

Documentation of the Thermal Energy Balance Equation used in the USNT Module of the NUFT Flow and Transport Code

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June 28, 2000

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1. Main Purpose and Some Issues

The main purpose of this document is to describe the thermal energy balance used in the USNT module of the NUFT code (Nitao, 1998) and its derivation. We also address several specific issues that have arisen within the Yucca Mountain Project. Since the reader may not be aware of these issues, we list them here in the form of questions.

Issue 1. Isn't the energy balance equation used by NUFT as described in the NUFT USNT manual (Nitao, 1998) incorrect because internal energy is used in the time derivative, or accumulation, term instead of enthalpy? Does the balance equation in NUFT assume constant pressure? Constant volume?

Issue 2. Does NUFT "double account" for heat transfer by mass transfer in the thermal conductivity?

Issue 3. Shouldn't the specific heat for the solid in the NUFT energy balance equation be specific heat, c_v , at constant volume, and not specific heat, c_p , at constant pressure?

The answer to all of these questions is in the negative. This document answers these issues by presenting a detailed and rigorous derivation of the thermal energy balance equation used in NUFT. From this derivation, we can answer these questions as follows.

Response to Issue 1. The internal energy in the time derivative term is correct under assumptions widely used in the literature and similar computer codes. The balance equation is based on established literature, such as in Bird et al. (1960), with the following common approximations made: that the viscous dissipation term, $(\tau : \nabla \mathbf{V})$, and the pressure gradient term, $(\mathbf{V} \cdot \nabla p)$, are negligible compared to other terms in the equation. The resulting balance equation is the same as given in the NUFT manual. In this document, we estimate the magnitude of the two neglected terms and show that they are, indeed, negligible for the Yucca Mountain system.

The balance equation used in NUFT dates back many years, at least to 1974 (Coats et al., 1974), in the thermal modeling of petroleum reservoirs and is still widely used in the petroleum industry. It is also the same equation in the TOUGH2 code (Pruess, 1991, see pp. 91-92), which is a thermal-hydrologic code also used in the Yucca Mountain

Project.

(Note: The assumption that the term $(\mathbf{V} \cdot \nabla p)$ is negligible does not mean that constant pressure is assumed – only that this particular term is neglected. In fact, pressure is a variable in all remaining terms in the equation in which it appears.)

Response to Issue 2. There is no double accounting for heat transfer in the thermal conductivity. As will be seen in our derivation and as described in the NUFT manual (Nitao, 1998), the thermal conductivity that is input to the NUFT model is the bulk thermal conductivity of the porous medium. The heat transfer due to diffusion and advection of mass are separate terms in the balance equation and are not part of the thermal conductivity. This point is clear from the balance equation described in the NUFT manual. Of course, it is up to the user to input thermal conductivity into the code, and *not* an effective transfer coefficient lumping together thermal conduction and heat transfer by mass movement.

Response to Issue 3. The conditions at the Yucca Mountain for the solid phase are closer to constant stress conditions than to constant volume conditions because of the weight of the thick overburden over the repository. As will be shown in the detailed derivation, under constant stress conditions the specific heat at constant pressure is more applicable than the specific heat at constant volume. The erroneous conclusion, that specific heat at constant volume should be used, is shown to arise from an incorrect derivation of the thermal energy equation that *ab initio* assumes that terms containing the solid velocity are negligible. When these terms are kept until the final step of the derivation, we show that, under constant pressure conditions, c_p , and not c_v , is the correct term in the thermal conduction equation,

(It is well-known that numerical values of c_p and c_v are only a few percent apart for geological materials. Moreover, highly respected references in the field of thermal conduction such as, Carslaw and Jaeger (1959), use c_p . It might, therefore, appear that a detailed discussion of this issue is not needed. However, we give a detailed discussion of this issue in order to give a complete documentation, and to resolve particular concerns within the Yucca Mountain Project.)

2. Introduction

NUFT solves the coupled partial differential equations which describe the flow and transport of multiple mass components and energy in a porous medium containing multiple fluid phases. These equations are obtained from differential mass and energy balances. The purpose of this document is to describe the derivation of one of these equations, the thermal energy balance equation. We will use as a starting point, the equation given in established literature and, then, describe and justify the approximations made for its use on the Yucca Mountain Project.

2.1. The Microscopic Level

In order to mathematically model flow and transport in a porous medium, we need to distinguish between *microscopic* versus *macroscopic* balance equations. The microscopic balance equations describe processes at and below the pore-scale level. The microscopic balance equations are obtained from averaging the mechanics of molecular motion over a microscopic representative elementary volume (μ REV) much larger than the mean free-path of the molecules and over a time interval when a sufficient number of particle collisions occurs (Hirschfelder et al., 1954).

A μ REV is associated at each point in a phase, so that, by suitable averaging, smooth thermodynamic fields for various quantities, such as temperature, stress, and chemical potentials of each mass component, are defined over the region occupied by the phase. Each μ REV is assumed to be wholly contained inside a phase, whether it be in a solid or fluid phase. Interfaces between the phases are often idealized as sharp surfaces at which boundary conditions must be specified. A more detailed analysis requires that interfaces be treated as transition zones between phases (Adamson, 1982).

A μ REV exists at a given point as long as fluxes in energy, mass, and momentum are sufficiently small. This condition can be expressed more precisely as requiring that the gradients in temperature, chemical potentials, and stress tensor, be small over the μ REV compared to the average value of the respective potentials over the μ REV (Kreuzer, 1981; Bear and Nitao, 1995). This assumption is often called “local thermodynamic equilibrium” in textbooks. Throughout this document we will assume that this condition is satisfied over the relevant physical domain. The assumption of local thermodynamic equilibrium allows us to use the results of classical thermodynamics at each infinitesimal volume within our domain and makes it possible to define the necessary equations of state that relate various properties within the

phases.

2.2. The Macroscopic Level

Each solid or fluid phase has a microscopic balance equation defined within the region occupied by that phase. that must be solved along with boundary conditions at interfaces between phases for the continuity of component mass and energy fluxes crossing the interfaces. In a porous medium, the solution of the resulting system is not practical because the geometry of the region occupied by the phases, and the interfaces between phases, is too complex. To avoid this difficulty, *macroscopic* governing equations are obtained by volume-averaging the microscopic balance equations (Bear and Bachmat, 1991).

At each point in the macroscopic continuum an elementary representative volume (REV) is assumed to exist. Volume-averaging of the microscopic equations is performed over each REV. The solutions to the resulting equations are volume-averaged physical quantities that are continuous over the domain. The size of the REV must be sufficiently large compared to the scale of significant spatial variations in physical and chemical properties and, therefore, is much larger than the size of the pores. A useful assumption, when valid, is local thermodynamic equilibrium at the macroscopic level. This means that the root-mean-square integral of the spatial variations in the microscopic thermodynamic potentials (temperature and the mass component chemical potentials) over each REV is small compared to the spatial variations of the macroscopic potentials within the REV. If this assumption is true, the thermodynamic state at the macroscopic level is representable by the macroscopic temperature and the macroscopic chemical potentials of each mass component (Nitao and Bear, 1996).

At the microscopic level each point lies within a single phase. However, at the macroscopic level, each point “contains” all fluid and solid phases and their properties. Hence, there is obviously a fundamental difference between the balance equations at the macroscopic and microscopic levels, which justifies the need to derive the balance equations at both scales.

2.3. Agenda

In this document, we first show how the microscopic thermal energy balance equation is derived and which terms are neglected in the NUFT code. We then show that the magnitude of the neglected terms are sufficiently small in describing the processes at Yucca Mountain. We, then, derive the

macroscopic equation by volume-averaging the microscopic equations.

(Quantities such as temperature and internal energy, are defined in thermodynamics under the assumption of thermodynamic equilibrium. However, systems where mass and heat transfer occurs, clearly, do not satisfy this criteria. Therefore a question arises as to how we can define these thermodynamic quantities under dynamic conditions. Moreover, how does the microscopic balance equation arise from the molecular level? Appendix A gives a brief treatment of these issues.)

3. Notational Convention

Throughout this document we subscribe to the following conventions for mathematical symbols.

1. We always denote quantities that are related to a particular fluid or solid phase by the use of subscripts. For example, θ_α is the volumetric fraction of the α -phase; and, θ_ℓ , θ_g , and θ_s are the volumetric fractions of liquid, gas, and solid phases, respectively.
2. In most cases, where it is understood that a particular fluid or solid phase is being discussed, the subscript denoting the phase will be dropped. This convention will be used, in particular, when we discuss microscopic equations.
3. We will always denote quantities that are related to a particular mass component by the use of superscripts. For example, ω^γ is the mass fraction of the γ -component within the phase under investigation; and, ω^a and ω^w stand for the mass fractions of air and water components, respectively.
4. Bold symbols denote vectors or tensors. Bold non-serif Latin symbols (such as \mathbf{T}) are always tensors.
5. Usually, but not always, upper-case symbols denote extensive quantities, and lower-case symbols denote intensive quantities. There are exceptions. Some upper-case symbols that do not represent extensive quantities are material velocity \mathbf{V} , absolute temperature T , intrinsic permeability K , phase saturation S_α , molecular mass M^γ , tortuosity tensor \mathbf{T}^* , and diffusivity \mathcal{D}^γ . Lower case symbols that do not represent intensive quantities are mass of a component m^γ , coordinate vector \mathbf{x}' of a microscopic point, coordinate vector \mathbf{x} of a macroscopic point, and cartesian coordinate x_i ,

4. Thermal Energy Balance Equation at the Microscopic Level

NUFT consists of several modules, each one solving the appropriate balance equations under a particular set of assumptions. The thermal-hydrological calculations for the Yucca Mountain system are modeled using the USNT module (Nitao, 1998). This module solves the general macroscopic mass and thermal energy balance equations for a multiple fluid phase system with multiple components. For the Yucca Mountain system the fluid phases are the aqueous phase and the gaseous phase. The two components modeled are air (considered as a single pseudo-component) and water. Both components may exist within either of the two phases.

The macroscopic balance equations solved by NUFT are obtained from volume-averaging the appropriate microscopic balance equations. For illustrative purposes and for its relative simplicity, we will in the first subsection consider the microscopic energy balance equation of a pure fluid phase. This phase can, for example, be a pure liquid consisting only of water or a pure gas consisting only of air. In the second subsection we consider the more complex multiple-component system appropriate to Yucca Mountain thermal-hydrologic calculations. After that, we show that a particular term, the term arising from diffusive mass transport against gravity, is zero. Lastly, we derive the thermal energy balance equation for a solid using the specific heat capacity, and show that under constant stress conditions the specific heat at constant pressure is the correct one to use, and not one at constant volume.

4.1. Balance Equation for a Pure Fluid

The thermal energy balance equation for a single, pure fluid phase (Bird et al., 1960, Eq. Q, p. 323) is

$$\frac{\partial \rho u}{\partial t} = -(\nabla \cdot \mathbf{q}) - (\nabla \cdot \rho u \mathbf{V}) - p(\nabla \cdot \mathbf{V}) - (\boldsymbol{\tau} : \nabla \mathbf{V}), \quad (4.1)$$

- p pressure,
- \mathbf{q} non-advective thermal energy flux,
- u specific internal energy of the fluid (internal energy per mass),
- \mathbf{V} mass-weighted fluid velocity,
- $\nabla \mathbf{V}$ second rank tensor, $\partial V_i / \partial x_j$,
- ρ mass density,
- $\boldsymbol{\tau}$ deviatoric stress tensor.

