1   TRANSPORT OF WATER BY ADVECTION AND DIFFUSION

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4   ABSTRACT

5   This investigation is concerned with transport of discrete particles in water

6   solutions occupying porous media. The solid boundary of a water solution is

7   employed as a frame of reference for defining particle velocities so that velocity

8   of the boundary is defined as zero in this frame of reference. Experimental

9   evidence shows that net flux of fluid particles is the sum of advection and

10   diffusion. Flux refers to velocity of *a reference volume* of a water solution as a

11   whole, not velocity of individual particles. The term "osmosis" is often used to

12   describe a combination of advection and diffusion. Advection in a particular

13   direction is flux of fluid particles driven by a force proportional to normal surface

14   forces in that direction on the boundary of a *reference volume* of a liquid water

15   solution as a whole, as well as body forces in that direction acting on mass within

16   a *reference volume.* Diffusion of liquid water particles in a particular direction is

17   flux proportional to the directional derivative of *kinetic energy* of water particles

18   per unit volume. *Kinetic energy* is due to particle velocities relative to the

19   boundary velocity. Models describing mass transport of fluid particles in water

20   solutions based on a definition of diffusion as flux of fluid particles relative to

21   *mean flux* do not predict fluxes relative to the solution boundary. Functions

22   describing conditions for fluid equilibrium do not describe fluid flux.

23

24   OBJECTIVES

25

26   An objective of this investigation is to show that net flux of a liquid water

27   solution is the sum of advection and diffusion. Another objective is to show that

28   definition of diffusion as a flux relative to mean flux is flawed, and the concept of

29   non-equilibrium thermodynamics for describing fluid flux is also flawed.

1   A particle is a mass that translates as a unit in a solution. No assumption
2   is made regarding its structure. For example, a particle could be a gas molecule
3   in a gaseous solution or a water cluster in a water solution.

4   Fluids, as defined here, are not treated as continua, as often is the case
5   for fluids discussed in fluid dynamics texts. Transport of particles in a soil water
6   solution is frequently assumed proportional to a directional derivative of a single
7   potential even though net flux in a particular direction may be driven by
8   directional derivatives of at least two significant potentials, that is, potentials
9   referring to energy associated with advection and energy associated with
10   diffusion.

11   A potential is the energy of particles per unit volume (or per unit mass) of
12   a solution. When referring to advection the potential refers to energy per unit
13   volume of particles in a *reference volume* of the solution as a whole, and when
14   referring to diffusion, a potential is energy per unit mass of a set of particles in a
15   *reference volume*. Net flux is equal to velocity of the centroid of a reference
16   volume as a whole and is equal to the sum of advection and diffusion.

17   The term *kinetic energy* refers to energy associated with particle velocities
18   in a frame of reference relative to the solid boundary of the fluid solution. A
19   directional derivative of a potential evaluates the driving force in a particular
20   direction. Kinetic energy, as defined here, is employed as a potential for diffusion
21   with dimensions of energy per unit mass.

22   Although most current investigators of flow in porous media employ the
23   term *gradient* when referring to a *directional derivative*, the distinctions in
24   meaning (for example) between $\frac{dp}{dx}$ and ∇p are emphasized here. A directional
25   derivative is used to evaluate a force driving particles in any particular direction at
26   a point in a fluid system; whereas a gradient evaluates the maximum driving
27   force at a particular point. Flux components described in most current literature
28   dealing with flux of liquid solutions in porous media are rarely the largest flux
29   components possible at points in a porous medium, although the driving force is
30   often incorrectly evaluated as a *gradient* of a potential.

1   To illustrate principles applying to net flux of liquid water in porous media,

2   a de-ionized liquid water solution occupying a stable porous medium is examined

3   theoretically and experimentally. Such a water solution is rarely, if ever, found in

4   soils or aquifers because water solutions found in soils or aquifers are not

5   de-ionized. A de-ionized water solution is examined here; because theoretically

6   only advection and diffusion of water particles are involved in this special case. It

7   is easier to focus attention on principles that apply to advection and diffusion of

8   liquid water for this special case.

9   Summing fluxes due to advection and diffusion is not sufficient to

10   evaluate net flux of water solutions in general. Cases where mixed fluid

11   phases (where each phase is often treated as a separate continuum) are not

12   discussed here. Flux of compressible fluids, *e.g.*, air or other gases, in

13   particular, is not discussed. The reader is referred to the text by Corey, A.T.

14   1994 for a discussion of advection of multiple phases. Driving force due to

15   directional derivatives of electrical potential is also not discussed. The reader

16   is referred to papers by Kemper, W.D. 1960, Olsen, H.W. 1985, and Malusis,

17   M.A., C.H. Shackelford and H.W. Olsen 2001 for a discussion of electrical

18   potentials in soil solutions.

19   This investigation ignores the effect of de-ionized water on the

20   geometry of fluid channels in porous media, such as, clay swelling in soils.

21   **Experiments with advection and diffusion in de-ionized liquid water solutions**

22   **occupying porous media (unaffected by a liquid water solution) are cited.**

23   **Conclusions based on theoretical analyses are presented if they have been**

24   **verified by published experimental observations.**

25

26   BACKGROUND

27

28   The earliest literature dealing with flux of liquid water through porous

29   media is by Henri Darcy 1856. A packed sand bed employed by Darcy in his

1 experiments contained fluid channels small enough that inertial resistance is
2 negligible, but large enough that net flux is dominated by advection. Inertial
3 resistance is neglected because net flux of water through the packed sand bed is
4 sufficiently small that inertia is not a significant factor. Du Plessis, J.P. 1994, has
5 provided rigorous theoretical and experimental research describing conditions
6 where this assumption is justified.

7 Darcy described net flux employing macroscopic variables, and described
8 the driving force for advection of a liquid water solution as the directional
9 derivative of *hydraulic head*. The term *macroscopic* implies that the flux
10 measured is averaged over a cross-section that includes solids as well as a liquid
11 solution. Hydraulic head is a potential, the directional derivative of which is
12 dimensionless, representing force per weight of water solution.

13 An equation, analogous to Darcy's equation, written in macroscopic units
14 with driving force per volume, rather than per weight of water solution is given by:

15

16
$$\boldsymbol{q_a} = -K_x \frac{d}{dx}(p + \rho g).$$
(1)

17

18 The flux vector evaluated by Eq. (1) is volume flux (referring to the solution as a
19 whole) per unit area per unit time, that is, it has dimensions of velocity.

