

The correct form of the energy balance for fully coupled
thermodynamics in water

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Abstract

The correct form of the energy balance for fully coupled thermodynamics is presented with examples of situations where a commonly used formulation based on conservation of enthalpy leads to erroneous results. Because liquid water has a negative Joule/Thomson coefficient at low temperatures, water cools as it compressed and heats as it expands. Conservation of enthalpy alone leads to water heating by 2 C per kilometer as it is brought up from depth. The corrected energy balance conserves methalpy, which is enthalpy plus gravitational potential energy. Although the erroneous form leads to small changes in the temperature profile for typical simulations, there are several instances where this effect may prove to be important. The most important impact of the erroneous form is probably in the field of geothermal energy production, where the creation of a few degrees of heat in a simulation could lead to miscalculation of power plant efficiencies.

1.0 Introduction

Advances in numerical modeling and computing speed over the past three decades have allowed the earth science community to explore many complex systems involving coupled heat and mass transfer in geologic systems. Examples include modeling of convection in oceanic crust [Fisher et al, 1990; Rees and Storesletten, 1995; Wilcox, 1998], groundwater flow near nuclear waste repositories [Pruess and Wang, 1990], geothermal energy [Hanano, 1998; Weir, 1994], geyser behavior [Ingebritsen and Rojstaczer, 1993], thermal development of oil fields [Wang, 1997], large scale lateral flow as found in both continental basins [Person et. al, 1996] and submarine accretionary systems [Screaton and Ge, 1997], and Martian hydrology [Travis et al., 2002].

The increased feasibility of coupled modeling and wealth of applications have led to a proliferation of coupled heat and mass transfer codes formulated as finite difference or finite element/volume schemes. These codes generally account for the conservation of fluid energy in one of two ways. The first approach (simpler thermodynamics) conserves internal energy of the fluid (a function of heat capacity and temperature) and has been adopted as the standard method since the dawn of coupled heat and mass transfer modeling [Narasimhan and Witherspoon, 1976; Strauss and Shubert, 1977; Voss, 1984]. The second approach conserves fluid enthalpy (fully-coupled thermodynamics) and employs steam table data [Haar et al., 1984] to evaluate enthalpy as a function of both pressure and temperature [Zyvoloski et al., 1997; Travis et al., 1991; Hayba and Ingebritson, 1994]. The steam table data set more accurately captures the true thermodynamic behavior of water and thus can be considered an advancement in the field. The fully-coupled approach is especially valid in large scale models where variation in the state variables leads to noticeable differences in fluid energy calculated by the two approaches. The fully-coupled approach has typically been implemented through a direct substitution of steam table enthalpy into the standard formulation of the energy balance. This method is completely valid for lateral flow systems, however for vertical flow this method fails to account for changes in the potential energy of the water.

In this paper we review the appropriate form of the energy balance to use in conjunction with the fully-coupled thermodynamics. Next, we present results obtained using both the corrected and uncorrected energy balance. Finally, we discuss some of the broader implications of the fully-coupled approach.

2.0 Theory

Confusion over the form of the energy balance in flow systems with fully-coupled fluid properties is not a new phenomenon. The problem has been dealt with previously, when Dodson [1971] and Ramberg [1971] presented replies to a paper by Waldbaum [1971]. Dodson [1971] notes that the thermodynamics literature typically defines specific enthalpy (h) as

$$h = C_p T + PV \quad (\text{EQ 1})$$

(C_p =specific heat capacity at constant pressure, T =temperature, P =pressure, V =specific volume). Furthermore, introductory thermodynamics texts are often mainly concerned with bench scale, non-flowing, and closed systems, leading to a simplification of isenthalpic (adiabatic) processes ($dh = 0$) where

$$d(C_p T) = - d(PV) \quad (\text{EQ 2})$$

The most obvious result of using Eq. 2 is that as pressure drops at a constant specific volume (i.e. incompressible fluid), temperature must rise if the process is to remain isenthalpic. The result of using Eq. 2 with the fully-coupled thermodynamics is that water flowing vertically will cool as it flows downward (to higher pressure) and heat as it flows upward. This is not the case for the simpler thermodynamics where internal energy (u)

$$u = C_p T \quad (\text{EQ 3})$$

is conserved, because the internal energy is independent of pressure.