For a fluid phase the deviatoric tensor, $\boldsymbol{\tau}$, is the viscous stress tensor.

The above equation is obtained from subtracting the kinetic energy balance equation from the total energy balance equation (Bird et al., 1960, p. 314). The kinetic energy balance equation is the direct result of the momentum balance equation (just as the mechanical energy equation, mechanical energy = kinetic energy + potential energy, is a corollary to Newton's second law). Hence, there are no kinetic energy and potential terms in the above equation.

For a pure fluid the non-advective thermal energy flux \mathbf{q} is due to thermal conduction alone and is usually treated using the Fourier law,

$$\mathbf{q} = -k\nabla T, \quad (4.2)$$

where k is the thermal conductivity of the fluid, and T is temperature.

The third term $-p(\nabla \cdot \mathbf{V})$ on the right-hand side of (4.1) can be written as

$$-p(\nabla \cdot \mathbf{V}) = -\nabla \cdot p\mathbf{V} + \mathbf{V} \cdot \nabla p. \quad (4.3)$$

We combine this term with the second term, $-(\nabla \cdot \rho u \mathbf{V})$, on the right-hand side of the same equation to obtain

$$-(\nabla \cdot \rho u \mathbf{V}) - p(\nabla \cdot \mathbf{V}) = -\nabla \cdot \rho h \mathbf{V} + \mathbf{V} \cdot \nabla p, \quad (4.4)$$

where $h = u + p/\rho$ is the specific enthalpy. Substituting these terms into (4.1), we have

$$\frac{\partial \rho u}{\partial t} = (\nabla \cdot k \nabla T) - (\nabla \cdot \rho h \mathbf{V}) + (\mathbf{V} \cdot \nabla p) - (\boldsymbol{\tau} : \nabla \mathbf{V}). \quad (4.5)$$

For many applications the last two terms $(\mathbf{V} \cdot \nabla p)$ and $-(\boldsymbol{\tau} : \nabla \mathbf{V})$ are negligible compared to the other terms. Later, we will demonstrate this fact for the Yucca Mountain system. Then, the following simplified thermal energy balance equation results,

$$\frac{\partial \rho u}{\partial t} = (\nabla \cdot k \nabla T) - (\nabla \cdot \rho h \mathbf{V}). \quad (4.6)$$

Equation (4.6) can also be obtained under a set of assumptions that are, perhaps, different than those used above. The total energy balance equation is given by (Bird et al., 1960, Eqt. N, p. 323)

$$\frac{\partial \rho(u + \frac{1}{2}V^2 + \varphi)}{\partial t} = -\nabla \cdot [\rho(h + \frac{1}{2}V^2 + \varphi)\mathbf{V}] - \nabla \cdot \mathbf{q} - \nabla \cdot [\boldsymbol{\tau} \cdot \mathbf{V}]. \quad (4.7)$$

If the viscous heating term $-(\nabla \cdot [\boldsymbol{\tau} \cdot \mathbf{V}])$ is neglected, and if the magnitude of the kinetic energy term, $\frac{1}{2}V^2$, and potential energy term, φ , is small

compared to the internal energy u , with their time and spatial derivatives being small, as well, compared to the derivatives of u , we may drop those terms to obtain,

$$\frac{\partial \rho u}{\partial t} = -\nabla \cdot (\rho h \mathbf{V}) - \nabla \cdot \mathbf{q}, \quad (4.8)$$

which is identical to (4.6) if the conduction flux, $\mathbf{q} = -k\nabla T$, is used.

4.2. Balance Equation for a Fluid Phase Consisting of Multiple Components

Because the thermal-hydrological calculation of the Yucca Mountain system consists of the transport of two components, air and water, (for Yucca Mountain thermal-hydrological calculations, air is treated as a single “pseudo-component”), we require the energy balance for a single fluid phase containing several components. The thermal energy balance equation for a given phase is (Bird et al., 1960, Eq. D, p. 562)

$$\rho \frac{Du}{Dt} = -(\nabla \cdot \mathbf{q}) - (\boldsymbol{\sigma} : \nabla \mathbf{V}) + \sum_{(\gamma)} (\mathbf{j}^\gamma \cdot \mathbf{f}^\gamma). \quad (4.9)$$

Recall that the subscript, γ , is over all mass components within the fluid phase. Also, all quantities refer to the particular phase under consideration. That is, instead of denoting quantities such as the density of a phase by ρ_α , we drop the subscript and simply use ρ . The term Du/Dt on the left-hand-side is the total time derivative defined by

$$\frac{Du}{Dt} \equiv \frac{\partial u}{\partial t} + (\mathbf{V} \cdot \nabla u). \quad (4.10)$$

The symbol \mathbf{f}^γ denotes the external force acting on per unit mass of the γ -component. The mass diffusion flux \mathbf{j}^γ of the γ -component is defined as (Bird et al., 1960, Eq. 16.1-9, p. 501),

$$\mathbf{j}^\gamma = \rho^\gamma \bar{\mathbf{V}}^\gamma, \quad (4.11)$$

where ρ^γ is the mass of the γ -component per mass of fluid, and $\bar{\mathbf{V}}^\gamma$ is the diffusion velocity (velocity relative to mass-weighted average velocity),

$$\bar{\mathbf{V}}^\gamma = \mathbf{V}^\gamma - \mathbf{V}, \quad (4.12)$$

(Bird et al., 1960, Eq. 16.1-3, p. 497) which is the mass-weighted velocity of the γ -component relative to the mass-weighted velocity \mathbf{V} of the fluid. It

is clear that (Bird et al., 1960, Eq. 16.1-1, p. 497),

$$\mathbf{V} = \frac{\sum_{(\gamma)} \rho^\gamma \mathbf{V}^\gamma}{\sum_{(\gamma)} \rho^\gamma} = \frac{1}{\rho} \sum_{(\gamma)} \rho^\gamma \mathbf{V}^\gamma. \quad (4.13)$$

The stress tensor σ is given by

$$\sigma = \tau + p\mathbf{I}, \quad (4.14)$$

where τ is the deviatoric tensor which, for a fluid, includes viscous shear, p is pressure, and \mathbf{I} is the unit tensor. (There are various different sign conventions for τ and σ , used in the literature. We use the same sign convention as Bird et al.(1960).)

The mass balance equation for a fluid phase is given by

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{V}) = 0. \quad (4.15)$$

We multiply both sides of this equation by u and add it to the left-hand side of (4.9). Then, using (4.10) gives

$$\begin{aligned} \frac{\partial \rho u}{\partial t} + \nabla \cdot (\rho u \mathbf{V}) &= -(\nabla \cdot \mathbf{q}) - (\sigma : \nabla \mathbf{V}) \\ &+ \sum_{(\gamma)} (\mathbf{j}^\gamma \cdot \mathbf{f}^\gamma). \end{aligned} \quad (4.16)$$

From (4.14) and the identity,

$$p\mathbf{I} : \nabla \mathbf{V} = p\nabla \cdot \mathbf{V}, \quad (4.17)$$

equation (4.16) becomes

$$\begin{aligned} \frac{\partial \rho u}{\partial t} + \nabla \cdot (\rho u \mathbf{V}) &= -(\nabla \cdot \mathbf{q}) - (\tau : \nabla \mathbf{V}) - (p\nabla \cdot \mathbf{V}) \\ &+ \sum_{(\gamma)} (\mathbf{j}^\gamma \cdot \mathbf{f}^\gamma). \end{aligned} \quad (4.18)$$

We subtract the term $\nabla \cdot (\rho u \mathbf{V})$ on both sides of the equation resulting in the term $-\nabla \cdot \rho u \mathbf{V}$ appearing on the right-hand side. The term $-p\nabla \cdot \mathbf{V}$ in the left-hand side of the equation is rewritten as

$$-p\nabla \cdot \mathbf{V} = -\nabla \cdot (p\mathbf{V}) + \mathbf{V} \cdot \nabla p. \quad (4.19)$$

Using this identity, we combine $-p\nabla \cdot \mathbf{V}$ with $-\nabla \cdot (\rho u \mathbf{V})$ to obtain

$$-\nabla \cdot (\rho u \mathbf{V}) - p\nabla \cdot \mathbf{V} = -\nabla \cdot (\rho h \mathbf{V}) + \mathbf{V} \cdot \nabla p, \quad (4.20)$$

where $h = u + p/\rho$ is the specific enthalpy. The thermal energy balance equation, (4.18), becomes

$$\begin{aligned} \frac{\partial \rho u}{\partial t} &= -(\nabla \cdot \mathbf{q}) - \nabla \cdot (\rho h \mathbf{V}) - (\boldsymbol{\tau} : \nabla \mathbf{V}) + (\mathbf{V} \cdot \nabla p) \\ &\quad + \sum_{(\gamma)} (\mathbf{j}^\gamma \cdot \mathbf{f}^\gamma). \end{aligned} \quad (4.21)$$

The thermal energy flux, \mathbf{q} , in (4.21) is composed of three terms (Bird et al., 1960, Eq.18.4-2, p. 566),

$$\mathbf{q} = \mathbf{q}^{(c)} + \mathbf{q}^{(d)} + \mathbf{q}^{(x)}. \quad (4.22)$$

(We may also add the radiative flux $\mathbf{q}^{(r)}$ to the above equation.)

The flux $\mathbf{q}^{(c)}$ is due to thermal conduction,

$$\mathbf{q}^{(c)} = -k\nabla T. \quad (4.23)$$

The flux $\mathbf{q}^{(d)}$ is due to species diffusion (Bird et al., 1960, Eq.18.4-3, p. 566),

$$\mathbf{q}^{(d)} = \sum_{(\gamma)} \left(\frac{\hat{h}^\gamma}{M^\gamma} \right) \hat{\mathbf{j}}^\gamma, \quad (4.24)$$

where M^γ is the molecular mass of the γ -component. The symbol \hat{h}^γ denotes the partial molar enthalpy of the γ -component and is defined by,

$$\hat{h}^\gamma \equiv \left(\frac{\partial H}{\partial N^\gamma} \right)_{p, T, N^{\delta \neq \gamma}}, \quad (4.25)$$

where $H = H(p, T, N^\delta)$ is the total fluid enthalpy, N^γ is the number of moles of the γ -component, and $N^{\delta \neq \gamma}$ denotes the moles of all components except the γ component.

