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On equations for the total suction and its matric and osmotic components

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ABSTRACT

A clear fundamental understanding of suctions is crucial for the study of the behaviour of plastic cement mortar and concrete, including plastic shrinkage cracking. In this paper, the expression relating the change in free energy of the pore water with an isothermal change in pressure is first derived. Based upon definitions of suctions, it is then shown that total, matric, and osmotic suctions can all be expressed in the same thermodynamic form. The widely accepted, but not yet satisfactorily validated, assumption that the total suction comprises matric and osmotic components is then confirmed theoretically. The well-known Kelvin equation for matric suction, and Morse and van't Hoff equations for osmotic suction are subsequently derived from the corresponding thermodynamic equations. The applicability of latter two equations in evaluating the osmotic suctions of cement mortar and concrete is highlighted.

1. Introduction

Plastic shrinkage cracking of cement mortar and concrete is primarily attributable to desiccation by evaporation from unprotected surfaces [1,2]. This causes high matric suction to develop in the pore water in the voids adjacent to these surfaces. Dissolved salts in the pore water generate osmotic suction, which can also contribute significantly to the total suction. Plastic shrinkage cracking occurs when the stress arising in the cement mortar or concrete due to a combination of suction and restraints of deformation such as reinforcement, prestressing ducts, or formwork reaches its strength.

Also, because plastic cement mortar and concrete are essentially frictional particulate materials, their behaviour, including plastic shrinkage cracking, is closely related to the interparticle stresses. These can be expressed as functions of suctions using existing soil mechanics models [3,4].

It is thus important to have a thorough fundamental understanding of suctions when studying plastic shrinkage cracking of cement mortar and concrete. The total suction has long been assumed to comprise only two components, namely the matric and osmotic suctions, and definitions of all three suctions have gained general acceptance [5, p. 65; 6,7, p. 166]. Equations based on thermodynamics that relate the three suctions individually to the partial pressure of the pore-water vapour have also long been available [8]. However, the interrelationship between these equations has not been stated explicitly, and the generally accepted subdivision of the total suction into matric and osmotic components has not been confirmed theoretically. The latter has been verified experimentally for soils by Krahn and Fredlund [9], but the verification is not considered conclusive, due mainly to relatively large experimental errors in the suction measurements [10,11].

In this paper, a detailed derivation of the expression relating the change in free energy of the pore water with an isothermal change in pressure is first presented. Definitions of the total, matric and osmotic suctions, which are adopted from the soil mechanics literature, are then introduced. Using the expression for the free energy and these definitions, it is shown explicitly that all of the suctions can be expressed in the same thermodynamic form. The widely accepted assumption that the total suction comprises matric and osmotic components is then confirmed theoretically. The Kelvin, Morse, and van't Hoff equations for matric and osmotic suctions are also derived from the corresponding thermodynamic equations.

2. Potential, suction, and free energy

The concept of potential has long been used in the study of electricity, magnetism, and mechanics, as well as in pore moisture studies. However, the analogous parameter, the free energy or thermodynamic potential, which is used in thermodynamics and physical chemistry, is more comprehensive than potential, and can be used to consider solid, liquid, and gaseous phases existing in equilibrium, as well as the effects of adsorptive force fields and temperature on the energy of pore moisture. The entropy, which is used in thermodynamics to describe energy changes associated primarily with the transformation of heat into other forms of energy, is even more comprehensive than the free energy, and could also be used as an alternative to potential in studies of pore moisture, but the associated criteria for energy changes and equilibria are too general to be very useful [8]. Entropy and potential are

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opposite in sign: during a spontaneous change in any system, its entropy always increases, while its potential always decreases.

The following analysis is accordingly based on the free energy of pore moisture. Additionally, pore moisture potentials can be expressed as heads, suctions (negative pressures), or in pF units [12]. In this paper, they are expressed as suctions.

3. Free energy of pore moisture

The absolute specific free energy, *f*, of water vapour, which is also termed the Gibbs free energy, is defined by [6,8,13, p. 697]

$$f = e + p \cdot v - T \cdot s \tag{1}$$

where *e* is the internal energy, *p* is the pressure, *v* is the specific volume, *T* is the absolute temperature, and *s* is the entropy of the system under consideration.

