \quad \text{(E6)}$$

We observe that the exchanges across the inlet and outlet sections can be separated into a number of components. If the REW is relative to a *first order stream*, the exchange across the REW mantle occurs only at the outlet. If the REW is relative to a *higher order stream*, there are two reaches converging at the inlet and there is a reach following further downstream at the REW outlet, i.e. the channel reach is communicating with the reaches of three neighbouring REWs. For example, with reference to Fig. 1(c), the channel reach of REW 5 is communicating with the reaches of REWs 3 and 4 at the inlet and with the reach of REW 7 at the outlet. In addition, the REW, which is the closest to the outlet, can interact across the external watershed boundary. With these considerations in mind, we rewrite eqns (E4) and (E5) in a general form:

$$e^{\mathrm{r}A} = \sum_{l} e_l^{\mathrm{r}A} + e_{\mathrm{ext}}^{\mathrm{r}A} \quad \text{(E7)}$$

$$I^{\mathrm{r}A} = \sum_{l} I_l^{\mathrm{r}A} + I_{\mathrm{ext}}^{\mathrm{r}A} \quad \text{(E8)}$$

where the summation extends over the neighbouring REWs (three in the case of a *higher order stream* and one in the case of a *first order stream*) and the second term on the r.h.s. is non-zero only for the REW next to the watershed outlet. In all the following balance equations the exchange term across the mantle is implicitly understood as a sum of these components. Next,

$$e^{\mathrm{r\ top}} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A_{\mathrm{top}}^{\mathrm{r}}}\mathbf{n}^{\mathrm{r}}\cdot[\rho(\mathbf{w}_{\mathrm{top}}^{\mathrm{r}}-\mathbf{v})]\mathrm{d}A\mathrm{d}\tau \quad \text{(E9)}$$

is the REW-scale mass exchange between the channel free surface and the atmosphere, and

$$I^{\mathrm{r\ top}} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A_{\mathrm{top}}^{\mathrm{r}}}\mathbf{n}^{\mathrm{r}}\cdot[\mathbf{i}-\rho(\mathbf{v}-\mathbf{w}_{\mathrm{top}}^{\mathrm{r}})\tilde{\psi}^{\mathrm{r}}]\mathrm{d}A\mathrm{d}\tau \quad \text{(E10)}$$

is the-respective non-convective flux term. Finally,

$$e^{\mathrm{r}j} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{\mathrm{or}}}\mathbf{n}^{\mathrm{r}j}\cdot[\rho(\mathbf{w}^{\mathrm{r}j}-\mathbf{v})]\mathrm{d}A\mathrm{d}\tau;\ j=\mathrm{s,o} \quad \text{(E11)}$$

is the mass exchange term of the channel reach with the saturated zone across the channel bed and with the o-subregion through lateral inflow, while

$$I^{\mathrm{r}j} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{\mathrm{r}j}}\mathbf{n}^{\mathrm{r}j}\cdot[\mathbf{i}-\rho(\mathbf{v}-\mathbf{w}^{\mathrm{r}j})\tilde{\psi}^{\mathrm{r}}]\mathrm{d}A\mathrm{d}\tau;\ j=\mathrm{s,o} \quad \text{(E12)}$$

is the non-convective interaction between the channel reach, the saturated zone and the o-subregion. Introduction of the previous defined quantities into the time-averaged balance law (eqn (E2)) and use of the definitions given by eqns (12)–(14) and (16), yields:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}(\langle\rho\rangle^{\mathrm{r}}m^{\mathrm{r}}\bar{\psi}^{\mathrm{r}}\xi^{\mathrm{r}}\Sigma) - (e^{\mathrm{r}A}\bar{\psi}^{\mathrm{r}} + I^{\mathrm{r}A})\Sigma - \langle\rho\rangle^{\mathrm{r}}m^{\mathrm{r}}\bar{f}^{\mathrm{r}}\xi^{\mathrm{r}}\Sigma \\ = \langle G\rangle^{\mathrm{r}}\xi^{\mathrm{r}}\Sigma + (e^{\mathrm{r\ top}}\bar{\psi}^{\mathrm{r}} + I^{\mathrm{r\ top}})\Sigma + (e^{\mathrm{rs}}\bar{\psi}^{\mathrm{r}} + I^{\mathrm{rs}})\Sigma \\ + (e^{\mathrm{ro}}\bar{\psi}^{\mathrm{r}} + I^{\mathrm{ro}})\Sigma\end{aligned} \quad \text{(E13)}$$

The use of REW-scale quantities, defined on the basis of averages, allows, after division by Σ, to recast the general balance equation for the channel reach:

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}(\rho^{\mathrm{r}}m^{\mathrm{r}}\psi^{\mathrm{r}}\xi^{\mathrm{r}}) - (e^{\mathrm{r}A}\psi^{\mathrm{r}} + I^{\mathrm{r}A}) - \rho^{\mathrm{r}}m^{\mathrm{r}}f^{\mathrm{r}}\xi^{\mathrm{r}} \\ = G^{\mathrm{r}}\xi^{\mathrm{r}} + (e^{\mathrm{r\ top}}\psi^{\mathrm{r}} + I^{\mathrm{r\ top}}) + (e^{\mathrm{rs}}\psi^{\mathrm{r}} + I^{\mathrm{rs}}) \\ + (e^{\mathrm{ro}}\psi^{\mathrm{r}} + I^{\mathrm{ro}})\end{aligned} \quad \text{(E14)}$$

In the following sections appropriate quantities will be introduced into eqn (E14), in order to state the balance laws for the four fundamental properties of mass, momentum, energy and entropy.

Conservation of mass

For the mass conservation along the spatial curve C^{r}, the microscale properties in eqn (E2) have to be chosen amongst the appropriate values for the mass balance from Table 2. The REW-scale r-subregion mass balance assumes according to eqn (E14) the following expression:

$$\frac{\mathrm{d}}{\mathrm{d}t}(\rho^{\mathrm{r}}m^{\mathrm{r}}\xi^{\mathrm{r}}) - e^{\mathrm{r}A} = e^{\mathrm{r\ top}} + e^{\mathrm{rs}} + e^{\mathrm{ro}} \quad \text{(E15)}$$

The second term on the l.h.s. accounts for the exchange of water between the channel reach and the neighbouring REWs as well as the external world across A (i.e. inflow and outflow discharge), whereas the terms on the r.h.s. represent the mass exchange with the atmosphere at the free surface (i.e. rainfall and open water evaporation), with the adjacent aquifer across the channel bed (i.e. recharge from groundwater) and with the overland flow region along the channel edge (i.e. lateral inflow).

Conservation of momentum

The REW-scale equation for conservation of momentum for the r-subregion is obtained after defining the-microscale properties according to Table 2:

$$\frac{d}{dt}(\rho^r m^r \mathbf{v}^r \xi^r) - (e^{rA}\mathbf{v}^r + \mathbf{T}^{rA}) - \rho^r m^r \boldsymbol{g}^r \xi^r = (e^{r\ top}\mathbf{v}^r + \mathbf{T}^{r\ top}) + (e^{rs}\mathbf{v}^r + \mathbf{T}^{rs}) + (e^{ro}\mathbf{v}^r + \mathbf{T}^{ro}) \quad \text{(E16)}$$

where:

$$\mathbf{T}^{rA} = \frac{1}{2\Delta t \Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{rA}} \mathbf{n}^{rA}\cdot[\mathbf{t} - \rho(\mathbf{v} - \mathbf{w}^{rA})\tilde{\mathbf{v}}^r]\mathrm{d}A\mathrm{d}\tau \quad \text{(E17)}$$

is the REW-scale momentum exchange term with the neighbouring REWs as well as the external world across the outlet and inlet sections on the mantle A. Furthermore,

$$\mathbf{T}^{r\ top} = \frac{1}{2\Delta t \Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^r_{top}} \mathbf{n}^{r}\cdot[\mathbf{t} - \rho(\mathbf{v} - \mathbf{w}^{r}_{top})\tilde{\mathbf{v}}^r]\mathrm{d}A\mathrm{d}\tau \quad \text{(E18)}$$

is the momentum transfer into the atmosphere on the channel free surface, and

$$\mathbf{T}^{rj} = \frac{1}{2\Delta t \Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{rj}} \mathbf{n}^{rj}\cdot[\mathbf{t} - \rho(\mathbf{v} - \mathbf{w}^{rj})\tilde{\mathbf{v}}^r]\mathrm{d}A\mathrm{d}\tau;\ j = \mathrm{s, o} \quad \text{(E19)}$$

are the REW-scale terms of momentum exchange with the saturated zone across the channel bed and with the regions of saturated overland flow along the channel edges.

Conservation of energy

The equation for conservation of energy for the channel reach is given, after the appropriate substitutions for the microscopic properties, by the expression:

$$\begin{aligned}\frac{d}{dt}\{\rho^r m^r [E^r + (v^r)^2/2]\xi^r\} &- \{e^{rA}[E^r + (v^r)^2/2] + \mathbf{T}^{rA}\cdot\mathbf{v}^r + Q^{rA}\} - \rho^r m^r(\boldsymbol{g}^r\cdot\mathbf{v}^r + h^r)\xi^r \\ &= \{e^{r\ top}[E^r + (v^r)^2/2] + \mathbf{T}^{r\ top}\cdot\mathbf{v}^r + Q^{r\ top}\} \\ &+ \{e^{rs}[E^r + (v^r)^2/2] + \mathbf{T}^{rs}\cdot\mathbf{v}^r + Q^{rs}\} + \{e^{ro}[E^r + (v^r)^2/2] \\ &+ \mathbf{T}^{ro}\cdot\mathbf{v}^r + Q^{ro}\}\end{aligned} \quad \text{(E20)}$$