The partial mass enthalpy, h^γ , may be defined by

$$h^\gamma \equiv \left(\frac{\partial H}{\partial m^\gamma} \right)_{p, T, m^{\delta \neq \gamma}}, \quad (4.26)$$

where m^γ is the mass of the γ -component. It is related to the partial molar enthalpy, \hat{h}^γ , by

$$h^\gamma = \hat{h}^\gamma / M^\gamma. \quad (4.27)$$

Therefore,

$$\mathbf{q}^{(d)} = \sum_{(\gamma)} h^\gamma \mathbf{j}^\gamma. \quad (4.28)$$

Substituting the various fluxes into (4.22) and (4.21), we obtain

$$\begin{aligned} \frac{\partial \rho u}{\partial t} = & \nabla \cdot (k \nabla T) - \nabla \cdot \left(\sum_{(\gamma)} h^\gamma \mathbf{j}^\gamma \right) - \nabla \cdot (\rho h \mathbf{V}) \\ & - (\boldsymbol{\tau} : \nabla \mathbf{V}) + (\mathbf{V} \cdot \nabla p) + \sum_{(\gamma)} (\mathbf{j}^\gamma \cdot \mathbf{f}^\gamma). \end{aligned} \quad (4.29)$$

The diffusive mass fluxes \mathbf{j}^γ for a binary (two-component) system is usually represented by Fick's law,

$$\mathbf{j}^\gamma = -\rho \mathcal{D}^\gamma \nabla \omega^\gamma, \quad (4.30)$$

where ω^γ is the mass fraction and \mathcal{D}^γ is the binary diffusion coefficient of the γ -species.

4.3. Diffusion Work Term for Gravitational Forces is Zero

The term $(\sum_{(\gamma)} \mathbf{j}^\gamma \cdot \mathbf{f}^\gamma)$ represents the work done by diffusion against an external force (The term corresponding to the work done by the bulk fluid was removed from the balance equation when we subtracted the mechanical energy balance from the total energy balance equation. The only remaining term for work against external forces is that relative to the motion of the bulk fluid, which, by definition, is the work done by diffusive mass fluxes.)

For Yucca Mountain simulations, the only external force is gravity. The term, \mathbf{f}^γ , is force per unit mass of the component. Therefore,

$$\mathbf{f}^\gamma = -g \nabla z, \quad (4.31)$$

where g is the local gravitational acceleration and z denotes the vertical coordinate (increasing upwards). We now show that the diffusion work term is zero if the only external force is gravity. Conceptually, this result follows from the fact that gravity acts on only the mass of each component while the net mass flux due to diffusion is zero. Therefore, no net work is done by mass diffusion.

First we show, formally, that the sum of the diffusion fluxes is zero,

$$\sum_{(\gamma)} \mathbf{j}^\gamma = 0. \quad (4.32)$$

From the definition of diffusive flux, we have from (4.11) and (4.12) that

$$\begin{aligned}
\sum_{(\gamma)} \tilde{\mathbf{j}}^\gamma &= \sum_{(\gamma)} \rho^\gamma (\mathbf{V}^\gamma - \mathbf{V}) \\
&= \sum_{(\gamma)} \rho^\gamma \mathbf{V}^\gamma - \left(\sum_{(\gamma)} \rho^\gamma \right) \cdot \mathbf{V} \\
&= \rho \mathbf{V} - \rho \mathbf{V} \\
&= 0,
\end{aligned} \tag{4.33}$$

where we used the definition of mass-weighted velocity \mathbf{V} ,

$$\mathbf{V} = \frac{\sum_{(\gamma)} \rho^\gamma \mathbf{V}^\gamma}{\sum_{(\gamma)} \rho^\gamma}, \tag{4.34}$$

and the identity,

$$\rho = \sum_{(\gamma)} \rho^\gamma. \tag{4.35}$$

Therefore, from (4.31) and (4.32), the gravitational work by diffusion is zero,

$$\sum_{(\gamma)} \tilde{\mathbf{j}}^\gamma \cdot \mathbf{f}^\gamma = - \left(\sum_{(\gamma)} \tilde{\mathbf{j}}^\gamma \right) \cdot (g \nabla z) = 0, \tag{4.36}$$

which is the desired result.

4.4. Balance Equation for a Solid Phase

The thermal energy balance, given by (4.9), for the fluid also applies to a solid. The demonstration that the mass-diffusion body force term is zero also applies to a solid. Moreover, energy transport by mass diffusion fluxes are sufficiently small in comparison to thermal conduction that they can be neglected. We have, therefore,

$$\rho \frac{Du}{Dt} = -(\nabla \cdot \mathbf{q}) - p(\nabla \cdot \mathbf{V}) - (\boldsymbol{\tau} : \nabla \mathbf{V}), \tag{4.37}$$

with the heat flux given by the Fourier law of conduction,

$$\mathbf{q} = -k \nabla T. \tag{4.38}$$

Because a computer code without mechanical coupling has no information regarding the velocity, \mathbf{V} , of the solid phase, these terms are usually neglected in thermal flow and transport codes. We could stop here, except that laboratory measurements of internal energy are not usually available.

Instead, the heat capacity of a solid is the relevant quantity that is measured. A solid sample is heated by the application of some heat flux, δQ , and the resulting change in temperature, δT , is measured. If the experiment is performed while the sample is constrained to a fixed volume (or, more precisely, a fixed strain) then the heat capacity, C_v , at constant volume is measured. If the sample is kept under a constant pressure (or, more precisely, fixed stress load), the heat capacity, C_p , at constant pressure is measured. We may represent these two definitions of heat capacity by the equations

$$\Delta Q|_v = C_v \Delta T, \quad (4.39)$$

and

$$\Delta Q|_p = C_p \Delta T. \quad (4.40)$$

Or more correctly,

$$\Delta Q|\epsilon = C_\epsilon \Delta T, \quad (4.41)$$

and

$$\Delta Q|\sigma = C_\sigma \Delta T, \quad (4.42)$$

where ϵ is strain, and σ is stress. The specific heat capacity c_p and c_v are the respective heat capacities, C_p and C_v , respectively, defined per unit mass of substance.

Because heating of the rock at the Yucca Mountain site occurs under approximately constant loading conditions from the weight of the overburden above the repository, one can argue that the constant pressure (or loading) specific heat is closer to reality than constant volume. Also, laboratory measurements under constant loading conditions is much easier to perform than those at constant volume.

In any case, for most substances, the values of c_p and c_v are only within a few percent of each other, and c_p is probably more commonly used than c_v . The work by Carslaw and Jaeger (1959), which is probably the most highly respected text in the field of heat conduction, uses c_p exclusively.

We now derive the thermal energy balance equation in term of c_p for heating under the constant stress conditions.

Consider an infinitesimal volume of rock in the field under a constant stress. Let q be the heat in the solid per unit mass of solid. Heating or cooling of the rock is assumed to take place as a reversible thermodynamic process. The rate of change, Dq/Dt , of heat in the volume is equal to the net heat flux applied to the volume which, in this case, is due to thermal conduction. Since the net thermal conduction flux for an infinitesimal system

per unit mass is $\frac{1}{\rho}\nabla\cdot k\nabla T$, we have

$$Dq/Dt = \frac{1}{\rho}\nabla\cdot k\nabla T. \quad (4.43)$$

This equation is a thermal energy balance equation and should, therefore, be the same as the balance equation, (4.37), derived earlier. In Appendix B we show that this is, indeed, the case.

Since the heating is assumed to occur under constant stress conditions, from the definition of c_σ we have that

$$Dq/Dt = c_\sigma DT/Dt. \quad (4.44)$$

Substituting into (4.43) we have the thermal energy balance equation in terms of c_σ as

$$\rho c_\sigma DT/Dt = \nabla\cdot k\nabla T. \quad (4.45)$$

Expanding the total derivative on the left-hand side we have

$$\rho c_\sigma \frac{\partial T}{\partial t} + \rho c_\sigma \mathbf{V} \cdot \nabla T = \nabla\cdot k\nabla T. \quad (4.46)$$

If the magnitude of the second term on the left-hand side is much smaller than the magnitude of the first term, i.e.,

$$|\mathbf{V} \cdot \nabla T| \ll \left| \frac{\partial T}{\partial t} \right|, \quad (4.47)$$

then we have the familiar heat conduction equation given by

$$\rho c_\sigma \frac{\partial T}{\partial t} = \nabla\cdot k\nabla T. \quad (4.48)$$

For an isotropic infinitesimal rock mass under an isotropic stress field with no shear c_σ is the same as c_p , and, we have

$$\rho c_p \frac{\partial T}{\partial t} = \nabla\cdot k\nabla T, \quad (4.49)$$

which is the desired thermal conduction equation in terms of c_p under constant solid pressure conditions.

Erroneous Argument for the Use of c_v Instead of c_p .

Some have argued that the use of c_v instead of c_p is more correct in the

equation for thermal conduction in a solid, even under constant stress conditions. In fact, many textbooks are somewhat cavalier in their treatment of this issue, perhaps, because the difference between c_v and c_p for many solids is only a few percent.

Before proceeding, we first rewrite equation (4.37) by using the mass balance equation and expanding the total time derivative to give the following form of the thermal balance equation,

$$\frac{\partial \rho u}{\partial t} + \nabla \cdot (\rho u \mathbf{V}) = -(\nabla \cdot \mathbf{q}) - p(\nabla \cdot \mathbf{V}) - (\boldsymbol{\tau} : \nabla \mathbf{V}). \quad (4.50)$$

The erroneous argument begins by neglecting all terms in the equation containing the solid velocity, \mathbf{V} , in order to obtain the equation,

$$\frac{\partial \rho u}{\partial t} = (\nabla \cdot k \nabla T). \quad (4.51)$$

From the well-known thermodynamic identity for the heat capacity at constant volume,

$$C_v = \left(\frac{\partial E}{\partial T} \right)_v, \quad (4.52)$$

we have that the specific heat capacity at constant volume is

$$\rho c_v = \left(\frac{\partial \rho u}{\partial T} \right)_v, \quad (4.53)$$

so that (4.51) becomes

$$c_v \frac{\partial T}{\partial t} = (\nabla \cdot k \nabla T). \quad (4.54)$$

Because this equation is different from (4.49), it is, then, concluded that (4.49) is incorrect and that c_v should be the factor multiplying the time derivative term, not c_p .

The error in the above argument is that *ab initio* the solid velocity terms are assumed to be negligible. This assumption is inconsistent with the assumed constant stress conditions since the solid will move during heating as it performs work against the applied stress. The derivation of (4.49) given above shows that the solid velocity terms are essential to deriving the balance equation under constant stress conditions, and when they are included the correct specific heat is seen to be c_p , and not c_v .

5. Simplifications to the Thermal Energy Balance Equation at the Microscopic Level

The macroscopic thermal energy equation solved by NUFT is derived from following simplified microscopic energy balance equation,

$$\frac{\partial \rho u}{\partial t} = (\nabla \cdot k \nabla T) - \nabla \cdot \left(\sum_{(\gamma)} h^{\gamma} \mathbf{j}^{\gamma} \right) - \nabla \cdot (\rho h \mathbf{V}), \quad (5.1)$$

which is obtained from (4.29) by neglecting the last three terms on the right-hand-side. The purpose of making these simplifications is to avoid unnecessary numerical computation by eliminating terms that are negligible compared to other terms in the equation.

The last term of (4.29) was shown to be zero when gravitation is the only external force. In this section the other two terms (4.29) that are neglected will be considered in detail in the context of Yucca Mountain. In particular, we will estimate upper bounds to the magnitude of these two terms and show that they have a negligible effect on model predictions.