20 Eq. (1) is often called Darcy's equation where the body force, g, is gravity.
21 Orientation of the cross-section, through which flux is evaluated, is arbitrary and
22 the variables employed are macroscopic. K is a coefficient called *hydraulic*
23 *conductivity* relating advective flux (in a direction normal to the cross-section
24 selected) to its driving force; g is a scalar representing potential energy per mass
25 resulting from position in a gravitational field, p is pressure, and ρ is fluid
26 density.

27 Directions of flux components evaluated by Eq. (1) are determined by
28 *directional derivatives* of the sum in parentheses, called piezometric pressure.

Fluxes evaluated by Eq. (1) represent components of flux driven by force evaluated with directional derivatives, not gradient operators.

An equation with a form similar to Eq. (1) may refer to a force unrelated to gravity, *e.g.,* a force driving diffusion. Fluxes evaluated by equations with the same form are additive because each flux can be expressed with the same dimensions by choosing a coefficient with appropriate dimensions. However, **potentials associated with advection and diffusion cannot be added because they are different functions of porous media.**

Driving forces for advection should be described as force per unit volume, because the potentials involved include energy resulting from surface forces that cannot be evaluated over an element of mass. Diffusion should be described as force per unit mass, because the component of flux evaluated is flux of particular particles, and the volume occupied by a set of particles is unknown.

The sum in parentheses in Eq. (1) is frequently referred to *as piezometric pressure p^**, a variable with dimensions of energy per volume Experience shows that Eq. (1) provides an acceptable evaluation of net flux in a particular direction in most agricultural soils and aquifers, because diffusion is usually an insignificant mechanism of transport compared to advection in soils and aquifers.

The coefficient employed in Eq. (1) is a function of fluid viscosity, as well as media properties, and should be adjusted for viscosity, a function of temperature. For advective flux in horizontal directions, the gradient of piezometric pressure reduces to a gradient of pressure only.

In evaluating a flux component with Eq. (1) in a real system, one may attempt to evaluate a flux component in a direction parallel to bedding planes of a geologic earth formation or perhaps through a membrane in a normal direction. Fluxes evaluated are in a direction chosen for convenience. When flux components resulting from directional derivatives, in general, are combined, they should refer to the same direction. Vectors such as fluxes or forces are indicated by symbols with bold font in this investigation.

Although, experience shows that Eq. (1) provides an acceptable evaluation of net flux in a particular direction over a large range of conditions, Eq. (1) fails to describe net flux in media such as membranes in living cells, shale layers where the petroleum industry currently extracts natural gas, or compacted clay layers used to retain dangerous chemicals in mining waste storage dumps. Eq. (1) also does not describe advective flux of compressible fluids through porous media, *e. g.*, gases, because it is impossible for a pressure difference to exist in gases without inducing diffusion as well as advection, and causing slippage at solid boundaries.

Advection in porous media

The definition of advection given above is a flux due to surface force on a *reference volume* of a liquid solution as a whole, plus a body force on mass within a *reference volume*. This defines advection at a point in a fluid system because a *reference volume* is defined at a point in space, that is, the centroid of a *reference volume*. Experience shows that if a finite advection is found at a point in the channels within a porous medium, advection will be found at all points within channels occupied by a liquid solution. However, fluxes of liquid solutions as a whole apparently approach zero at solid boundaries. This does not imply that velocity of individual particles is necessarily zero at a boundary.

Flux velocities at other points in a liquid water solution are found to be inversely proportional to the distance normal to the surface of solids. Such velocity distributions, called *viscous flux*, result in angular deformation of *reference volumes*, and resistance to viscous flux is found to be proportional to rate of angular deformation of *reference volumes*.

Diffusion through plant membranes

Plant scientists often regard net flux of particles through plant membranes as being proportional to directional derivatives of *activity*, where *activity* is a potential with dimensions of energy per unit mass, referring to a particular

particle. Although transport of individual particles evaluated by the directional derivatives of potentials with dimensions of energy per unit mass evaluates mass transport due to diffusion, mass transport due to advection is not evaluated.

Many plant scientists apparently consider that directional derivatives of *activity* evaluate forces that can drive advection, as well as diffusion. They apparently believe surface forces*, e.g.*, pressure and viscous resistance, are accounted for by employing directional derivatives of *activity* to evaluate forces driving advection as well as diffusion.

However, pressure is normal force per unit area and viscous resistance is tangential surface force per unit area. Surface force can be evaluated on the surface of volumes, not on elements of mass. Consequently, there is no logical way to apply activity as a potential for evaluating advection. Such a potential is useful for evaluating mass flux of particular particles, a process defined as *diffusion*.

When plant scientists discover an occasional particle with insufficient *activity* to have arrived inside a plant by diffusion, they often assume the energy difference allowing it to have passed a plant membrane must have been created by the *pumping action of living cells*. Apparently, many plant scientists think plant membranes do not permit advection that could provide transport of particles larger than water clusters through root hairs without *pumping by a vital process*.

Advective fluxes capable of allowing particles larger than water particles to pass through plant membranes against an *activity* difference, unrelated to a process of living organisms, are possible. However, because fluid channels through root hairs are likely to be small enough to impede advection, diffusion is probably the primary mechanism of transport through root hairs in most cases.

Diffusion

The scientific community has long recognized that diffusion as well as advection contributes significantly to net flux in porous media having very *small* fluid channels. Investigators have differed concerning the definition of diffusion. It

1 was originally regarded as a flux of particles relative to a solid matrix, and later
2 incorrectly defined as flux relative to *a moving stream*.

3 The earliest experiments dealing specifically with diffusion are
4 experiments conducted by Graham, T. 1833 regarding diffusion of gases through
5 plaster-of-Paris, a porous medium with extremely small fluid channels. Graham
6 likely regarded advection through plaster-of-Paris to be negligible compared to
7 diffusion.

8 To insure diffusion was the flux measured in his experiments, Graham
9 manually held the pressure of each gas employed equal on both sides of a
10 porous plug of plaster of Paris and measured flux components through a cross-
11 section normal to gravity. Theoretically, such flux components are due to
12 diffusion only.