The variation in temperature with pressure at constant enthalpy is known as the Joule-Thomson coefficient and is defined as

$$\mu_j = (dT/dP)_h \quad (\text{EQ 4})$$

The Joule-Thomson coefficient can also be expressed as

$$\mu_j = (T\alpha - 1)V/C_p \quad (\text{EQ 5})$$

(α =thermal expansivity at constant pressure) [Waldbaum, 1971]. For water, μ_j is negative at temperatures below approximately 250. C, and this term amounts to an increase in temperature of 2.2 C per 10 MPa drop in pressure at 20 C. Figure 1 shows the magnitude of the Joule-Thomson coefficient as a function of temperature at four different pressures, generated from the NIST/ASME steam properties database [NIST 2002]. An interesting

point is that for the non-ideal gases hydrogen and helium (where α does not equal $1/T$), μ_j is negative at room temperature causing decompressing hydrogen to heat [Kestin, 1979].

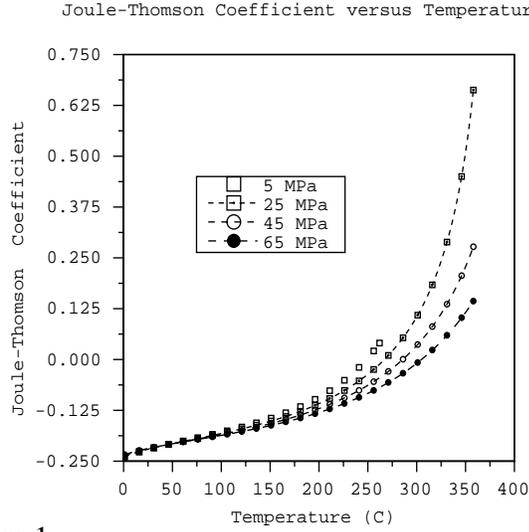


Figure 1

The simplification introduced by conserving only enthalpy in a flowing system ignores changes in both kinetic and potential energy. Assuming that kinetic energy in porous systems is negligible, the quantity which must be conserved in the fully couple porous flow models is given by

$$h_o = C_p T + P V + g z \quad (\text{Eq 6})$$

where h_o is termed *enthalpy* after Kestin [1979]. Using this formulation, when water flows vertically due to pressure gradients that are small relative to the hydrostatic gradient,

$$\frac{\partial}{\partial z}(P V) = \frac{\partial}{\partial z}(g z) \quad (\text{Eq 7})$$

and there are no significant differences from solutions made using Eq. 3. In fact, for flow in any direction driven by small pressure gradients the correction is negligible. However, when vertical pressure gradients are large relative to the hydrostatic gradient or for large lateral pressure gradients, use of Eq. 6 can lead to results that differ from the simple case by several degrees.

3.0 Example Simulations

In this section we present simulations that demonstrate the behavior of both the corrected (Eq. 6) and uncorrected (Eq. 1) enthalpy conservation statements and compare these results to simulations performed using the traditional conservation of internal energy (Eq. 3). Simulations are run using the finite elements code FEHMN [Zyvoloski et al., 1997] and the integrated finite difference code MAGHNUM [Travis et al., 2002] with modifications to explore the different scenarios. The unmodified codes use Eq. 1 for enthalpy. To simulate Eq. 6 we add the $g z$ term in the appropriate subroutine. Eq. 3 is sim-

ulated using a lookup table in which we specify internal energy solely as a function of temperature.