5.1. Estimation of the Effect of Viscous Heating Term

5.1.1. Viscous Heating during Infiltration

In this subsection we consider the term $-\boldsymbol{\tau} : \nabla \mathbf{V}$, which represents irreversible thermal energy dissipation from viscous shear during fluid flow. For Newtonian fluids, this term is always non-negative because it can be written as the sum of squares (Bird et al., 1960, p. 82). For relatively simple systems (such as flow and heat transfer between parallel plates) the dimensionless group, called the Brinkman number (Bird et al., 1960, p. 278),

$$Br = \frac{\mu(V/D)^2}{k(T_o - T_1)/D^2}, \quad (5.2)$$

can be used to estimate the relative effect of viscous dissipation over thermal conduction. Here, μ is dynamic viscosity of the fluid, k is thermal conductivity of the fluid, $(T_o - T_1)/D$ is the characteristic temperature gradient, and D is a characteristic length. Small values of Br indicates that any heat generated by viscous dissipation will be carried off by thermal conduction, and, hence, has little effect. However, for more complicated problems, a more detailed analysis is needed.

The standard Brinkman number is for a single fluid system. Also, it presumes that the characteristic length D for viscous dissipation is the same

at that for thermal conduction. For Yucca Mountain the system is not single phase system, but involves heat transfer through a fractured porous medium consisting of solid and fluid phases. At Yucca Mountain the largest fluid velocity gradients (which are the source of viscous dissipation) are in the fractures where the velocities are the highest. The characteristic length for viscous dissipation should be the fracture aperture. Thermal conduction occurs from the fractures to the matrix block and then over the scale of the distance from the repository to the ground surface. We, therefore, cannot use an analysis based on the standard Brinkman number.

In order to estimate the relevant importance of viscous heating for liquid flow down a system of fractures, we consider a two-dimensional system of idealized vertical fractures that are of the same aperture b and spaced a distance a apart from each other. We assume that b is much smaller than a , i.e., $b \ll a$. The fractures extend from the ground surface to the water table, which is at depth, d_{wt} , from the surface. The amount of viscous heating released per unit volume (W/m^3) inside the fraction is approximately given by (Bird et al., 1960, eq 9.4-3, p. 278),

$$q_v = \mu \left(\frac{V_f}{b} \right)^2, \quad (5.3)$$

where b is the aperture of the fracture and V is the velocity of the fluid inside the fracture.

We will estimate the rise in temperature due to viscous heating. Note that the vertical temperature profile approximately satisfies the steady-state heat conduction equation with the source term due to viscous heating,

$$\frac{d}{dz} ak \frac{d\Delta T_v(z)}{dz} = bq_v. \quad (5.4)$$

where $\Delta T(z)$ denotes the rise in the vertical temperature profile above the ambient conditions due to viscous heating. Solving this equation we have

$$\Delta T_v(z) = \frac{1}{2} bq_v z^2 / ak, \quad (5.5)$$

where z is the depth below the ground surface. Setting $z = d_{wt}$, the increase in temperature at the water table is therefore,

$$\Delta T_v = \frac{1}{2} bq_v d_{wt}^2 / ak = \frac{1}{2} \frac{(b/a) \mu \left(\frac{V_f}{b} \right)^2}{k/d_{wt}^2}. \quad (5.6)$$

To be conservative with regards to flow velocity, we assume that the fractures are filled with fluid. The velocity for flow between parallel plates under a gravity pressure gradient is well known and is given by

$$V_f = \frac{b^2}{12\mu}\rho g. \quad (5.7)$$

Let q_{inf} stand for the assumed constant specific volumetric infiltration flux ($\text{m}^3/\text{m}^2\text{-s} = \text{m/s}$) over the repository. All of this flux is assumed to occur in the fractures. Thus, we must have

$$bV_f = aq_{inf}, \quad (5.8)$$

or, equivalently,

$$a = bV_f/q_{inf}. \quad (5.9)$$

This constraint on spacing, a , between flowing or “active” fractures arises as follows – the larger the flux into each fracture the fractures that have flow must be spaced farther apart in order for the total infiltration flux to be satisfied.

Substituting into the expression for a into (5.5), we obtain the following expression for the temperature rise at the water table,

$$\Delta T_v = \frac{(q_{inf}/b)\mu \left(\frac{V_f}{b}\right)}{k/d_{wt}^2}. \quad (5.10)$$

Substituting for V_f from (5.7), we have

$$\Delta T_v = \frac{q_{inf}\rho g/12}{k/d_{wt}^2}. \quad (5.11)$$

We use the following parameter values for the flow of liquid water,

q_{inf}	100 mm/y
b	100 μm
ρ	$1 \times 10^3 \text{ kg/m}^3$
μ	$8.7 \times 10^{-4} \text{ Nt-s/m}^2$
k	1.2 (W-m/ $^\circ\text{K}$)
d_{rep}	350m
d_{wt}	600m

The resulting increase in temperature at the water table is estimated to be

$$\Delta T_v \approx 0.8^\circ\text{C}. \quad (5.12)$$

Using a similar formula as for the water table, the temperature rise at the repository is given by

$$\Delta T_v \approx 0.3^\circ C. \quad (5.13)$$

The above values are conservative because we have only included conductive heat transfer to the ground surface and have neglected heat transfer to the water table. The rise in temperature is relatively small compared to repository temperatures and, therefore, viscous heating due to infiltration may be neglected.

5.1.2. Viscous Heating during Buoyant Gas Convection

Buoyant gas convection is another possible source of gas flow which could potentially lead to viscous dissipation. In order to estimate gas velocities, we consider the approximately cylindrical column of heated region of rock created by the repository. To be conservative we consider the column to extend 50 m above and below the repository and treat the column as being uniformly heated to a temperature of 130° C. The flow of gas is driven by the difference between the pneumatic head of the column of height H in the repository to the pneumatic head Δp of the same column height away from the repository at a distance R approximately 1 km away from the central vertical repository axis. Thus, the pneumatic gradient due to the density difference is

$$(\Delta p/\Delta z) = [\rho_g|_{25^\circ C} - \rho_g|_{130^\circ C}] g. \quad (5.14)$$

The bulk intrinsic permeability K_b is estimated by the formula for flow between parallel plates,

$$K_f = \phi_f b^2/12, \quad (5.15)$$

where b is fracture aperture and ϕ_f is fracture porosity (volume of fractures / bulk volume).

The Darcy flux, $\phi_f \mathbf{V}_f$, flowing through the repository is

$$\begin{aligned} \phi_f \mathbf{V}_f &= (K_f/\mu_g) \left(\frac{H}{R+H} \right) (\Delta p/\Delta z) \\ &= \phi_f (b^2/12\mu_g) \left(\frac{H}{R+H} \right) [\rho_g|_{25^\circ C} - \rho_g|_{130^\circ C}] g, \end{aligned} \quad (5.16)$$

where \mathbf{V}_f is fracture gas, and we have assumed that all of the flow occurs in the fractures. The factor $[H]/(R+H)$ accounts for the resistance encountered by gas flowing horizontally from the outer boundary to the center of the repository.

Note that the fracture porosity in (5.16) cancels and the resulting equation gives the fracture gas velocity,

$$\mathbf{V}_f = (b^2/12) \left(\frac{H}{R+H} \right) [\rho_g|_{25^\circ C} - \rho_g|_{130^\circ C}] g. \quad (5.17)$$

Using an analysis similar to the case of infiltration, we solve for the temperature rise to obtain

$$\Delta T_v \approx \frac{(H/d_{rep})(b/a)\mu \left(\frac{V_f}{b}\right)^2}{2k/d_{rep}^2}. \quad (5.18)$$

Substituting the following values into (5.17),

b	100 μm
H	100 m
$b/a (= \phi_f)$	0.01
d_{rep}	350 m
k	1.2 W-m/ $^\circ\text{K}$
μ_g	1.8×10^{-5} Nt-s/m ²
$\rho_g _{25^\circ C}$	1.18 kg/m ³
$\rho_g _{130^\circ C}$	0.88 kg/m ³

we have $\mathbf{V}_f = 1.2 \times 10^{-5}$ m/s = 390m/y. Substituting this value into (5.18) we have the following estimate for the upper bound to the temperature rise from viscous heating,

$$\Delta T_v \approx 4 \times 10^{-5} \text{ }^\circ\text{C}. \quad (5.19)$$

5.1.3. Viscous Heating during Vapor Generation

Yet another source of gas flow is the release of steam generated inside matrix blocks. Viscous heating from steam flow can occur both inside the matrix and the fractures.

We consider an idealized system of parallel fractures spaced distance a apart. For steam to be generated the gas pressure in the matrix must be equal to or less than the saturation pressure $p_{sat}(T_m)$ where T_m is the temperature of the matrix. From Darcy's law the velocity V_s of steam flowing out of the matrix is approximately given by

$$V_s = \frac{K_m}{\mu} \Delta p / (\phi_m a / 2), \quad (5.20)$$

where ϕ_m is matrix porosity, K_m is matrix permeability, and $\Delta p = p_{sat}(T_m) - p_{amb}$ is the increase in gas pressure, and p_{amb} is the ambient pressure at the repository.

In order to calculate viscous heating due to flow of steam within the matrix, the flow is idealized as passing through a set of parallel tubes of diameter d equal to the mean pore diameter of the matrix. Porosimetry measurements indicate that d is on the order of 80 nanometer (80×10^{-9} m) for welded tuff at Yucca Mountain. The magnitude of viscous heating per unit volume inside a tube is given approximately by

$$|\boldsymbol{\tau} : \nabla \mathbf{V}| \sim \mu \left(\frac{V_s}{d} \right)^2. \quad (5.21)$$

The magnitude of heat being transported in the tube by advection per unit length of the tube is

$$|\nabla \cdot \rho_s h \mathbf{V}| \sim \rho_s V_s h_s / a, \quad (5.22)$$

where ρ_s is steam density. From (5.21) and (5.22), the ratio of the viscous heating to the heat transported by advection is, therefore,

$$\frac{|\boldsymbol{\tau} : \nabla \mathbf{V}|}{|\nabla \cdot \rho_s h \mathbf{V}|} \sim a \mu V_s / (d^2 \rho_s h_s). \quad (5.23)$$

Substituting for V_s from (5.20), we obtain

$$\frac{|\boldsymbol{\tau} : \nabla \mathbf{V}|}{|\nabla \cdot \rho_s h \mathbf{V}|} \sim K_m \Delta p / (2d^2 \phi_m \rho_s h_s). \quad (5.24)$$

Numerical simulations of the Yucca Mountain repository show that the temperature of the two phase boiling zone does not exceed 130 °C. Therefore, we use the following typical values with thermophysical properties at 130°C,

K_m	$1 \times 10^{-18} \text{ m}^2$
ϕ_m	0.10
d	$80 \times 10^{-9} \text{ m}$
a	0.3m
$h_s _{130^\circ\text{C}}$	$2.7 \times 10^6 \text{ J/kg}$
$\rho_s _{130^\circ\text{C}}$	1.50 kg/m^3
μ_g	$1.8 \times 10^{-5} \text{ Nt-s/m}^2$
$p_{sat} _{130^\circ\text{C}}$	$2.7 \times 10^5 \text{ Pa}$
p_{amb}	$0.89 \times 10^5 \text{ Pa}$

The upper bound to the ratio of viscous heating to advective transport is estimated from (5.24) to be

$$\frac{|\boldsymbol{\tau} : \nabla \mathbf{V}|}{|\nabla \cdot \rho h \mathbf{V}|} \approx 3.5 \times 10^{-5}. \quad (5.25)$$

Therefore, viscous heating in the steam generation zone is negligible compared to advective transport of energy so it can be ignored in the balance equation.

