Non-Isothermal Transport of Immiscible Fluids at Low Capillary Numbers: Surface and Line Contributions to the Driving Force

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We derive the entropy production for transport of heat and two immiscible fluids in an inelastic porous material. The representative volume elements are described by their entropy, energy, volume, and masses. The Gibbs equation defines their temperature, pressure, and chemical potentials. Constitutive equations that follow from the entropy production can be written for a continuous path in state space. There are three independent driving forces and conjugate fluxes, one for transport of heat and two for transport of two immiscible fluids. The forces contain contributions from surface and line energies, contributions that are important at low capillary numbers. The equations predict a Soret effect and can be used to compute thermal osmosis. They provide an explanation for observations known for a long time, that there are deviations from Darcy's law at low capillary numbers (1-4) for transport in clay, soil, and even through glass beads. We find how volume flow arises, not only from changes in the pressure, but also from changes in the porosity, or saturation of the wetting fluid, temperature, and chemical potentials. We discuss how the relations can be tested by non-equilibrium molecular dynamics simulations or experiments.

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