Differentiating Eq. (1), gives

$$\mathrm{d}f = \mathrm{d}e + p \cdot \mathrm{d}v + v \cdot \mathrm{d}p - T \cdot ds - s \cdot dT \tag{2}$$

Also, according to the first law of thermodynamics

$$\mathrm{d}e = \mathrm{d}q - dw \tag{3}$$

where d*q* is the amount of heat taken in by the system, and d*w* is the total work performed by the system.

The heat, d*q*, is equal to *T*·d*s* in any reversible process, while d*w* can, in general, be separated into the work of expansion, *p*·*dv*, against *p* and other mechanical work, $\mathrm{d}w_\mathrm{m}$.

Combining Eqs. (2) and (3), gives

$$\mathrm{d}f = -s \cdot \mathrm{d}T + v \cdot \mathrm{d}p - dw_\mathrm{m} \tag{4}$$

Applying Eq. (4) to a finite isothermal change in the system from any state *A* to another state *B*, yields

$$\Delta f = \int_A^B df = f_B - f_A = \int_A^B vdp - \int_A^B dw_\mathrm{m} \tag{5}$$

where Δ*f* is the change in *f* corresponding to the change from state *A* to state *B*. State *A* is thus an arbitrary datum for Δ*f*.

It is now assumed that the water vapour is an ideal gas, so that

$$pv = RT \tag{6}$$

where *R* is the gas constant for water vapour (461.9 J/kg K). This is a good assumption for water vapour in the range of practical interest [13–15].

If no work is performed during the isothermal change apart from a change in *p*, that is, if $\mathrm{d}w_\mathrm{m}$ equals zero, Eq. (5) becomes

$$\Delta f = \int_A^B vdp = RT \int_A^B \frac{dP}{P} = RT \ln\left(\frac{p_B}{p_A}\right) = \frac{R_\mathrm{u}T}{M} \ln\left(\frac{p_B}{p_A}\right) \tag{7}$$

where R_u is the universal gas constant (8.314 J/mol K), and *M* is the molar mass of water vapour.

Eq. (7) shows that the *f* of water vapour increases with an isothermal increase in pressure, and vice versa. Since, at equilibrium, the *f* of water vapour in contact with pore water must equal that of the pore water [8], Eq. (7) also applies to the latter.

For convenience in the subsequent analysis, Eq. (7) can be written as

$$\rho \Delta f = -\frac{R_\mathrm{u}T}{\mathrm{V}} \ln\left(\frac{p_A}{p_B}\right) \tag{8}$$

where *ρ* is the density of pure water, and *V* is the molar volume of pure water. The product, *ρ*Δ*f*, in Eq. (8) is equal to the potential of the pore water and thus the negative of the suction, both expressed as a stress.

Eq. (8) represents the special case of an isothermal process during which the total work is performed is by a change in *p* only. This is a good approximation of typical processes in pore moisture [6,8]. Consequently, Eq. (8) can be used to evaluate the total, matric, and osmotic suctions in pore moisture, and to clarify their interrelationship and significance.

4. Thermodynamic equations for total, matric, and osmotic suctions

Free, pure water is used as the datum in pore moisture energy relationships. The total, matric, and osmotic suctions can thus be evaluated as follows [6,8].

The total suction, *ψ*, is the amount of work that must be done per unit quantity of pure water in order to transport reversibly and isothermally an infinitesimal quantity of water from a pool of pure water at a specified elevation at atmospheric pressure to the pore water at the point under consideration. Combining this with Eq. (8) gives

$$\psi = -\frac{R_\mathrm{u}T}{V} \ln\left(\frac{p_\mathrm{e}}{p_0}\right) \tag{9}$$

where p_e is the partial pressure of the water vapour in equilibrium with the pore water, and p_0 is the partial pressure of water vapour in equilibrium with free, pure water at the same temperature (Fig. 1).

The matric suction, ψ_m, is the amount of work that must be done per unit quantity of pure water in order to transport reversibly and isothermally an infinitesimal quantity of water from a pool containing a solution identical in composition to the pore water at the elevation and the external gas pressure of the point under consideration to the pore water. Eq. (8) then becomes

$$\psi_\mathrm{m} = -\frac{R_\mathrm{u}T}{V} \ln\left(\frac{p_\mathrm{e}}{p_1}\right) \tag{10}$$

where p_1 is the partial pressure of the water vapour in equilibrium with a solution identical in composition with the pore water (Fig. 1).