5.2. Estimation of the Effect of the Pressure Gradient Term

The pressure gradient term, $V \cdot \nabla p$, arose from combining of the energy transport term, $-\nabla \cdot \rho u \mathbf{V}$, with the volumetric work term, $-p \nabla \cdot \mathbf{V}$, in order to obtain an enthalpy transport term, $-\nabla \cdot \rho h \mathbf{V}$. The term, $V \cdot \nabla p$, is significant if the magnitude of the pressure gradient in the direction of flow times the magnitude of the flow velocity is sufficiently large.

The largest pressure gradients and flow velocities occur when steam generated by water boiling in the matrix causes pressurization of the pores within matrix blocks.

We consider the same two-dimensional system of fractures considered in the previous subsection on viscous heating. The magnitude of the pressure gradient term for steam flowing out of the matrix is estimated as

$$|\mathbf{V} \cdot \nabla p| \sim V_s \Delta p / a. \quad (5.26)$$

The magnitude of the advective term is estimated as

$$|\nabla \cdot \rho h \mathbf{V}| \sim \rho_s h_s V_s / a. \quad (5.27)$$

The ratio of these two terms is

$$\frac{|\mathbf{V} \cdot \nabla p|}{|\nabla \cdot \rho h \mathbf{V}|} \sim \frac{\Delta p}{\rho_s h_s}. \quad (5.28)$$

We use the same following parameter values as in the subsection in viscous heating.

K_m	$1 \times 10^{-18} \text{ m}^2$
ϕ_m	0.10
$h_s _{130^\circ C}$	$2.7 \times 10^6 \text{ J/kg}$
$\rho_s _{130^\circ C}$	1.50 kg/m^3
$p_{sat} _{130^\circ C}$	$2.7 \times 10^5 \text{ Pa}$
p_{amb}	$0.89 \times 10^5 \text{ Pa}$

We, then, obtain the following estimated upper bound to the ratio of the pressure gradient term to the advective term

$$\frac{|\mathbf{V} \cdot \nabla p|}{|\nabla \cdot \rho h \mathbf{V}|} \leq 0.04, \quad (5.29)$$

demonstrating that the pressure gradient term may be neglected in the balance equation.

6. Flux Boundary Conditions and Source Terms

In this section we derive the appropriate boundary conditions and source terms corresponding to the thermal balance equation. We first derive the boundary conditions.

Equation (5.1) can be written in the form

$$\frac{\partial \rho u}{\partial t} = -\nabla \cdot \mathbf{q}_e \quad (6.1)$$

where we define the thermal flux,

$$\mathbf{q}_e = -k \nabla T + \sum_{(\gamma)} h^\gamma \mathbf{j}^\gamma + \rho h \mathbf{V}. \quad (6.2)$$

From the definition, $\mathbf{j}^\gamma = \rho^\gamma (\mathbf{V}^\gamma - \mathbf{V})$, the flux \mathbf{q}_e can be written as

$$\mathbf{q}_e = -k \nabla T + \sum_{(\gamma)} \rho^\gamma h^\gamma \mathbf{V}^\gamma. \quad (6.3)$$

We first determine the flux passing through a surface \mathcal{S} of infinitesimal area, that, possibly, defines a discontinuity in fluid properties. Consider two surfaces \mathcal{S}_ϵ and $\mathcal{S}_{-\epsilon}$ on both sides of the surface that are a distance ϵ from the surface in question, \mathcal{S} . Integrating (6.1) over the volume enclosed by the two surfaces, applying the divergence theorem, and letting ϵ approach zero, we have

$$\mathbf{q}_e \cdot \nu \Big|_1 = \mathbf{q}_e \cdot \nu \Big|_2, \quad (6.4)$$

where the subscripts 1 and 2 denote the different properties at the two sides of the surface and ν is the normal vector on the surface. This relationship states that the flux \mathbf{q}_e is conserved across surfaces (subject to the approximations made in deriving (6.1)). From the definition of \mathbf{q}_e , this equation is,

$$\left(-k \nabla T \cdot \nu + \sum_{(\gamma)} \rho^\gamma h^\gamma \mathbf{V}^\gamma \cdot \nu \right) \Big|_1 = \left(-k \nabla T \cdot \nu + \sum_{(\gamma)} \rho^\gamma h^\gamma \mathbf{V}^\gamma \cdot \nu \right) \Big|_2. \quad (6.5)$$

The relationship can also be rewritten as

$$(\mathbf{q}_h \cdot \nu + \sum_{(\gamma)} h^\gamma \mathbf{q}^\gamma \cdot \nu) \Big|_1 = (\mathbf{q}_h \cdot \nu + \sum_{(\gamma)} h^\gamma \mathbf{q}^\gamma \cdot \nu) \Big|_2, \quad (6.6)$$

where \mathbf{q}_h is heat flux and $\mathbf{q}^\gamma = \rho^\gamma \mathbf{V}^\gamma$ is the mass flux of the γ -component across the surface. Thus, the mass flux of a γ -component gives rise to the thermal energy flux equal to $h^\gamma \mathbf{q}^\gamma$.

Therefore, the proper boundary condition at a surface \mathcal{S} is

$$(-k \nabla T \cdot \nu + \sum_{(\gamma)} \rho^\gamma h^\gamma \mathbf{V}^\gamma \cdot \nu) \Big|_{\mathcal{S}} = q_h|_{\mathcal{S}} + \sum_{(\gamma)} (h^\gamma q^\gamma)|_{\mathcal{S}}, \quad (6.7)$$

where $q_h|_{\mathcal{S}}$ is the specified heat flux at the boundary surface \mathcal{S} , $q^\gamma|_{\mathcal{S}}$ are the specified mass fluxes, and $h^\gamma|_{\mathcal{S}}$ are the specified partial enthalpies.

We now derive source terms to the thermal energy balance equation. Suppose there is a point source of heat q_{oh} and point sources of component mass fluxes, q_o^γ , located at a microscopic point ξ' . Consider a sphere \mathcal{S}_ϵ of radius ϵ centered at ξ' . From arguments similar to above, the thermal energy flux, $q_e|_{\mathcal{S}}$, coming out of this sphere is given by

$$q_e \Big|_{\mathcal{S}_\epsilon} = \int_{\mathcal{S}_\epsilon} \mathbf{q}_e \cdot \nu dS = \int_{\mathcal{S}_\epsilon} q_h dS + \int_{\mathcal{S}_\epsilon} \sum_{(\gamma)} h^\gamma q^\gamma dS. \quad (6.8)$$

As ϵ approaches zero, we have

$$q_e = q_{oh} + \sum_{(\gamma)} h_o^\gamma q_o^\gamma. \quad (6.9)$$

Therefore, the thermal energy source term for a point source is given by

$$q_e(\mathbf{x}') = (q_{oh} + \sum_{(\gamma)} h_o^\gamma q_o^\gamma) \cdot \delta(\mathbf{x}' - \xi'), \quad (6.10)$$

where $\delta(\mathbf{x}' - \xi')$ is the Dirac delta function. From this expression, the term for a general distribution of sources is

$$q_e(\mathbf{x}') = q_{ho}(\mathbf{x}') + \sum_{(\gamma)} h_o^\gamma(\mathbf{x}') q_o^\gamma(\mathbf{x}'), \quad (6.11)$$

where the following functions in space are specified: heat flux $q_{ho}(\mathbf{x}')$, component mass fluxes $q_o^\gamma(\mathbf{x}')$, and partial mass enthalpies $h_o^\gamma(\mathbf{x}')$.

7. Thermal Energy Balance Equation at the Macroscopic Level

In this section we derive the macroscopic thermal balance equation by volume-averaging the microscopic balance equation derived earlier.

7.1. Volume-Averaging the Microscopic Equation

We can rewrite the thermal energy balance equation, (5.1), in the following form

$$\frac{\partial \rho u}{\partial t} = -\nabla \cdot \mathbf{q}_e, \quad (7.1)$$

where we define the total thermal flux

$$\mathbf{q}_e \equiv -k\nabla T + \sum_{(\gamma)} h^\gamma \mathbf{j}^\gamma + \rho h \mathbf{V}. \quad (7.2)$$

The macroscopic thermal energy balance equation is obtained by volume-averaging this equation. In particular, we will need to average over each of the fluid and solid phases, separately. The actual formula for the volumetric phase average of some microscopic quantity $e(\mathbf{x}', t)$ defined over some α -phase is (Bear and Bachmat 1991, Eq. 1.3.5, p 32)

$$\bar{e}(\mathbf{x}, t) = \frac{1}{U_o(\mathbf{x})} \int_{U_{o\alpha}(\mathbf{x}, t)} e(\mathbf{x}', t) dU_\alpha(\mathbf{x}'). \quad (7.3)$$

Here $U_o(\mathbf{x})$ denotes the volume of the REV centered at the macroscopic point \mathbf{x} and $U_{o\alpha}(\mathbf{x}, t)$ is the region occupied by the α -phase that inside the REV. We also need to define the intrinsic phase average by (Bear and Bachmat, 1991, Eq. 1.3.3)

$$\bar{e}^\alpha(\mathbf{x}, t) = \frac{1}{U_{o\alpha}(\mathbf{x})} \int_{U_{o\alpha}(\mathbf{x}, t)} e(\mathbf{x}', t) dU_\alpha(\mathbf{x}'). \quad (7.4)$$

It follows (Bear and Bachmat, 1991, Eq. 1.3.6) that

$$\bar{e} = \theta_\alpha \bar{e}^\alpha, \quad (7.5)$$

where θ_α is the volumetric fraction of the α -phase, i.e.,

$$\theta_\alpha \equiv U_{o\alpha}(\mathbf{x}, t)/U_o(\mathbf{x}, t), \quad (7.6)$$

the volume of the α -phase divided by bulk volume. The following relationship regarding the volumetric fractions are true,

$$\sum_{(\alpha)} \theta_\alpha = 1, \quad \theta_\alpha = S_\alpha \phi, \quad \theta_s = 1 - \phi, \quad (7.7)$$

where ϕ is porosity, S_α is saturation, and the subscript s in θ_s denotes the solid phase.

For the Yucca Mountain thermal-hydrology problem there are two fluid phases gas (g), liquid (ℓ), and solid (s). We will use the subscript α to denote the appropriate phase.

The average surface integral of a quantity e defined at the interface between two phases will be denoted by

$$\overline{e}^{\alpha\beta}(\mathbf{x}, t) = \frac{1}{S_{\alpha\beta}(\mathbf{x})} \int_{S_{\alpha\beta}(\mathbf{x}, t)} e(\mathbf{x}', t) dS_{\alpha\beta}(\mathbf{x}'), \quad (7.8)$$

where $S_{\alpha\beta}$ is the surface between the phases α and β within the REV and $S_{\alpha\beta}$ is its surface area.