13 Graham evidently regarded diffusion as flux of particular particles relative
14 to the solid material forming the boundary of gaseous mixtures. The fluxes he
15 measured are with respect to the porous medium used for his experiments, not
16 flux relative to a *moving stream.* Graham regarded diffusion as flux of particular
17 particles because he stated that *diffusive flux is inversely proportional to the*
18 *square root of particle mass.*

19 Experience of numerous subsequent investigators has confirmed
20 Graham's findings, *e.g.,* Hoogschagen, J. 1953, and Knaff, G. and
21 E.U. Schlunder 1985. But many investigators have also discovered that diffusive
22 flux of liquid water particles is found experimentally to increase with temperature,
23 *e. g.*, the diffusive fluxes measured by Corey, A.T., W.D. Kemper and J.H. Dane.
24 2010.

25

26 ### Fick's equation

27 The first equation for evaluating diffusion was proposed by Fick, A. 1855,
28 following experiments with isothermal diffusion of solutes in liquids. Fick found
29 that rate of molar diffusion of a solute in a particular direction within a liquid
30 solution is proportional to the directional derivative of its concentration in an

1 isothermal liquid water solution. Experience of numerous subsequent
2 investigators has shown this rule also applies to flux of isothermal ideal gases
3 through porous media. The same rule applies to diffusion of solutes in liquids as
4 for particles in an ideal gaseous solution, according to van't Hoff, J.H. 1887.
5 Evidently solutes, unlike solvents, are not part of a semi-crystalline lattice that
6 restricts translation of solvents. However, at room temperatures only a small
7 fraction of solvents translate in three dimensions in a water solution.

8 An equation presented by Bird, R.B., W.E. Stewart and E.N. Lightfoot
9 1960, rewritten in terms of macroscopic variables applied to isothermal diffusion
10 through porous media, is:

11

12 $$\boldsymbol{q}_d = -\sum_i (D_i \frac{d(c_i/c)}{dx}) . \qquad (2)$$

13

14 D_i is a coefficient with dimensions of length squared per time, and c_i is the
15 concentration of a particular particle that translates in three dimensions, $\boldsymbol{c}$ is total
16 concentration, and $\boldsymbol{q}_d$ is a *vector* with dimensions of velocity that represents the
17 sum of diffusive fluxes in a solution.

18 Fick's equation, as originally written, evaluates molar flux, and the driving
19 potential is concentration rather than mole fraction, so Fick's original equation is
20 non-linear, **but it is not incorrect**. Eq. (2) employs the Bird, R.B., W.E. Stewart
21 and E.N. Lightfoot 1960 driving potential, mole fraction, rather than
22 concentration, to evaluate volume fluxes rather than molar fluxes. **Coefficients in**
23 **Eq. (2) are not the same as the coefficient for a molar flux in Fick's original**
24 **equation,** because the coefficients employed are, mole fraction, rather than
25 concentration *per se*. However, the coefficients employed are functions of fluid
26 properties that vary with viscosity, which is a function of temperature, as well as
27 other media properties. Eq. (2) is assumed to provide a **sum of linear**
28 **relationships** associated with volume fluxes rather than mole fluxes.

1   Although Fick derived his original equation following experiments with

2   isothermal diffusion of solutes in liquid solutions, an analogous equation can be

3   derived from probability considerations. The number of particles with a particular

4   mass passing a unit area is equal to the product of volume flux and the

5   concentration of such particles in a unit volume. The potential for diffusion

6   includes kinetic energy of individual particles per unit volume. Each coefficient D_i

7   in Eq. (2) applies to particles with a particular mass. The coefficients are

8   sometimes referred to as diffusivities.

9   The potential for advection, including pressure, is normal surface force

10   averaged over the boundary of reference volumes as well as body force acting

11   on mass within reference volumes as a whole. Potentials for advection and

12   diffusion are different functions of porous media. However, fluxes proportional to

13   directional derivatives for both advection and diffusion are additive, if expressed

14   in the same dimensions. The sum of advective and diffusive fluxes is evaluated

15   by choosing appropriate coefficients.

16

17   **Diffusion defined as a flux relative to mean velocity**

18   Authors employing non-equilibrium thermodynamics (NET), among others,

19   have adopted a model for mass transport that defines diffusion as a flux relative

20   to *mean* flux. This definition (first proposed by Maxwell, J.C. 1866) is currently

21   widely accepted and is employed in most current literature dealing with mass

22   transport*, e.g.*, Krishna, R. and J.A. Wesselingh 1997, although these authors

23   (like numerous others) cannot verify transport models, based on this theory, with

24   experimental results. Altevogt, A.S., D.E. Rolston and R.T. Venterea 2003

25   conclude, based on their experiments, that the subject requires additional

26   research. Investigators, *e.g.*, Farr, J.M. 1993, and Auvermann, B.W. 1996 find

27   that experimental data in published literature do not support transport models

28   based on the concept that diffusion is a flux relative to *mean flux*. Farr attempted

29   to define a diffusion equation that would be consistent with the definition of

30   diffusion as a flux relative to *mean flux*. Success is obtained by this approach

over a narrow range of fluid particle sizes only. According to Corey, A.T. and B.W. Auvermann 2003 the problem is the model, not Fick's equation.

A model for mass transport by a combination of advection and diffusion, employing the concept that diffusion is a constituent flux relative to *mean flux,* is currently widely accepted, especially by chemical engineers. Chemical engineers get their concepts concerning mass transport largely from a textbook on Transport Phenomena by Bird, R.B., W.E. Stewart and E.N. Lightfoot (1960, 2002). This model is based on the assumption that transport by diffusion for all particles in a solution sum to zero so that *mean flux*, sometimes referred to as *motion of the flowing stream*, is unaffected by diffusion.

Many authors apparently believe that mass flux is evaluated by the Navier-Stokes equation for fluid advection. For example, Bird, R. B., W. E. Stewart and E. N. Lightfoot 1960 assume *mean* mass flux is given by the Navier-Stokes equation in the form:

$$\rho \frac{D\boldsymbol{v}}{Dt} = -\nabla p + \rho \boldsymbol{g} + \mu(\nabla \cdot \nabla \boldsymbol{v}). \qquad (3)$$

Apparently these authors believe Eq. (3) evaluates *barycentric velocity* because they use the symbol for *barycentric velocity* in this equation rather than the symbol for volume flux.

Eq. (3) is incorrect; because **this equation equates mass times acceleration to forces acting on** *reference volumes*, **not on** *reference masses.* Another problem with Eq. (3) arises when applied to viscous flux in porous media in a particular direction. When a flux component is evaluated in a particular direction, use of a three-dimensional operator to evaluate viscous resistance to flux through a porous medium is inappropriate; because **the direction of the applicable viscous resistance is in a direction parallel to solid boundaries only.**

Viscous flux is two-dimensional; **flux components normal to solid boundaries do not exist.**

Viscous flux at solid boundaries is found to be zero, so that *slippage* that occurs with gases in the general case is zero for all cases analyzed here. **This investigation is concerned with flux of water particles in de-ionized liquid water solutions.** Advective fluxes described here are viscous fluxes.