The osmotic suction, *π*, is the amount of work that must be done per unit quantity of pure water in order to transport reversibly and isothermally an infinitesimal quantity of water from a pool of pure water at a specified elevation at atmospheric pressure, to a (large) pool containing a solution identical in composition with the pore water at the point under consideration, but in all other respects identical to the reference pool (Fig. 1). Combining this with Eq. (8) yields

$$\pi = -\frac{R_\mathrm{u}T}{\mathrm{V}} \ln\left(\frac{p_1}{p_0}\right) \tag{11}$$

In Eqs. (9)–(11), p_e, p_1, p_0 are based on the absolute pressure datum. They can be converted into the atmospheric pressure datum by subtracting 101.325 kPa.

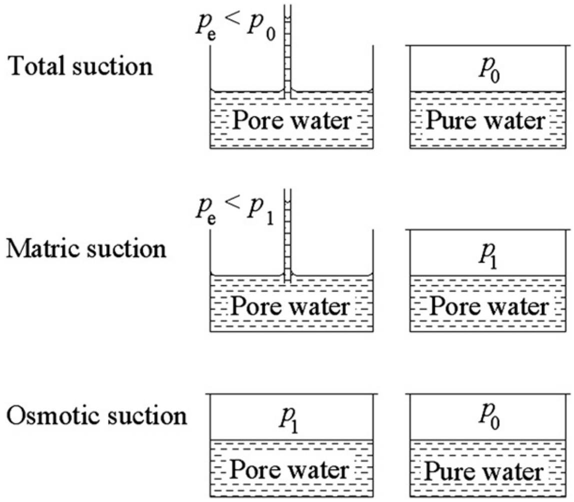

Fig. 1. Total, matric and osmotic suction (after [16]).

Eq. (9) is frequently used to express ψ as a function of vapour pressure [5,10]. The ratio, p_e/p_0, closely approximates the relative humidity, h [17,18]. Fig. 2, which is derived from Eq. (9), shows that ordinary temperature variation has little effect on the total suction. However, the latter varies from zero at a h of 100% to very high values at even slightly lower relative h. For example, a h of about 94% at a temperature of 20 °C corresponds to a suction of about 8 MPa.

The matric suction, ψ_m, is related to the pore radius, r, by the well-known Laplace equation [15,19,20, pp. 21–23],

$$\psi_m = \frac{2\gamma}{r}\cos(\theta) \tag{12}$$

where γ is the surface tension of the pore water, and θ is the contact angle between the pore wall and the spherical interface between the pore water and pore air. (For free droplets of pore moisture, θ equals zero and r becomes the droplet radius.)

Combining Eqs. (10) and (12) gives the well-known Kelvin equation [15,19,20, pp. 24–25],

$$\frac{2\gamma}{r}\cos(\theta) = -\frac{R_uT}{V}\ln\left(\frac{p_e}{p_1}\right) \tag{13}$$

Excellent experimental confirmation has been obtained for Eq. (13) [21,22], which can remain valid to within a few percent even for temperatures approaching the critical point [15].

Eq. (11), the general expression for osmotic suction, can be obtained thermodynamically in several different ways. It is independent of any theory or mechanism of osmotic pressure, and is theoretically exact [14, p. 252]. Osmotic suctions determined experimentally and using Eq. (11) for sucrose solutions at 30 °C [14, pp. 242–253] are compared in Fig. 3. It can be seen that, notwithstanding the assumptions of ideal behaviour, Eq. (11) is in excellent agreement with the experimental data at all concentrations.

5. Morse and van't Hoff equations

The well-known Morse and van't Hoff equations for π, which were originally empirical, can be derived from Eq. (11) [14, pp. 250–253].

Raoult's law [6,14, pp. 232–233] states that the fraction reduction of the vapour pressure of a solvent due to the addition of a solute, is equal to the mole fraction of the solute in the solution. This gives

$$\frac{p_0 - p_1}{p_0} = x_1 = \frac{n_1}{n_0 + n_1} \tag{14}$$

where x_1 is the mole fraction of the solute, and n_0 and n_1 are the numbers of moles of solvent and solute, respectively.

By definition, ideal solutions obey Raoult's law exactly for all concentrations and all temperatures. All dilute solutions obey Raoult's law approximately, but it is probable that only solutions that have zero heat of dilution and in which there is no volume change when the components are mixed in the liquid state obey it exactly.