Let e , now, be a quantity defined over the α -phase which is zero outside of the α -phase. The average of its time derivative is given by (Bear and Bachmat, 1991, Eq. 2.3.12)

$$\begin{aligned} \frac{\partial \overline{e}}{\partial t} &= \frac{\partial \overline{e}}{\partial t} - \sum_{(\beta)} \overline{e \mathbf{V}_{\alpha\beta} \cdot \boldsymbol{\nu}}^{\alpha\beta} \frac{S_{\alpha\beta}}{U_o} \\ &= \frac{\partial \theta_\alpha \overline{e}^\alpha}{\partial t} - \sum_{(\beta)} \overline{e \mathbf{V}_{\alpha\beta} \cdot \boldsymbol{\nu}}^{\alpha\beta} \frac{S_{\alpha\beta}}{U_o}, \end{aligned} \quad (7.9)$$

where $\mathbf{V}_{\alpha\beta}$ is the velocity of the interface between the α and the β phases. The sum over β in the last term of the above equation is over all phases that are on contact with the α -phase.

Let \mathbf{G} be a vector quantity defined over the α -phase which is zero outside of the α -phase. The average of the divergence of \mathbf{G} is (Bear and Bachmat, 1991, Eq. 2.3.29)

$$\overline{\nabla \cdot \mathbf{G}} = \theta_\alpha \overline{\nabla \cdot \mathbf{G}^\alpha} = \nabla \cdot \theta_\alpha \overline{\mathbf{G}^\alpha} + \sum_{(\beta)} \overline{\mathbf{G} \cdot \boldsymbol{\nu}}^{\alpha\beta} \frac{S_{\alpha\beta}}{U_o}, \quad (7.10)$$

We now average this equation by integrating over an α -phase and dividing by the volume of the REV, $U_o(\mathbf{x})$. The averaging theorem, (7.9), is applied to the left-hand-side of balance equation and the theorem, (7.10), to the right-hand-side, to obtain the macroscopic thermal balance equation of a particular α -phase,

$$\begin{aligned} \frac{\partial \theta_\alpha \overline{\rho u}^\alpha}{\partial t} - \sum_{(\beta)} \overline{\rho u \mathbf{V}_{\alpha\beta} \cdot \boldsymbol{\nu}}^{\alpha\beta} \frac{S_{\alpha\beta}}{U_o} = \\ - \nabla \cdot (\theta_\alpha \overline{\mathbf{q}_e}^\alpha) - \sum_{(\beta)} \overline{\mathbf{q}_e \cdot \boldsymbol{\nu}}^{\alpha\beta} \frac{S_{\alpha\beta}}{U_o}. \end{aligned} \quad (7.11)$$

The second terms on both the left and right-hand sides of the equation are combined so that

$$\frac{\partial \theta_\alpha \overline{\rho u}^\alpha}{\partial t} = -\nabla \cdot (\theta_\alpha \overline{\mathbf{q}_e}^\alpha) + \sum_{(\beta)} f^{\beta \rightarrow \alpha}, \quad (7.12)$$

where we define the following symbol,

$$f^{\beta \rightarrow \alpha} = -\frac{1}{U_o} \int_{\mathcal{S}_{\alpha\beta}} (\mathbf{q}_e - \rho u \mathbf{V}_{\alpha\beta}) \cdot \boldsymbol{\nu} dS_{\alpha\beta}. \quad (7.13)$$

To see the meaning of this symbol, the integrand in the above integral, when expanded, is

$$\begin{aligned} (\mathbf{q}_e - \rho u \mathbf{V}_{\alpha\beta}) \cdot \boldsymbol{\nu} = \\ -k \nabla T \cdot \boldsymbol{\nu} + \sum_{(\gamma)} h^\gamma \mathbf{j}^\gamma \cdot \boldsymbol{\nu} + \rho u (\mathbf{V} - \mathbf{V}_{\alpha\beta}) \cdot \boldsymbol{\nu} + p \mathbf{V} \cdot \boldsymbol{\nu}. \end{aligned} \quad (7.14)$$

The first term is the conductive flux across the interface $\mathcal{S}_{\alpha\beta}$ between the α and β phases. The second term is the energy flux carried by mass diffusion. The third term is the energy carried by advection due to the velocity of the fluid relative to the velocity of the interface. The last term is the work done on the surface by fluid pressure forces. Hence, $f^{\beta \rightarrow \alpha}$ is the thermal energy flux (per unit bulk volume) going from the β -phase to the α -phase. This term describes, for example, the energy transfer between phases when a phase change takes place such as during evaporation or condensation of components.

Expanding the flux average $\overline{\mathbf{q}_e}^\alpha$, in (7.12) we have

$$\overline{\mathbf{q}_e}^\alpha = -\overline{k}^\alpha \nabla T^\alpha + \sum_{(\gamma)} \overline{h^\gamma}^\alpha \overline{\mathbf{j}^\gamma}^\alpha + \overline{\rho}^\alpha \overline{h}^\alpha \overline{\mathbf{V}}^\alpha. \quad (7.15)$$

The higher order phase averages of the form

$$\overline{\overline{\rho h}}^\alpha, \overline{\overline{\rho h \mathbf{V}}}^\alpha, \text{ etc.} \quad (7.16)$$

have been neglected. In particular we will neglect, $\overline{\overline{\rho h \mathbf{V}}}^\alpha$, which is the dispersion of heat. Here, the deviation, \mathring{e} , of a microscopic quantity e , is defined as the difference between the quantity e and its average. In this case,

$$\mathring{e}(\mathbf{x}', t; \mathbf{x}) \equiv e(\mathbf{x}') - \overline{e}^\alpha(\mathbf{x}). \quad (7.17)$$

It can be shown that average of a product uv is given by

$$\overline{uv}^\alpha = \overline{u}^\alpha \overline{v}^\alpha + \overline{u'v'}^\alpha. \quad (7.18)$$

In order to re-express the diffusion fluxes $\overline{\mathbf{j}}^{\gamma\alpha}$, NUFT and many other porous media flow and transport codes use the phenomenological, macroscopic version of Fick's law,

$$\overline{\mathbf{j}}^{\gamma\alpha} = -\overline{\rho}^\alpha \overline{\mathcal{D}}^{\gamma\alpha} \mathbf{T}_\alpha^* \nabla \overline{\omega}^{\gamma\alpha}, \quad (7.19)$$

where \mathbf{T}_α^* is the tortuosity coefficient (Bear and Bachmat, 1991, p. 129).

Similarly, for the thermal conduction flux, we use

$$\overline{\mathbf{q}}^{(c)\alpha} = -\overline{k}^\alpha \mathbf{T}_\alpha^* \nabla \overline{T}^\alpha. \quad (7.20)$$

Substituting into (7.15), the averaged thermal flux is

$$\overline{\mathbf{q}}_e^\alpha = -\overline{k}^\alpha \mathbf{T}_\alpha^* \nabla \overline{T}^\alpha + \sum_{(\gamma)} \overline{h}^{\gamma\alpha} \overline{\mathbf{j}}^{\gamma\alpha} + \overline{\rho}^\alpha \overline{h}^\alpha \overline{\mathbf{V}}^\alpha. \quad (7.21)$$

Upon substituting (7.15) into (7.12) we obtain the simplified macroscopic thermal energy balance equation for any α -phase within the REV,

$$\begin{aligned} \frac{\partial \theta_\alpha \overline{\rho}^\alpha \overline{u}^\alpha}{\partial t} &= \nabla \cdot (\theta_\alpha \overline{k}^\alpha \mathbf{T}_\alpha^* \nabla \overline{T}^\alpha) - \nabla \cdot (\theta_\alpha \sum_{(\gamma)} \overline{h}^{\gamma\alpha} \overline{\mathbf{j}}^{\gamma\alpha}) \\ &\quad - \nabla \cdot (\theta_\alpha \overline{\rho}^\alpha \overline{h}^\alpha \overline{\mathbf{V}}^\alpha) + \sum_{(\beta)} f^{\beta \rightarrow \alpha}. \end{aligned} \quad (7.22)$$

As mentioned before, the fluxes, $f^{\beta \rightarrow \alpha}$, represent internal energy fluxes coming from another β -phase in contact with the α -phase. Since these fluxes are internal to the REV, the net sum of these fluxes is zero. Therefore, we may sum the energy balance equation, (7.22), over all phases and the $f^{\beta \rightarrow \alpha}$ will sum to zero and no longer be present.

To illustrate this point, consider a two fluid phase (g, ℓ), single solid phase (s) system. The thermal energy balance equations are

$$\mathcal{B}_g = f^{s \rightarrow g} + f^{\ell \rightarrow g}, \quad (7.23)$$

$$\mathcal{B}_\ell = f^{s \rightarrow \ell} - f^{\ell \rightarrow g}, \quad (7.24)$$

$$\mathcal{B}_s = -f^{s \rightarrow \ell} - f^{s \rightarrow g}, \quad (7.25)$$

where \mathcal{B} represents all terms (time derivative and transport) in the balance equation except those for fluxes between phases. Adding these three equations we obtain

$$\mathcal{B}_g + \mathcal{B}_\ell + \mathcal{B}_s = 0. \quad (7.26)$$

Note that because we now have only a single balance equation, rather than the original three, we have more unknowns than equations. To reduce the number of unknowns, the assumption of local thermodynamic equilibrium is necessary. In particular, without thermodynamic equilibrium one has the individual temperatures for each phase, \bar{T}^s , \bar{T}^g , and \bar{T}^ℓ , which is fine if we have three energy balance equations. However, with a single energy balance equation we need to assume that the three temperatures are equal

$$\bar{T}^s = \bar{T}^g = \bar{T}^\ell. \quad (7.27)$$

That is, we need to assume thermal equilibrium between phases. For a porous medium this condition is satisfied except in extreme cases outside the physical regimes encountered at Yucca Mountain.