where:

$$E^r = \bar{E}^r + \overline{(\tilde{v}^r)^2}^r/2 \quad \text{(E21)}$$

is the REW-scale internal energy of the channel reach and

$$h^r = \bar{h}^r + \overline{\tilde{\boldsymbol{g}}^r\cdot\tilde{\mathbf{v}}^r}^r \quad \text{(E22)}$$

is the REW-scale energy supply, consisting of the external supply in addition to the energy supply due to fluctuations of velocity and gravity at the sub-REW-scale. Next, the REW-scale interaction terms are defined:

$$Q^{rA} = \frac{1}{2\Delta t \Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{rA}} \mathbf{n}^{rA}\cdot\{\mathbf{q} + \mathbf{t}\cdot\tilde{\mathbf{v}}^r - \rho(\mathbf{v} - \mathbf{w}^{rA}) \times [\tilde{E}^r + (\tilde{v}^r)^2/2]\}\mathrm{d}A\mathrm{d}\tau \quad \text{(E23)}$$

is the energy transfer from the channel reach across the mantle at the outlet and inlet cross-sections,

$$Q^{r\ top} = \frac{1}{2\Delta t \Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{r}} \mathbf{n}^{r}\cdot\{\mathbf{q} + \mathbf{t}\cdot\tilde{\mathbf{v}}^r - \rho(\mathbf{v} - \mathbf{w}^{r}_{top}) \times [\tilde{E}^r + (\tilde{v}^r)^2/2]\}\mathrm{d}A\mathrm{d}\tau \quad \text{(E24)}$$

is the energy exchange with the atmosphere at the channel free surface, and

$$Q^{rj} = \frac{1}{2\Delta t \Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{rj}} \mathbf{n}^{rj}\cdot\{\mathbf{q} + \mathbf{t}\cdot\tilde{\mathbf{v}}^r - \rho(\mathbf{v} - \mathbf{w}^{rj}) \times [\tilde{E}^r + (\tilde{v}^r)^2/2]\}\mathrm{d}A\mathrm{d}\tau;\ j = \mathrm{s, o} \quad \text{(E25)}$$

are the energy transfer terms into the s-subregion across the channel bed, and the saturated overland flow region along the channel edges.

Balance of entropy

The balance of entropy for the channel reach is given, after appropriate substitution for respective microscopic quantities into eqn (E2), by the expression:

$$\frac{d}{dt}(\rho^r m^r \eta^r \xi^r) - (e^{rA}\eta^r + F^{rA}) - \rho^r m^r b^r \xi^r = L^r\xi^r + (e^{r\ top}\eta^r + F^{r\ top}) + (e^{rs}\eta^r + F^{rs}) + (e^{ro}\eta^r + F^{ro}) \quad \text{(E26)}$$

where:

$$\eta^r = \bar{\eta}^r \quad \text{(E27)}$$

$$b^r = \bar{b}^r \quad \text{(E28)}$$

$$L^r = \langle L\rangle^r \quad \text{(E29)}$$

are the REW-scale entropy, and the REW-scale terms for entropy supply and internal generation of entropy, respectively, while the entropy exchange terms,are defined as follows:

$$F^{rA} = \frac{1}{2\Delta t \Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{rA}} \mathbf{n}^{rA}\cdot[\mathbf{j} - \rho(\mathbf{v} - \mathbf{w}^{rA})\tilde{\eta}^r]\mathrm{d}A\mathrm{d}\tau \quad \text{(E30)}$$

is the entropy exchange with the neighbouring REWs and the external world across the mantle A at the outlet and inlet, while

$$F^{r\ top} = \frac{1}{2\Delta t \Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{r}} \mathbf{n}^{r}\cdot[\mathbf{j} - \rho(\mathbf{v} - \mathbf{w}^{r}_{top})\tilde{\eta}^r]\mathrm{d}A\mathrm{d}\tau \quad \text{(E31)}$$

is the entropy exchange with the atmosphere across the channel free surface. Finally, the term defined as

$$F^{\mathrm{r}j} = \frac{1}{2\Delta t\Sigma}\int_{t-\Delta t}^{t+\Delta t}\int_{A^{\mathrm{r}j}}\mathbf{n}^{\mathrm{r}j}\cdot[\mathbf{j}-\rho(\mathbf{v}-\mathbf{w}^{\mathrm{r}j})\tilde{\eta}^{\mathrm{r}}]\mathrm{d}A\mathrm{d}\tau \quad j=\mathrm{s},\mathrm{o} \tag{E32}$$

expresses the entropy exchange of the channel reach with the s- and the o-subregions.