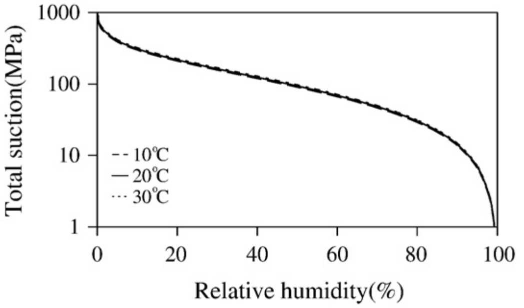

Fig. 2. Variation of total suction with relative humidity and temperature.

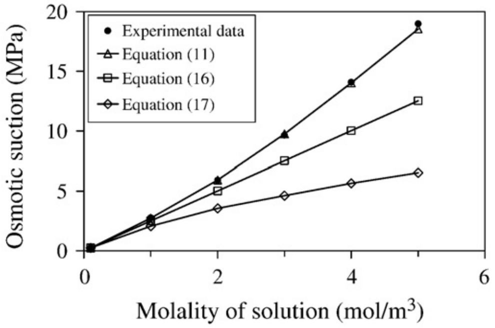

Fig. 3. Comparison of experimental and theoretical osmotic suctions.

Subtracting unity from both sides of Eq. (14) and combining the result with Eq. (11) gives, for ideal solutions,

$$\pi = -\frac{R_uT}{V}\ln(1 - x_1) \tag{15}$$

If the solution is also dilute, x_1 is small, and $\ln(1-x_1)$ and x_1 approximate to $-x_1$ and n_1/n_0, respectively. Combining these approximations with Eq. (15) gives the Morse equation,

$$\pi = \frac{R_uT}{V}x_1 = \frac{R_uT}{V\frac{n_0}{n_1}} = \frac{R_uT}{V_1} \tag{16}$$

where V_1 is the volume of solvent per mole of solute.

For extremely dilute solutions, V_1 in Eq. (16) can be replaced by the volume, V_2, of the solution containing 1 mol of solute. This gives the van't Hoff equation,

$$\pi = \frac{R_uT}{V_2} = cR_uT \tag{17}$$

where c is the molar concentration of solute.

Eqs. (16) and (17) are compared to Eq. (11) and sucrose solution data [14, p. 243] in Fig. 3. This shows that the van't Hoff equation is valid for only very dilute solutions, while the Morse equation is valid for slightly higher concentrations. Suarez [23, pp. 118–119] comments that the van't Hoff equation breaks down rapidly for concentrations above 0.2 mol/m^3, while the Morse equation is reasonably accurate to at least 0.5 mol/m^3. Consequently, the van't Hoff and Morse equations may not be suitable for evaluating the osmotic suctions of cement mortar and concrete. Osmotic suctions of up to 0.5 MPa, corresponding to molar concentration of 205 mol/m^3, have been measured in cement mortars without additives immediately after mixing [24].

6. Relationship between total, matric, and osmotic suctions

Eq. (9) for the total suction can be rewritten as follows:

$$\psi = -\frac{R_uT}{V}\ln\left(\frac{p_e}{p_1}\frac{p_1}{p_0}\right) = -\frac{R_uT}{V}\ln\left(\frac{p_e}{p_1}\right) - \frac{R_uT}{V}\ln\left(\frac{p_1}{p_0}\right) \tag{18}$$

Substituting Eqs. (10) and (11) in Eq. (18) then gives

$$\psi = \psi_m + \pi \tag{19}$$

Eq. (19) shows theoretically, on the basis of thermodynamics, that the total suction equals exactly the sum of the matric and osmotic suctions.

7. Conclusions

A theoretical derivation of the interrelationship between the total, matric, and osmotic suctions based on thermodynamics has been presented in this paper. It has been shown that the total, matric, and osmotic suctions can be expressed in terms of very similar thermodynamic equations, and that the total suction comprises only the matric and osmotic suctions. The widely accepted assumption that this is so has thus been confirmed theoretically, and the Kelvin, Morse, and van't Hoff equations for matric and osmotic suctions have been derived from the corresponding thermodynamic equations.

The concepts underlying the equations commonly used to estimate total, matric, and osmotic suctions, which are crucial for the study of the behaviour of plastic cement mortar and concrete, including plastic shrinkage cracking and other relevant behaviours, have thus been both clarified and unified.