The single thermal energy balance equation is obtained by summing (7.22) over all phases to give,

$$\begin{aligned} \frac{\partial}{\partial t} \left(\sum_{(\alpha)} \theta_\alpha \bar{\rho}^\alpha \bar{u}^\alpha \right) &= \nabla \cdot \left(\sum_{(\alpha)} \theta_\alpha \bar{k}^\alpha \mathbf{T}_\alpha^* \nabla \bar{T}^\alpha \right) - \nabla \cdot \left(\sum_{(\alpha)} \sum_{(\gamma)} \theta_\alpha \bar{h}^{\gamma\alpha} \bar{\mathbf{j}}^{\gamma\alpha} \right) \\ &\quad - \nabla \cdot \left(\sum_{(\alpha)} \theta_\alpha \bar{\rho}^\alpha \bar{h}^\alpha \bar{\mathbf{V}}^\alpha \right). \end{aligned} \quad (7.28)$$

Instead of the most general form of the balance equation for the solid, for the Yucca Mountain site, we wish, instead, to use the form given by (4.49) for heating under constant stress conditions. By volume-averaging the equation using the techniques given above, we have the balance equation for the solid phase,

$$\bar{\rho}^s \bar{c}_p^s \theta_s \frac{\partial \theta_s \bar{T}^s}{\partial t} = \nabla \cdot \theta_s \bar{k}^s \mathbf{T}_s^* \nabla \bar{T}^s. \quad (7.29)$$

Using this equation and specializing equation (7.28) to a gas-liquid-solid system, we have

$$\begin{aligned} \bar{\rho}^s \bar{c}_p^s \frac{\partial \theta_s \bar{T}}{\partial t} + \frac{\partial}{\partial t} (\theta_g \bar{\rho}^g \bar{u}^g + \theta_\ell \bar{\rho}^\ell \bar{u}^\ell) &= \\ \nabla \cdot (\mathbf{k}_B \nabla \bar{T}) - \nabla \cdot \left[\sum_{\gamma=a,w} (\theta_\gamma \bar{h}^{\gamma g} \bar{\mathbf{j}}^{\gamma g} + \theta_\ell \bar{h}^{\gamma \ell} \bar{\mathbf{j}}^{\gamma \ell}) \right] & \\ - \nabla \cdot (\theta_g \bar{\rho}^g \bar{h}^g \bar{\mathbf{V}}^g + \theta_\ell \bar{\rho}^\ell \bar{h}^\ell \bar{\mathbf{V}}^\ell), & \end{aligned} \quad (7.30)$$

where $\gamma = a, w$ represents the sum over the air (a) and water (w) components. From equation (7.19), the diffusive mass fluxes are given by

$$\bar{\mathbf{j}}^{\gamma\alpha} = -\bar{\rho}^\alpha \bar{\mathcal{D}}^{\gamma\alpha} \nabla \bar{\omega}^{\gamma\alpha}, \quad \alpha = g, \ell; \gamma = a, w. \quad (7.31)$$

Here, we assumed local thermodynamic equilibrium so that,

$$\bar{T}^s = \bar{T}^g = \bar{T}^\ell = \bar{T}. \quad (7.32)$$

The effective ‘‘bulk’’ thermal conductivity, which we denote by \mathbf{k}_B , is defined as the tensor

$$\mathbf{k}_B = \theta_s \bar{k}^s \mathbf{T}_s^* + \theta_g \bar{k}^g \mathbf{T}_g^* + \theta_\ell \bar{k}^\ell \mathbf{T}_\ell^*. \quad (7.33)$$

The bulk thermal conductivity, k_B , is a constitutive coefficient which must be measured experimentally as a function of the fluid phase volumetric fractions, θ_α . The same condition applies to the tortuosity coefficient in the mass diffusion laws given by (7.19).

The Darcy fluxes for each fluid phase is equal to $\theta_\alpha \mathbf{V}_\alpha$, and they are obtained from Darcy’s law,

$$\theta_\alpha \bar{\mathbf{V}}^\alpha = -\frac{K k_{r\alpha}}{\bar{\mu}^\alpha} (\nabla \bar{p}^\alpha + \bar{\rho}^\alpha \mathbf{g} \nabla z). \quad (7.34)$$

The symbol K is the intrinsic permeability of the porous medium, and $k_{r\alpha}$ is the relative permeability of the phase.

7.2. Thermal Radiation

The thermal balance equation in NUFT includes fluxes due to thermal radiation on surface faces of computational cells, such as on waste packages and drift walls. Radiation fluxes between two surface faces, 1 and 2, are given by

$$q^{(e)} = A_1 C [(T_1)^4 - (T_2)^4], \quad (7.35)$$

where A_1 is the surface area of face 1 and C is a user-specified coefficient whose value is usually set to $(F\sigma)$, where F is the so-called view factor and σ is the Stefan-Boltzmann constant. The value of the view factor F depend on the geometry of the system and, also, includes the emissivities of the surfaces. The absolute temperatures, T_1 and T_2 , are those of the respective surfaces. The above equation is valid for wide variety of black and non-black body systems (Bird et al., 1960, pp. 438-447).

7.3. Final Macroscopic Thermal Balance Equation used in the NUFT Code

The NUFT code solves the balance equation (7.30) with the following simplifications,

1. The solid density, $\bar{\rho}^s$, is a constant, ρ_s .
2. The bulk thermal conductivity \mathbf{k}_B is a scalar, k_B .
3. The tortuosity coefficient \mathbf{T}_α^* for mass diffusion is a saturation and porosity-dependent scalar.

Then, the macroscopic thermal energy balance equation used in the NUFT code is

$$\begin{aligned} \rho_s c_p(\bar{T}) \frac{\partial \theta_s \bar{T}}{\partial t} + \frac{\partial}{\partial t} (\theta_g \bar{\rho}^g \bar{u}^g + \theta_\ell \bar{\rho}^\ell \bar{u}^\ell) = \\ \nabla \cdot (k_B \nabla \bar{T}) - \nabla \cdot \sum_{\gamma=a,w} (\theta_\gamma \bar{h}^{\gamma g} \bar{\mathbf{j}}^{\gamma g} + \theta_\ell \bar{h}^{\gamma \ell} \bar{\mathbf{j}}^{\gamma \ell}) \\ - \nabla \cdot (\theta_g \bar{\rho}^g \bar{h}^g \bar{\mathbf{V}}^g + \theta_\ell \bar{\rho}^\ell \bar{h}^\ell \bar{\mathbf{V}}^\ell). \end{aligned} \quad (7.36)$$

When the equation in the documentation of the NUFT USNT module (Nitao, 1998) was written, only a constant specific heat, c_p , option was available; in which case, the first term on the left hand side can be rewritten as $\partial \rho_s c_p \theta_s (\bar{T} - T_o) / \partial t$ where T_o is an arbitrary reference temperature, which is the form given in the manual. More recent versions of NUFT have a temperature-dependent specific heat option which is implemented into the balance equation in the manner given by (7.36).

Also, NUFT solves for saturations instead of volumetric fractions. Substitution of the following relationships between volumetric fraction and saturation,

$$\theta_s = 1 - \phi, \quad \theta_\alpha = S_\alpha \phi, \quad (7.37)$$

into (7.36) gives the actual equation given in the NUFT USNT manual (Nitao, 1998).

8. List of Mathematical Symbols

Latin Symbols

b fracture aperture (m),

Br	Brinkman dimensionless group,
B_α	terms in the thermal energy balance equation of α -phase, not including fluxes between phases (J/m^3),
c_p	specific heat capacity at constant pressure ($\text{J}/\text{kg}\cdot^\circ\text{K}$),
c_v	specific heat capacity at constant volume ($\text{J}/\text{kg}\cdot^\circ\text{K}$),
c_σ	specific heat capacity at constant stress ($\text{J}/\text{kg}\cdot^\circ\text{K}$),
c_ϵ	specific heat capacity at constant strain ($\text{J}/\text{kg}\cdot^\circ\text{K}$),
C_p	heat capacity at constant pressure, ($\text{J}/^\circ\text{K}$),
C_v	heat capacity at constant volume ($\text{J}/^\circ\text{K}$),
C_σ	heat capacity at constant stress ($\text{J}/^\circ\text{K}$),
C_ϵ	heat capacity at constant strain ($\text{J}/^\circ\text{K}$),
D^γ	free diffusion coefficient of the γ -component (m^2/s),
E	internal energy (J),
f	subscript for fracture property,
$f^{\beta\rightarrow\alpha}$	heat flux from β -phase to α -phase in an REV divided by the REV volume (W/m^3),
\mathbf{f}^γ	external force per mass of the γ -component (Nt/kg),
g	subscript for gas phase,
g	gravitational acceleration (m/s^2),
G	Gibbs free energy (J),
\mathbf{G}	arbitrary vector quantity,
h	specific enthalpy, $u + p/\rho$ (J/kg),
h^γ	partial mass enthalpy of the γ -component (J/kg),
\hat{h}^γ	partial molar enthalpy (J/mol),
H	enthalpy, $E + pU$ (J),
\mathbf{I}	unit, or identity, tensor,
\mathbf{j}^γ	diffusive mass flux of the γ -component ($\text{kg}/\text{s}\cdot\text{m}^2$),
k	thermal conductivity ($\text{W}\cdot\text{m}/^\circ\text{K}$),
k_B	bulk thermal conductivity ($\text{W}\cdot\text{m}/^\circ\text{K}$),
$k_{r\alpha}$	relative permeability of the α -phase,
K	intrinsic permeability (m^2),
K_f	fracture intrinsic permeability (m^2),
K_m	matrix intrinsic permeability (m^2),
ℓ	subscript for liquid phase,
m	subscript for matrix property,
m^γ	mass of the γ -component (kg),
M^γ	molecular mass of the γ -component (kg/mol),
n^γ	number density of the γ -component, no. of molecules of the component per volume ($\text{molecules}/\text{m}^3$),

N^γ	moles of the γ -component (mol),
p	pressure (Nt/m ²),
q	specific heat flux (W/m ²),
q_H	repository specific heat flux (W/m ²),
\mathbf{q}	thermal specific energy flux vector (W/m ²),
Q	heat flux (W),
R	gas constant (J/°K-mol),
s	subscript for solid phase,
\mathbf{s}	vector coefficient depending on the spatial distribution of phases in an REV (1/m),
\hat{s}^γ	partial molar entropy of the γ -component (J/mol-°K),
S	entropy (J/°K),
S_α	phase saturation, equal to volume of α -phase / total void volume (m ³ /m ³),
$S_{\alpha\beta}(\mathbf{x})$	surface area of the surface $\mathcal{S}_{\alpha\beta}(\mathbf{x})$ (m ²),
$\mathcal{S}_{\alpha\beta}(\mathbf{x})$	interface between a α -phase and a β -phase within an REV centered at \mathbf{x} ,
t	time (s),
T	temperature, units of °K, unless stated otherwise,
u	specific internal energy (J/kg),
U	volume (m ³),
$U_o(\mathbf{x})$	volume of the REV centered at \mathbf{x} (m ³),
$\mathcal{U}_o(\mathbf{x})$	REV centered at point \mathbf{x} ,
$U_{o\alpha}(\mathbf{x})$	the volume of the region $\mathcal{U}_{o\alpha}(\mathbf{x})$ (m ³),
$\mathcal{U}_{o\alpha}(\mathbf{x})$	the region occupied by the α -phase in an REV centered at point \mathbf{x} ,
v	specific volume (m ³ /kg),
\hat{v}^γ	partial molar volume of the γ -component (m ³ /mol),
V	magnitude of velocity (m/s),
\mathbf{V}	velocity vector (m/s),
\mathbf{V}_α	velocity vector of the α -phase (m/s),
$\mathbf{V}_{\alpha\beta}$	velocity vector of the interface between the α and β phases (m/s),
x_i	the i -th cartesian coordinate (m),
\mathbf{x}	coordinate vector of macroscopic point (m),
\mathbf{x}'	coordinate vector of microscopic point (m),
x^γ	mole fraction of the γ -component (mol/mol),
z	vertical coordinate that increases upwards (m).