Definition of diffusion as a flux that sums to zero, when the summation is over all constituents in a solution, contradicts the definition of diffusion employed by investigators, *e.g.*, Graham T. 1833, Fick A. 1855, van't Hoff, J.H. 1887, or Glasstone, S., K.J. Laidler and H. Eyring 1941, each of whom describe diffusion processes that do not sum to zero.

The concept of diffusion, as originally conceived by Graham and Fick, is not diffusion as postulated by the Maxwell-Stefan model for diffusion. Krishna, R. and J. A. Wesselingh 1997 state that *Fick's law of diffusion postulates a linear dependence of diffusion flux with respect to the molar average mixture velocity.* The original papers by Fick, A. 1855 do not justify such a definition of diffusion as *Fick's law of diffusion*.

Fick defined diffusion as a flux responding to a directional derivative of concentration in a frame of reference attached to the fluid boundary, not as a flux relative to *mean velocity*. Fick's papers also do not support the conclusion appearing in the Krishna, R. and J.A. Wesselingh 1997 **Abstract:** *The Maxwell-Stefan formulation provides the most general and convenient, approach for describing mass transport,* because **this formulation fails to predict mass transport where diffusion is a significant mechanism of transport (Farr, 1993, Auvermann, 1996).**

Self-diffusion of liquid water

Glasstone, S., K.J. Laidler and H. Eyring 1941 show experimentally, as well as analytically, that Eq. (2) applies to solvents, as well as solutes, in a liquid water solution, provided the concentration entered in Eq. (2) is proportional to the

1 concentration of particles that translate in three dimensions. Glasstone, S., K. J.

2 Laidler and H. Eyring 1941 have found this concentration to be approximated by

3 an exponential function of temperature. Only a small fraction of solvents translate

4 in three dimensions at room temperature, but at boiling temperature all solvents

5 enter the gaseous phase and translate in three dimensions. Diffusion of solvents

6 is called *self-diffusion* by Glasstone, S., K.J. Laidler and H. Eyring 1941.

7   Temperature, *per se*, is not a potential, the directional

8 derivative of which is proportional to a driving force for diffusion in a particular

9 direction, but the actual driving force, for *self-diffusion* of liquid water, increases

10 with temperature in two ways: The number of moles per unit volume that

11 translate in three dimensions increases with temperature, and kinetic energy of

12 each particle in this set also increases with temperature.

13   The interpretation of Corey, A.T. and B.W. Auvermann 2003 that

14 temperature is a force potential for diffusion applies only to solutes in a liquid, or

15 to molecules of an ideal gas, where concentration of particles that translate in

16 three dimensions is a constant proportional to temperature.

17   According to Glasstone, S., K.J. Laidler and H. Eyring 1941, *self-diffusion*

18 of water is given by:

19
$$\boldsymbol{q}_{d_w} = -D_w \frac{d(c_w/c)}{dx}.$$
(4)

20

21 Fluxes evaluated by Eq. (4) are fluxes of liquid water in particular directions due

22 to self-diffusion. Fluxes evaluated by Eq. (4) have dimensions of volume per unit

23 area per unit time, or velocity; the coefficients have dimensions of length squared

24 per unit time; c_w is concentration of water particles that translate in three

25 dimensions; c is total concentration of water particles.

26

27   **Total potential**

28   Historically, investigators have attempted to evaluate net flux in porous

29 media by defining a single potential the directional derivative of which supposedly

evaluates the force driving diffusion as well as advection. Such an equation, developed by soil scientists, is the *total potential* equation. This equation is derived by adding potentials referring to diffusion as well as advection.

Corey, A.T. and W.D. Kemper 1961 show, with a simple thought experiment, that such an equation does not predict direction or magnitude of net flux. They state that a valid potential for this purpose, in terms of water variables only, does not exist because magnitude and direction of fluxes depend on medium as well as fluid properties. Corey, A.T. and A. Klute 1985 show that adding potentials associated with advection, as well as diffusion, involves adding potentials with unlike dimensions. Adding such potentials gives physically meaningless numbers.

Non-equilibrium thermodynamics

Groenevelt, P.H., and G.H. Bolt 1969 proposed a *total potential* based on a generalized Gibbs function having dimensions of energy per unit mass. The directional derivative of this potential includes terms proportional to force inducing advection as well as diffusion. Groenevelt and Bolt refer to their theory as NET, meaning *non-equilibrium thermodynamics*.

Gibbs' function was originally developed to describe equilibrium conditions in a fluid system where neither gravity nor a pressure gradient is a significant factor. de Groot, S. R. and P. Mazur 1962 suggested that this theory could be extended to apply to flux, provided the flux was sufficiently slow. NET is based on the concept that force acting on fluid as a whole in a particular direction is the directional derivative of a function describing conditions at equilibrium.

One might conclude this theory is valid from a statement made in the text by Zemansky, M. W. and R. N. Dittman 1997. See **section 11.6,** where they state that the *gradient of chemical potential can be thought of as the driving force for the flow of matter.*

A theoretical development that might appear to lead to this conclusion is provided in **section 11.6.** However, this development applies to flux of particles of

a given size through a membrane that blocks flux of all other particles so this development applies to diffusion only. It does not apply to advection where the applicable driving force is given by Newton's second law of motion applied to a *reference volume* of the solution as a whole.

The fact that temperature is a variable in a generalized Gibbs function precludes this function from being a valid potential for evaluating mass flux. Temperature is a function of total energy that includes heat energy, only a fraction of which is kinetic energy, in the general case. The directional derivative of temperature does not correlate with mass flux, even though this derivative has the same dimensions as the directional derivative of kinetic energy.

A somewhat less obvious reason that flux of water does not correlate with difference in temperature is that Gibbs' function does not include the mass of the particle per unit volume. Newton's second law states that force on a *reference volume* in motion is proportional to rate of change of momentum. Momentum depends on mass as well as velocity. However, Gibbs' function for fluids at equilibrium includes no term for molecular mass per unit volume. It includes terms for concentration of each particle but not their mass.