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References

[1] W. Lerch, Plastic shrinkage, J. ACI 53 (8) (1957) 797–802.

[2] P.H. Morris, P.F. Dux, Cracking of plastic concrete, Aust. J. Civil Eng. 1 (1) (2003) 17–21.

[3] V.N.T. Dao, P.H. Morris, P.F. Dux, Plastic cracking of concrete: the roles of osmotic and matric suctions, in: R.K. Dhir, T.A. Harrison, M.D. Newlands (Eds.), Cement Combinations for Durable Concrete — Proc. of 6th Intl. Congress on “Global Construction: Ultimate Concrete Opportunities”, Dundee, Scotland, July 2005, Thomas Telford, 2005, pp. 407–416.

[4] V.N.T. Dao, Early-age Cracking of Concrete, PhD Thesis, The University of Queensland, 2007.

[5] D.G. Fredlund, H. Rahardjo, Soil Mechanics for Unsaturated Soils, John Wiley & Sons, New York, 1993.

[6] Review Panel, Engineering Concepts of Moisture Equilibria and Moisture Changes in Soils, in: G.D. Aitchison (Ed.), Moisture Equilibria and Moisture Changes in Soils Beneath Covered Areas, Butterworths & Co. (Australia), Sydney, 1965, pp. 7–21.

[7] J.K. Mitchell, Fundamentals of Soil Behavior, 2nd ed.John Wiley & Sons, New York, 1993.

[8] N.E. Edlefsen, A.B.C. Anderson, Thermodynamics of soil moisture, Hilgardia 15 (2) (1943) 31–298.

[9] J. Krahn, D.G. Fredlund, On total, matric and osmotic suction, Soil Sci. 114 (5) (1972) 339–348.

[10] E.C. Leong, S. Tripathy, H. Rahardjo, Total suction measurement of unsaturated soils with a device using the chilled-mirror dew-point technique, Geotechnique 53 (2) (2003) 173–182.

[11] A.M. Ridley, W.K. Wray, Suction Measurement: a Review of Current Theory and Practices, in: E.E. Alonso, P. Delage (Eds.), Unsaturated Soils (Sols non saturés) — Proc. of 1st Intl. Conf. on Unsaturated Soils, UNSAT'95, A.A. Balkema, Rotterdam, 1996, pp. 1293–1322.

[12] D. Croney, J.D. Coleman, Soil structure in relation to soil suction (pF), J. Soil Sci. 8 (1) (1954) 75–84.

[13] Y.A. Çengel, M.A. Boles, Thermodynamics: an Engineering Approach, 5th ed. McGraw-Hill Higher Education, Boston, 2006.

[14] S. Glasstone, D. Lewis, Elements of Physical Chemistry, 2nd rev. ed.Macmillan & Company, London, 1963.

[15] J.G. Powles, On the validity of the Kelvin equation, J. Phys. A (Mathematical and General), 18 (9) (1985) 1551–1560.

[16] D.G. Fredlund, How negative can pore-water pressures get? Geotech. News 9 (3) (1992) 44–46.

[17] W. Brutsaert, Evaporation into the Atmosphere: Theory, History, and Applications, Reidel Publishing Co., Boston, 1982.

[18] J.R. Philip, Evaporation, and moisture and heat fields in the soil, J. Meteorol. 14 (1957) 354–366.

[19] K.P. Galvin, A conceptually simple derivation of the Kelvin equation, Chem. Eng. Sci. 60 (16) (2005) 4659–4660.

[20] G. Barnes, I. Gentle, Interfacial Science: an Introduction, Oxford University Press, New York, 2005.

[21] V.K. La Mer, R. Gruen, A direct test of Kelvin's equation connecting vapour pressure and radius of curvature, Trans. Faraday Soc. 48 (5) (1952) 410–415.

[22] J.C. Fisher, J.N. Israelachvili, The direct experimental verification of the Kelvin equation for capillary condensation, Nature 277 (5697) (1979) 548–549.

[23] D.L. Suarez, Thermodynamics of the soil solution, in: D.L. Sparks (Ed.), Soil Physical Chemistry, CRC Press, Boca Raton, 1999, pp. 97–134.

[24] P.H. Morris, P.F. Dux, Suctions, fracture energy, and plastic cracking of cement mortar and concrete, ACI Mater. J. 102 (6) (2005) 390–396.