Greek Symbols

$\delta(\mathbf{x}' - \xi')$	Dirac delta function centered at ξ' ,
ϵ, ϵ_{ij}	strain tensor (m/m),
∇e	gradient of a scalar quantity, e , defined as the vector with components, $\partial e / \partial x_i$,
$\nabla \mathbf{G}$	gradient of a vector quantity, \mathbf{G} , defined as the second-rank tensor with components, $\partial G_i / \partial x_j$,
$\nabla \cdot \mathbf{G}$	divergence of a vector quantity, defined as $\sum_i \partial G_k / \partial x_i$,
μ	dynamic viscosity of a fluid phase (Nt-s/m ²),
μ^γ	chemical potential of the γ -component (J/mol),
ν	unit normal vector at a surface,
ν_α	unit outward normal vector of surface of the α -phase,
ω^γ	mass fraction of the γ -component, equal to mass of component divided by mass of phase (kg/kg),
ϕ	porosity (m ³ /m ³),
ϕ_f	fracture porosity (m ³ /m ³),
ϕ_m	matrix porosity (m ³ /m ³),
ρ	mass density (kg/m ³),
$\hat{\rho}$	molar density (mol/m ³),
θ_α	volumetric fraction of the α -phase, equal to volume of phase divided by bulk volume (m ³ /m ³),
σ, σ_{ij}	stress tensor (Nt/m ²),
τ	deviatoric stress tensor (Nt/m ²).

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A. Appendix: Origin of the Thermal Energy Balance Equation from Statistical Mechanics

This exposition follows the discussion in Chp. 9 of Hirschfelder et al. (1954). The derivation of the energy balance begins with a system of N molecules defined over the $6N$ -dimensional phase space given by the positions of the molecules

$$\mathbf{r} = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N), \quad (\text{A.1})$$

and their momenta

$$\mathbf{p} = (\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N). \quad (\text{A.2})$$

The molecules are considered as point particles with no internal degrees of freedom. Only two-body forces between molecules is considered so that the

potential energy $\Phi(\mathbf{r})$ of the system is of the form

$$\Phi(\mathbf{r}) = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N \varphi(\mathbf{r}_{ij}). \quad (\text{A.3})$$

Although the discussion in Hirschfelder et al. (1954) is for a system of identical molecules, Irving and Kirkwood (1950) have extended the derivation to a system with multiple molecular species.

The statistical distribution of the motion the molecules in phase space is described by the probability distribution function, $f^{(N)}(\mathbf{r}, \mathbf{p}, t)$, which satisfies the Liouville equation (Eq. 9.4-1 of Hirschfelder et al., 1954). The usual microscopic quantities can be defined in terms of this function as follows.

The probability per unit volume that the k -th molecule is at point \mathbf{r} is given by the following integral over phase space, (\mathbf{r}, \mathbf{r}) ,

$$\overline{\delta(\mathbf{r}_k - \mathbf{r})} = \frac{1}{N!} \int \int \delta(\mathbf{r}_k - \mathbf{r}) f^{(N)}(\mathbf{r}, \mathbf{p}, t) d\mathbf{r} d\mathbf{p}. \quad (\text{A.4})$$

The total number density at the point \mathbf{r} is defined as

$$n(\mathbf{r}, t) = \sum_{k=1}^N \overline{\delta(\mathbf{r}_k - \mathbf{r})}. \quad (\text{A.5})$$

It is the average number of molecules per volume. The mass density of the γ -species of the system is defined as

$$\rho(\mathbf{r}, t) = \sum_{k=1}^N \overline{m_k \delta(\mathbf{r}_k - \mathbf{r})}, \quad (\text{A.6})$$

where m_k is the mass of the k -th molecule. The momentum density is

$$\rho(\mathbf{r}, t) \mathbf{V}(\mathbf{r}, t) = \sum_{k=1}^N \overline{p_k \delta(\mathbf{r}_k - \mathbf{r})}, \quad (\text{A.7})$$

where p_k is the momentum of the k -th molecule and \mathbf{V} is the mass-weighted average velocity of the molecules. The kinetic energy density associated with the molecules is given by

$$\sum_{k=1}^N \overline{\left(\frac{p_k^2}{2m} \right) \delta(\mathbf{r}_k - \mathbf{r})}. \quad (\text{A.8})$$

In order to obtain the kinetic energy associated only with the random motion of the molecules, we need to subtract the kinetic energy $\frac{1}{2}\rho V^2$ due to bulk

motion of the molecules. Therefore, the kinetic energy density associated with only the random motion of molecules is given by

$$n(\mathbf{r}, t)u_K(\mathbf{r}, t) = \sum_{k=1}^N \overline{\left(\frac{p_k^2}{2m}\right)} \delta(\mathbf{r}_k - \mathbf{r}) - \frac{1}{2}\rho V^2. \quad (\text{A.9})$$

The potential energy, unlike the previous quantities, is not localized to an individual molecule, but depends on the forces acting between them. The approximation is made that one-half the potential energy $\varphi(r_{ij})$ is localized at each molecule. The definition of the potential energy density is, then, given by

$$n(\mathbf{r}, t)u_\Phi(\mathbf{r}, t) = \sum_{i=1}^N \sum_{j=1}^N \overline{\varphi_{ij} \delta(\mathbf{r}_k - \mathbf{r})}. \quad (\text{A.10})$$

The total internal energy per molecule is the sum of the kinetic energy due to random motion and the potential energy. That is,

$$u(\mathbf{r}, t) = u_K(\mathbf{r}, t) + u_\Phi(\mathbf{r}, t). \quad (\text{A.11})$$

To go further we must define the lower order distribution $f^{(1)}(\mathbf{r}, \mathbf{p}, t)$ as the integral of $f(\mathbf{r}, \mathbf{p}, t)$ over all position and momentum coordinates of all molecules except for one. Similarly, $f^{(2)}(\mathbf{r}, \mathbf{p}, t)$ is the integral over all position and momentum coordinates except for two molecules. It can be shown, under certain assumptions, that the mass density of each species of molecules, mean (mass-weighted) velocity, kinetic energy, and potential energy at a point can be defined by expectation values using the probability distributions $f^{(1)}$ and $f^{(2)}$.

The Liouville equation can be used to obtain the rate of change of the expectation value of the internal energy, $u(\mathbf{r}, t)$. The resulting expression (Eq. 9.4-34 of Hirschfelder et al., 1954), is the desired balance equation for thermal energy,

$$\frac{\partial}{\partial t}(nu) + \nabla \cdot (nu\mathbf{V}) + \nabla \cdot \mathbf{q} - (\boldsymbol{\sigma} : \nabla \mathbf{V}) = 0. \quad (\text{A.12})$$

The heat flux vector \mathbf{q} is given by

$$\mathbf{q} = \mathbf{q}_K + \mathbf{q}_\Phi, \quad (\text{A.13})$$

where \mathbf{q}_K is the kinetic energy contribution and \mathbf{q}_Φ is the potential energy contribution. The symbol $\boldsymbol{\sigma}$ denotes the stress tensor and is the negative of the pressure tensor \mathbf{P} used by Hirschfelder et al (1954).

The operator ‘:’ used in the balance equation is defined by

$$A : B \equiv \sum_i \sum_j A_{ij} B_{ji}, \quad (\text{A.14})$$

where A and B are any rank-two tensors. Hence, the term $\boldsymbol{\sigma} : \nabla \mathbf{V}$ in the above energy balance equation is defined by

$$\boldsymbol{\sigma} : \nabla \mathbf{V} = \sum_i \sum_j \sigma_{ij} \frac{\partial V_j}{\partial x_i}. \quad (\text{A.15})$$

B. Appendix: Derivation of the Solid Thermal Energy Balance Equation using the First Law of Thermodynamics

We consider the heating of the solid sample of fixed mass, m , and initial volume, U_o , heated by a heat flux, δQ . The sample is assumed to be sufficiently small that the temperature and tensorial stress field within the sample is approximately uniform. The heating is assumed to take place as a reversible thermodynamic process.

From the first law of thermodynamics we have

$$\delta Q = dE + \delta W, \quad (\text{B.1})$$

where dE is the change in internal energy. The term δW is the work done by heating. It does not include body forces such as gravitation because heating does no direct work against gravity. It only includes the work done against the stress field. (Note: The gravitational force can affect loading on the “sample” volume through the momentum balance equation; and, therefore, indirectly affects the magnitude of the stress acting upon it. But, again, the work is done against the resulting stress field and not, against the gravitational force itself. To duplicate field conditions in the laboratory the loading must replicate stress conditions in the field, including those induced by gravity. Moreover, the sample must be sufficiently small such that gravitational forces will not create non-uniform stresses within the sample.)

The work term δW is given by (Landau and Lifshitz, 1970)

$$\delta W = U_o \sum_{i,j} \sigma_{ij} d\epsilon_{ij}, \quad (\text{B.2})$$

where σ_{ij} and ϵ_{ij} are the components of the stress and strain tensors of the solid, respectively. From (B.1), the rate of change of heat in the sample is given by

$$DQ/Dt = DE/Dt + DW/Dt. \quad (\text{B.3})$$

We will now use the identity (Bear and Bachmat, 1991, Eq. 2.1.12),

$$D\epsilon_{ij}/Dt = \frac{1}{2} \left(\frac{\partial V_i}{\partial x_j} + \frac{\partial V_j}{\partial x_i} \right). \quad (\text{B.4})$$

Taking the total derivative of (B.2), we have

$$DW/Dt = U_o \sum_{i,j} \sigma_{ij} D\epsilon_{ij}/Dt. \quad (\text{B.5})$$

Substituting the expression for $D\epsilon_{ij}/Dt$ from (B.4) into this equation, simple algebra shows that the result is

$$DW/Dt = U_o \boldsymbol{\sigma} : \nabla \mathbf{V}. \quad (\text{B.6})$$

From (B.3), the rate of change of heat is given by

$$DQ/Dt = DE/Dt + DW/Dt. \quad (\text{B.7})$$

Substituting DW/Dt from (B.6) into this equation, we have

$$DQ/Dt = DE/Dt + U_o \boldsymbol{\sigma} : \nabla \mathbf{V}. \quad (\text{B.8})$$

Dividing by the fixed mass, m , of the solid volume, we have

$$Dq/Dt = Du/Dt + \frac{1}{\rho} \boldsymbol{\sigma} : \nabla \mathbf{V}, \quad (\text{B.9})$$

where q is the heat flux per unit mass.

From (4.37) we have

$$Du/Dt + \frac{1}{\rho} \boldsymbol{\sigma} : \nabla \mathbf{V} = \frac{1}{\rho} \nabla \cdot k \nabla T. \quad (\text{B.10})$$

Therefore, this equation and (B.9) implies that

$$Dq/Dt = \frac{1}{\rho} \nabla \cdot k \nabla T. \quad (\text{B.11})$$

This equation is the same as (4.43), which is what we wished to derive.

(It is important to emphasize that the above derivation applies only to a reversible process. Otherwise, the heat, Q , would not be unique function of time, and it's total time derivative would be meaningless. To make this point clear, some authors use the following result from the second law of thermodynamics,

$$T DS/Dt = DQ/Dt, \quad (\text{B.12})$$

to rephrase the equations in terms of entropy instead of heat.)