<center>Mean Flux</center>

Definition of diffusion as a flux relative to *mean flux* apparently began with Maxwell, J.C. 1866, although investigators often referred to diffusion as a flux relative to the *velocity of a flowing stream,* or the *bulk-flow velocity*. This concept continues to be employed in recent studies, *e.g.*, de Groot, S.R. and P. Mazur 1962, Cunningham, R.E. and Williams, R.J. 1980, Krishna R. and A. Wesselingh 1997. This definition is also accepted by soil physicists employing non-equilibrium thermodynamic theory, *e.g.*, Groenevelt, P.H. and G.H. Bolt, 1969. It is accepted by many chemical engineers, having been adopted by the authors of a popular chemical engineering textbook, Bird, R.B., W.E. Stewart, and E. N. Lightfoot 1960, 2002.

1

2   Reasoning based on a definition of diffusion as velocity relative to *mean*
3   *velocity*, or velocity of a *flowing stream*, leads to the conclusion that the vector
4   sum of diffusion velocities is zero. This definition contradicts diffusion as
5   interpreted by pioneers, *e.g.,* Graham T. 1833 and A. Fick 1855, because they
6   defined fluxes that do not sum to zero as diffusion.

7   Use of *mean velocity* as a reference velocity for defining diffusion is
8   adopted by de Groot, S.R. and P. Mazur 1962 who state in their text book,
9   dealing with non-equilibrium thermodynamics, that *an equation describing flux is*
10   *independent of the frame of reference in which the flux is defined*. They use this
11   relationship to justify defining diffusion as a flux relative to *mean flux*.

12   However, the mathematical principle quoted in their text applies only to
13   fluxes that are independent of the frame of reference to which they apply. It does
14   not apply to fluxes that contribute to *reference velocities*. One may arrive at this
15   conclusion by considering limiting cases in which *mean flux* results from diffusion
16   only, as for the gas fluxes measured by Thomas Graham 1833.

17   Transport by diffusion only is described in most elementary texts dealing
18   with chemistry. Students are taught that net flux of a constituent in a particular
19   direction is proportional to the directional derivative of chemical potential. **This**
20   **theory does not describe transport due to advection.** Advection in a particular
21   direction must be evaluated by a potential having dimensions of energy per unit
22   volume, because advection is a flux that results from force per unit volume.

23   Historically, authors of textbooks dealing with elementary fluid mechanics
24   usually assume the fluids examined are homogeneous so that flux of a reference
25   volume is evaluated with an equation that employs a *total derivative* to evaluate
26   mass acceleration. The so-called *total derivative* is a function of channel
27   dimensions and time, as a reference particle moves in time and space. It is
28   assumed that this derivative is a function of space variables and time only, so
29   that the rate of change of density is assumed to be zero. This assumption is valid

for homogeneous fluids only where density is a constant in time and space. It is not valid for evaluating mass acceleration of interest to plant and soil scientists.

The basic equation that applies to advective flux is Newton's second law of motion, that is, **force equals mass times acceleration**. However, the *derivative* of non-homogeneous fluids is a function of density, as well as the space variables and time, as mass continuity requires. Systems where diffusion, as well as advection, is significant cannot employ the so-called *total derivative* as described in elementary texts dealing with hydraulics or fluid mechanics, because this description assumes the fluid is homogeneous, that is, density is constant in a reference volume that moves in space and time.

In the general case, resistance forces include fluid inertia and viscous resistance, indicated by the rate of change of shape of a reference volume. Resistance to divergence of flow must be accounted for in formulating equations describing many flow systems*, e. g.*, open channels or rivers. The assumptions one can make depend on the application under investigation.

Textbooks dealing with hydraulics refer to the energy of a unit weight of water solution as a whole as *pressure head*, *elevation head*, and *velocity head* with dimensions of length. Analogous variables are listed in the Bernoulli equation expressed as energy per unit volume (Zemansky, M.W. and R.N. Dittman, 1997). The directional derivative of each energy variable in the Bernoulli equation is a force in a particular direction inducing advection in that direction because these are variables referring to a reference volume as a whole.

Driving forces for advection include normal force acting on the boundary of a reference volume, as well as body force acting on mass within a reference element with constant volume. In the general case, resistance to divergence of flow must be accounted for in formulating equations describing many flow systems*, e.g.*, open channels or rivers. However, this requirement can be neglected for most cases involving flux in porous media.

Pressure is often treated as an intensive variable at a point in space, referring to the centroid of a *reference volume.* Pressure due to random motion of

1

2 particles per unit volume of an ideal gas is two-thirds the kinetic energy of the

3 particles, because pressure is a normal surface force only, whereas kinetic

4 energy includes motion in three dimensions. Zemansky, M.W. and R.N. Dittman

5 1997 provide a rigorous derivation of this relationship. Experimental evidence

6 verifying this conclusion has been conducted with gas molecules of known

7 structure and mass, but it is assumed that the relationship applies for other

8 particles in liquid solutions as well.

9

10   **Forces driving advection**

11   One of the forces driving a reference volume of a water solution in a

12 particular direction is proportional to a directional derivative of pressure; another

13 is a body force, usually gravity, acting on mass within a *reference volume*. Both

14 of these forces drive a *reference volume* of a fluid solution as a whole. Pressure

15 is a normal surface force averaged over the boundary of a reference volume.

16   Kinetic energy refers to velocity of particles that have no preferred

17 direction so kinetic energy is a scalar; but the directional derivative of kinetic

18 energy of particular particles evaluates force that drives diffusion in a particular

19 direction.

20

21   ANALYSIS

22

23   Net flux, in the special case investigated here, results from advection and

24 diffusion as described above for non-homogeneous fluids. For a case of interest

25 to soil and plant scientists, a suitable reference volume for evaluating net flux

26 must be a volume element; **a surface stress cannot be averaged over the surface**

27 **of a fluid particle consisting of mass occupying an undefined space.**

28   Experience shows that resistance to fluid inertia may be neglected for flux

29 through most porous media. Resistance due to divergence of flow may also be

30 neglected because net flux in what is called porous media is very slow compared

18

1 to net flux in general. Rate of divergence is also too slow to cause a measurable

2 resistance.

3   Plant and soil scientists cannot assume a liquid solution is homogeneous;

4 they must deal with transport of individual particles across membranes. The

5 same is true for engineers dealing with leakage of dangerous chemicals, *e.g.*,

6 chemicals that may be radioactive, through compacted clay barriers. The Navier-

7 Stokes equation, in its original form, is inadequate to describe flux of individual

8 particles.