We model simple upward flow driven by a fixed pressure gradient. The domain is a simple two-dimensional box, 1000 m on each side, composed of a homogeneous porous medium (Figure 1). The computational grid is composed of 2500 nodes with spacing of

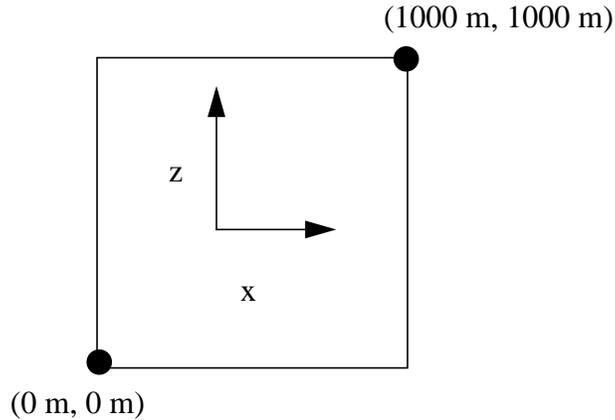


Figure 2 Model domain

approximately 4 m in both the horizontal and vertical directions. The bottom of the domain ($z=0$) is fixed at 11.5 MPa and 20 C, while the top of the domain ($z=1000\text{m}$) is fixed at 1.0 MPa and 20 C. The side boundaries are no-flow with respect to both heat and mass. Permeability (κ) is set to $1 \times 10^{-10} \text{ m}^2$, porosity is set to 0.2, and thermal conductivity is set to $0.1 \text{ W}/(\text{m K})$ to limit thermal conduction effects. Via Darcy's law

$$q = -\frac{k}{\mu}(\nabla(P) - \rho\vec{g}) \quad (\text{EQ } 8)$$

(q =volume flux, μ =fluid viscosity, ρ =fluid density, \vec{g} =gravitational vector) these parameters generate a one-dimensional upward volume flux of $q = 6.3 \times 10^{-5} \text{ m/s}$. FEHMN results for the three cases are shown in Figure 3. Also shown on Figure 3 are the MAGNUM results for for corrected (Eq. 6) and uncorrected (Eq. 1) simulations. The codes show nearly identical responses and suggest that this problem may be widespread in current coupled heat and mass transfer simulators that use the enthalpy formulation for energy conservation.