9   A few years ago petroleum engineers were interested only in advection;

10 production of petroleum liquids by diffusion was not deemed profitable. Now that

11 horizontal drilling is feasible, petroleum engineers must deal with transport in

12 strata with very small permeabilities so that fluxes observed can be affected by

13 diffusion.

14 <div align="center">**Reference volumes**</div>

15   Reference volumes (*fluid particles*) that can be assumed to obey Newton's

16 second law of motion for a flux of interest to plant and soil scientists must apply

17 to flux of fluids with a variety of particles. A *reference volume* assumed to obey

18 Newton's second law varies with density. A *reference volume* must include

19 particles with sizes that may approach the dimensions of flow channels in some

20 cases.

21   A *reference volume*, for this analysis, is assumed to be large enough to

22 contain a *representative* concentration of each particle included in the solution as

23 a whole. *Representative* is in italics because concentration and density vary from

24 one region to another. A question arises as to the size of a *region* as well as the

25 size needed to define a valid *reference volume*. A detailed discussion of what

26 constitutes a valid *reference volume* for fluids in porous media is found in a text

27 by Bear, J. 1972.

28   *Reference volumes* employed here are usually assumed to have

29 dimensions significantly larger than individual particles. However, the dimensions

30 are usually assumed to be small compared to dimensions of fluid channels in

1 porous media where advective flux is given by Eq. (1). It is possible for the
2 dimensions of *reference volumes* to approach the size of fluid channels in some
3 porous media. Impedance of advective flux is expected to depend on the ratio of
4 the dimensions of a *reference volume* to dimensions of fluid channels.
5
6 <p align="center">**Volume and mass flux**</p>
7   Volume flux has dimensions of velocity, but it is not a velocity from a
8 mathematical perspective because flux refers to motion of many constituents in a
9 *reference volume* rather than to a point in space. However, volume flux is
10 assumed to have the same magnitude and direction as velocity of the centroid of
11 a *reference volume* at a point in space so this velocity is employed to represent
12 net volume flux. **Net volume flux (designated by** U **) is equal to the sum of**
13 **diffusion indicated by the symbol** U_d **and advection indicated by** U_a **.**
14   Although mass flux does not have dimensions of velocity, mass flux is
15 assumed to be equal to velocity of the center of mass of a *reference volume*
16 designated by V, called *barycentric velocity*. Volume flux and *barycentric velocity*
17 are independent variables as the thought experiment (Fig.1) indicates.
18   The Navier-Stokes equation assumes resistance to viscous flux is
19 proportional to rate of angular deformation of *reference volumes*. For viscous
20 flux, motion of *reference volumes* with respect to a particular direction is entirely
21 two-dimensional because there can be no component of flux normal to a solid
22 boundary. For flux in porous media, Eq. (3) is rewritten as:
23

24
$$\rho \frac{Du_a}{Dt} = -\frac{dp^*}{dx} + \mu(\frac{\partial u_a^2}{\partial y^2} + \frac{\partial u_a^2}{\partial z^2}). \qquad (5)$$

25

26 Symbol x in Eq. (5) is a length in an arbitrary direction and coordinates y and z
27 are normal to x. Eq. (5) evaluates a component of volume flux rather than mass
28 flux because driving and resistance forces in this equation are surface forces.
29

<p align="center">20</p>

Force driving diffusion

2   Diffusion differs from advection in that diffusion refers to transport of

3   individual particles rather than transport of *reference volumes* as a whole.

4   However, diffusion contributes to net volume flux as well as net mass flux for this

5   analysis. Kinetic energy per mole increases with temperature. Concentration of

6   moles per unit volume is constant at a particular temperature in an ideal gas. For

7   fluids in general, including liquids, number of moles that translate in three

8   dimensions is also constant at a particular temperature.

9

10   **Other mechanisms of transport**

11   Flux through fluid channels approaching the dimensions of *reference*

12   *volumes* is force acting on a subset of particles with dimensions smaller than fluid

13   channels in porous media evaluated by Eq. (1). Flux that needs to be evaluated

14   in this case can be different from advection as defined here; because particles in

15   this subset may be smaller than larger particles present in a *reference volume* as

16   a whole that are totally blocked by the solid boundary.

17   Consider a mixture of particles of equal mass that differ only in respect to

18   color. For example, half of the particles occupying a portion of a particular space

19   are red and another half of this space is occupied by blue particles. When the

20   mixture reaches equilibrium, the red particles and the blue particles will be

21   equally distributed. This motion is a flux in response to a force per unit volume on

22   particles with a particular color because the motion is due to a directional

23   derivative of mass per unit volume which is proportional to concentration of

24   particles with a particular color in this case.

25   However, we may regard the motion as a response to a derivative of

26   entropy, a potential with the same dimensions as the potential associated with

27   diffusion. Theory indicates that entropy approaches a maximum at equilibrium.

28

29

30

Transport of liquid solutions in aquifers

Experience shows the dominant force per unit volume producing net flux in a particular direction in agricultural soils and aquifers is usually the directional derivative of piezometric pressure, the potential in Eq. (1). Dimensions of fluid channels in agricultural soils and aquifers apparently are large enough that only advection is significant. Research to date indicates diffusion is insensitive to channel dimensions over a large range of pore sizes, and is usually much less important than advection.

Kinetic energy related to pressure

Pressure in liquid solutions is different from the sum of partial pressures because pressure in liquid solutions includes normal force resulting from inter-molecular forces at the boundary of reference volumes as well as rate of change of momentum of translating particles crossing normal to the boundary of *reference volumes*. The component of pressure resulting from the change of momentum of translating particles is proportional to their kinetic energy, and is apparently proportional to the vapor pressure of a solvent.

Vapor pressure of water (as a function of temperature) is found in any edition of the Handbook of Chemistry and Physics. Eq. (4) in terms of macroscopic variables is rewritten by substituting vapor pressure for concentration:

$$q_{d_w} = -\mathcal{D}_w \frac{dp_{v_w}}{dx}. \tag{6}$$

This substitution is permissible because experience shows that vapor pressure of water solutions is proportional to concentration of water particles that can translate in three dimensions (Corey, A.T., W.D. Kemper and J.H. Dane 2010).

Rewriting the driving force for diffusion as a directional derivative of a potential with dimensions of energy per volume, rather than as a dimensionless fraction, requires that dimensions of the coefficient must also change so the flux

1 evaluated has dimensions of volume flux and can be combined with advective

2 flux evaluated by Darcy's equation. Vapor pressure and piezometric pressure

3 cannot be added, because $\mathcal{D}_w$ and K_x are different functions of a porous

4 **medium even though they have the same dimensions.**

5 \

6 **Experiments verifying Eq. (6)**

7 Corey, A.T., W.D. Kemper and J.H. Dane 2010 show the contribution of

8 diffusion to net flux of liquid water particles in a particular direction is proportional

9 to a directional derivative of water vapor pressure. Corey, A.T., W.D. Kemper and

10 J.H. Dane 2010 measured net flux of liquid water through two different

11 membranes, each of which had fluid channels small enough to insure that

12 diffusion is significant, but large enough that Eq. (1) evaluates advection with

13 sufficient accuracy in both membranes. Eq. (1) does not evaluate net flux

14 because it does not evaluate diffusion, a significant flux through both membranes

15 investigated.

16 Detailed description of the apparatus and methods employed is provided

17 by Corey, A.T., W.D. Kemper and J.H. Dane 2010. The membranes were

18 manufactured by Dow Chemical for desalination purposes so they were designed

19 to provide as little resistance as possible, consistent with the necessity of

20 removing most of the salt from liquid water solutions efficiently. Apparently, this

21 requires manufacturing porous media with channels having as little *tortuosity* as

22 possible.

23 It is first determined experimentally that Eq. (1) provides an acceptable

24 evaluation of advection over the range of temperatures and membranes

25 employed in each experiment provided the hydraulic coefficient is adjusted for

26 mean temperature in each experiment. Advection in one direction and diffusion in

27 the other direction is then induced by imposing a large temperature difference

28 across vertical membranes. Net flux is measured directly. Diffusive flux is

29 calculated as the difference between net flux and advective flux.

1   Correlation between net flux and temperature difference imposed across

2   the membranes employed is negligible because the apparatus employed

3   provides no control over the fraction of energy dissipated by conduction. Heat as

4   defined here is total energy per unit mass that includes vibration or spin of

5   particles. Flux of that portion of total energy per unit mass that includes only

6   vibration and spin does not contribute to mass flux.

7   Diffusive flux, plotted as a function of water vapor pressure, fits a straight

8   line passing through the origin in each experiment, indicating that self-diffusion of

9   particles in a particular direction is proportional to the directional derivative of

10   water vapor pressure, and that net flux of water particles is the sum of advection

11   and self-diffusion.

12   **Net flux**

13   Assuming evidence provided by Corey, A.T., W.D. Kemper and J.H. Dane

14   2010 is sufficient to state that net flux of de-ionized liquid water is, in fact, equal

15   to the sum of advection and diffusion, a question arises as to whether or not a

16   single potential can be found such that the directional derivative correlates with

17   net flux in the same manner as the sum of advection and diffusion.

18   Such a potential is not the sum of unlike potentials appearing in equations

19   (1) and (6). Though the directional derivatives of these potentials when multiplied

20   by their respective coefficients have the same dimensions, **the coefficients are**

21   **different functions of the porous medium.** The only way directional derivatives of

22   the sum of two unlike potentials are proportional to net flux is for the products of

23   coefficients and directional derivatives of potentials to be additive. However, the

24   potentials for advection and diffusion cannot be added **because they are different**

25   **functions of the porous media.**

26   A single potential necessary to provide the correct evaluation of net flux is

27   necessarily a function of the coefficients for each flux mechanism. Furthermore,

28   any derivative of a sum of potentials would have to account for the fact that the

29   coefficients are strongly dependent on the direction chosen. For these reasons,

1 evaluation of the sum of diffusion and advection as a flux driven by a directional

2 derivative of a single potential is impossible.

3   **Consideration of mass continuity requires including source terms in**

4 **reference volumes.** The so-called "total" derivative does not apply to non-

5 homogeneous fluids. This fact is explained in the text by Streeter, V. L. 1948, and

6 is the reason modern textbooks dealing with fluid dynamics, *e.g.*, Turner,

7 J.S.1973, employ a term evaluating momentum flux in their flux equations that is

8 not found in Eq. (5). The fact that Eq. (5) applies only to homogeneous fluids has

9 been pointed out by Brenner, H. 2006, and by Greenshields, C.J. and

10 J.M. Reese 2006.

11   Deriving an advective flux equation applicable for non-homogenous fluids

12 requires applying Newton's second law of motion, that is, *force is equal to the*

13 *rate of change of momentum.* For force on a reference volume of fluid with a

14 density gradient this is:

15
$$\frac{d(\rho \boldsymbol{u})}{dt} \equiv \rho \frac{d\boldsymbol{u}}{dt} + \boldsymbol{u}\frac{d\rho}{dt} .$$

16 The time derivative of $\boldsymbol{u}$ is acceleration, which we assume is negligible, but the

17 time derivative of density is not zero for cases where a significant density

18 variation exists. Corey, A. T. and S. D. Logsden 2005 show that this derivative is

19 related to a density variation in a particular direction by:

20

21
$$u_a \frac{d\rho}{dt} \equiv u_a \left(\frac{d\rho}{dx}\frac{dx}{dt}\right) \equiv u_a{}^2 \frac{d\rho}{dx} . \qquad (6)$$

22

23 Eq. (5) is re-written to apply for an advective flux in porous media as:

24

25
$$\boldsymbol{u}_a{}^2 \frac{d\rho}{dx} = -\frac{dp*}{dx} + \mu\left(\frac{\partial^2 \boldsymbol{u}_a{}^2}{\partial y^2} + \frac{\partial^2 \boldsymbol{u}_a{}^2}{\partial z^2}\right) . \qquad (7)$$

26

Eq. (7) can be regarded as a version of Stokes equation for viscous flux in porous media, because inertial resistance is set to zero, but this equation is theoretically applicable to fluids with a single particle species only.

Eq. (7) contains two independent driving forces but only a single resisting force. The two independent driving forces make Eq. (7) impractical for evaluating advection in porous media in any case, but impossible where particles with more than a single particle mass are involved. Density gradients can be significant for cases where more than a single particle mass is involved, and the single resistance function applies only to homogeneous fluids where diffusion is not a significant mechanism of transport.

According to the Dusty-Gas Model presented by Mason, E.A., and A.P. Malinauskas, 1983, lighter particles transfer momentum in a particular direction to heavier particles upon contact, so the resistance function that involves only directional derivatives normal to the solid boundary is insufficient in the general case.