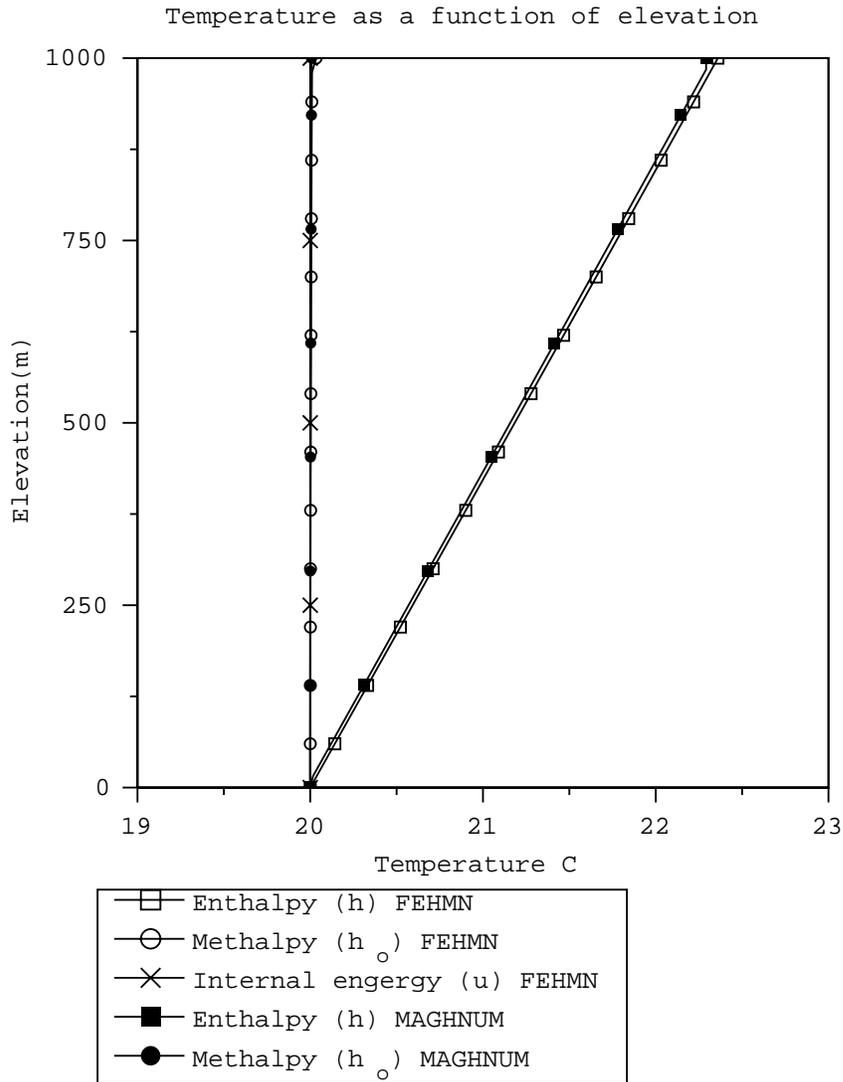


Figure 3 Results of the example simulations

4.0 Discussion

Because the spurious generation of heat from Eq.1 relies on mass transport across a pressure gradient, this error is only seen when conductive heat transfer is small relative to advective transport. Thus, only with high flow rates and/or low thermal conductivities will one see erroneous output from the uncorrected models. Convection cells using typical properties for earth materials run with and without the correction show no significant differences in heat transfer or fluid velocities.

Cases where the correction may prove important include models of geothermal extraction that involve relatively rapid extraction of deep water from boreholes, large-scale

convection in low thermal-conductivity materials in extraterrestrial environments, and seafloor convection that involves bottom water (2 C) entering the crust at high flow rates.

In the first case, the uncorrected model would add 2 degrees celcius per kilometer to modeled temperatures in the extracted water, leading to overestimates of energy efficiencies for a geothermal powerplant. This could have potentially devastating consequences for the economic feasibility of such installations. In the second case, the uncorrected model would tend to dampen convection, leading to underestimates of heat and mass transport in extraterrestrial systems where our understanding may be solely based on such models. The final case is quite interesting because it led to the discovery of the error in our codes. Bottom water is quite near the freezing point, and by miscalculating the pressure/temperature relationship, water flowing into the crust from the seafloor in the model is cooled and may eventually freeze. Freezing causes codes such as FEHMN to crash as the temperature of the fluid goes beyond the limits of the fluid properties.

5.0 Conclusions

We have presented the correct form of the energy balance to use when modeling the fully coupled thermodynamics of liquid water, conserving methalpy instead of the standard thermodynamics textbook conservation of enthalpy. Methalpy includes a term in the energy balance for gravitational potential energy.

Because the variation in temperature with pressure at constant enthalpy, the Joule/Thomson coefficient, is negative below about 250 C at moderate pressures, water undergoing expansion in this P/T range will heat, while water being compressed will cool. Coincidentally, at 20 C and low P, the correction for the gravitational potential energy almost exactly cancels the Joule/Thomson effect leading to nearly isothermal upflow or downflow.

Without the correction for gravitational potential energy, models that conserve enthalpy can exhibit strange behavior due to the Joule-Thomson effect. Water rising in a borehole will heat by approximately 2 C per kilometer, while water being drawn down into a fractured system will cool by approximately 2 C per kilometer. Miscalculation of withdraw temperatures for geothermal power plants may significantly impact operating efficiencies. Simulations of focused convection into the seafloor may lead to freezing.

The non-linear relationship between pressure, temperature, and the Joule/Thomson coefficient combined with competing effects of thermal conductivity and flowrate lead us to suggest that simulations performed with only conservation of enthalpy should be examined on a case-by-case basis to determine the significance of the correction.

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