A thought experiment

The fact that net mass flux and advective flux are different variables, and that Eq. (5) does not evaluate net mass flux is demonstrated by the following thought experiment: Diffusion in a closed space is employed to illustrate that even for this limiting condition, such that motion of *reference volumes* is completely blocked, transport of mass by diffusion only is still possible. The upper sketch depicts such a space where the center of mass of particles in the space is moving to the right by diffusion. The bottom sketch of the same space depicts the motion that has occurred after the center of mass has reached an equilibrium position, so the center of mass and centroid coincide.
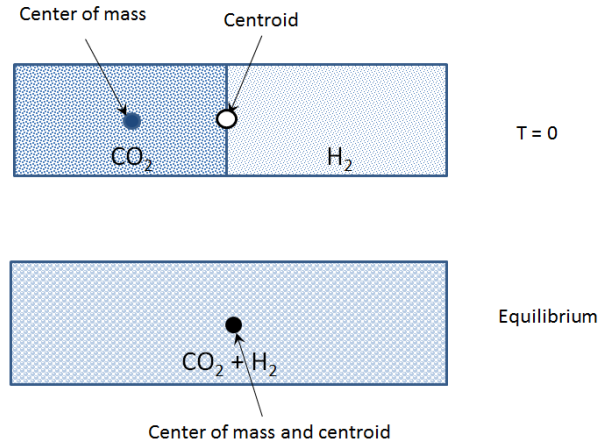
Fig.1. Diffusion in a closed space - a thought experiment

No experimental evidence is cited that either hydrogen or carbon dioxide molecules form particles as defined above (and as depicted in Fig. 1) in gaseous solutions, but we assume hydrogen gas molecules diffuse faster than carbon dioxide gas molecules. Graham's law of diffusion indicates the center of mass is moving to the right in the upper sketch because hydrogen gas molecules diffuse faster than carbon dioxide gas molecules. Pressure is greater on the left side during motion of the center of mass before equilibrium is established. At equilibrium, pressure is again constant and net mass flux ceases, but the center of mass has moved to coincide with the centroid, **a movement not predicted by Eq. (5).**

The pressure gradient that develops during motion of the center of mass is cancelled by a force exerted on the fluid body by the solid boundary, because the centroid cannot move in a closed space, no advection is possible. In other words, a mass flux may occur without any advection; so **volume flux and mass flux are independent variables.**

CONCLUSIONS

Results of the Corey, A.T., W.D. Kemper and J.H. Dane 2010 experiments, as well as the thought experiment depicted above, show that evaluating net flux due to advection and diffusion requires evaluating advection

27

1 and diffusion independently. **Eq. (5) does not evaluate** *mean flux* **if diffusion**
2 **occurs.** A single flux equation to evaluate net flux where diffusion as well as
3 advection exists usually requires too many independent variables to be practical
4 for use in the general case where fluid particles with multiple masses are
5 involved.

6   The Corey, A.T., W.D. Kemper, and J.H. 2010 experiments show
7 advection of de-ionized liquid water is sometimes evaluated with acceptable
8 accuracy by Eq. (1) even where diffusion also is significant. These experiments
9 show **self-diffusion of liquid water particles in a de-ionized solution is proportional**
10 to the vapor pressure of a water solution.

11   Net flux of a particular particle in a water solution in porous media, in a
12 particular direction, is accomplished by first **determining flux of the particle**
13 **associated with advection of the water solution as a whole in a particular**
14 **direction and adding the diffusive flux in that direction.**

15   For a special case where advective flux is approximated with sufficient
16 accuracy by Eq. (1), an appropriate equation can be written as:

17

$$q_{i_x} = -\frac{c_i}{c} K_w \frac{dp_w^*}{dx} - \mathcal{D}_i \frac{dp_{v_i}}{dx} \qquad (8)$$

18

19

20 For the particular case of flux of de-ionized liquid water, Eq. (8) reduces to:

21

$$q_{w_x} = -K_{w_x} \frac{dp_w^*}{dx} - \mathcal{D}_{w_x} \frac{dp_{v_w}}{dx} \qquad (9)$$

22

23

24 The driving forces in equations (8) and (9) are evaluated by *directional*
25 *derivatives, not gradient operators.*

26   Equations (8) and (9) apply to flux of water constituents in a de-ionized
27 liquid water solution where the water cluster is theoretically the only particle
28 transported by self-diffusion. Eq. (9) is verified by experimental evidence for net

flux of liquid water provided by Corey, A.T., W.D. Kemper and J.H. Dane 2010. This equation can be applied to a special case of transport of water constituents in liquid water solutions through porous media with channels small enough that diffusion is significant, but large enough that Eq. (1) provides an adequate evaluation of advection.

Need for additional research

Additional research is needed to evaluate flux of liquid solutions through porous media, *e.g.,* shale, compacted clay layers, or membranes that separate living cells such as in capillaries in the mammalian cardiovascular or plant systems. Research appearing in the literature to date does not show clearly where transport of a reference volume is evaluated with sufficient accuracy by an equation relating advective flux to the directional derivative of piezometric pressure. A rule that describes conditions under which Eq. (1) evaluates advective flux with acceptable accuracy is needed.

LIST OF SYMBOLS

Symbol	Variable	Dimensions
∇	Gradient operator	L^{-1}
$\boldsymbol{v}$	barycentric velocity	LT^{-1}
M	molecular mass	M
$\boldsymbol{u}$	volume flux	LT^{-1}
$\boldsymbol{u}_a$	advective volume flux	LT^{-1}
$\boldsymbol{u}_d$	diffusive volume flux	LT^{-1}
$\boldsymbol{q}$	macroscopic volume flux	LT^{-1}
$\boldsymbol{q}_a$	macroscopic advective flux	LT^{-1}
$\boldsymbol{q}_d$	macroscopic diffusive flux	LT^{-1}
$\boldsymbol{q}_{d_w}$	water diffusive flux	LT^{-1}
p	pressure	$ML^{-1}T^2$
p^*	piezometric pressure	$ML^{-1}T^2$
ρ	density	ML^{-3}

29

1	T	Kelvin temperature	ML^2T^{-2}
2	t	time	T
3	c	concentration	L^{-3}
4	μ	viscosity	$ML^{-3}T$
5	K	Darcy conductivity	$M^{-1}L^3T^{-3}$
6	$\mathcal{D}$	diffusion coefficient	$M^{-1}L^3T^{-3}$
7	D	Fick's diffusion coefficient	$L^2\,T^{-1}$

8 The dimensions listed in this list are dimensions in the mass, length, and time

9 system for designating dimensions.

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