Soil Wetting as a Spontaneous Process
by Lyle Prunty
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Spontaneous processes occur in the direction allowed by the second law of thermodynamics. The wetting of soil is such a process. Other examples include cooling of an object initially at elevated temperature, escape of a compressed gas, and flow of a river. Although the initial condition in each of the above instances can be restored, doing so requires auxiliary devices and energy. In each instance the surroundings of the system will be forever different even though the system itself has been restored to its original state.

The conservation of energy principle is inadequate, alone, to determine the final equilibrium state of a system undergoing spontaneous changes. Time elapsed before an isolated system comes to equilibrium may be great or small, but the direction of change is invariant. The second law of thermodynamics is consistent with the direction of change in all known spontaneous processes. There are many equivalent ways to state the second law of thermodynamics. Two often-used statements are those of Clausius and Kelvin-Planck (Moran and Shapiro, 1992).

When free water is absorbed into dry soil heat is evolved. When the process is conducted at constant temperature the quantity of heat is known as the heat of wetting. In the theory of coupled heat and water flow in unsaturated soil, heat of wetting is often included in the energy equation. The theory developed by deVries (1958) and Philip and deVries (1957) seems to be the most widely used formulation of coupled heat and water flow theory. The objective of this paper is to clarify the proper role of heat of wetting in such theory. Application of the laws of thermodynamics and concepts of spontaneous and reversible thermodynamic processes are central to the development.

Reversible, Irreversible, and Spontaneous Wetting

The capillary tube model of Fig. 1 provides a way to visualize reversible wetting. In Fig. 1, the nonwetting portion of the horizontal capillary is filled with water. The meniscus just touches the wetting part of the tube and the surface tension force \(2\pi r\gamma\) just balances the gravitational force \(mg\) on mass \(m = \rho_l \pi r^2 l\).
A control volume (Fig. 1) defines the system to which the first law
\[ \Delta E = q + w \]  \hspace{1cm} (1)
will be applied. In a reversible displacement \( dz \) work \( w \) done on the system is
\[ mgdz = -2\pi r \gamma dz = -\frac{2\gamma}{r} \pi r^2 dz = -\frac{2\gamma}{r} dV. \] \hspace{1cm} (2)
Heat \( q \) conjugate to \( w \) enters the system at constant temperature and may be written \( q = \rho \Lambda dV \), where \( \Lambda \) is specific internal energy of adsorption. In the capillary tube model
\[ -\frac{2\gamma}{r} = P = \rho \psi_r \] \hspace{1cm} (3)
where \( P \) is capillary pressure and \( \psi_r \) (J/kg) is water potential in the capillary soil with pore radius \( r \). In going from the dry to saturated condition the
volume of water taken into the capillary soil (the wetting portion of the tube of Fig. 1) is \( V_w = \pi r^2 l \). If the bulk volume of the capillary soil is \( V_b \) then the energy change per unit bulk volume in going from dry to saturated is

\[
\Delta E = q + w = \rho(\psi_r + \Lambda)(V_w/V_b) = \rho(\psi_r + \Lambda)\theta_{sat}. \tag{4}
\]

Heat input to the system during any process can be found from (1) as

\[
q = \Delta E - w. \tag{5}
\]

This \( q \) depends on the work done on the system during the process. It is instructive to consider \( q \) for reversible \((q_r)\), nonreversible \((q_n)\), and spontaneous \((q_s)\) wetting from dryness to saturation.

For the reversible process, work per unit bulk volume \( V_b \) is found from (2) and (3) to be \( w_r = \rho \psi_r \theta_{sat} \), so with (4)

\[
q_r = \rho(\psi_r + \Lambda)\theta_{sat} - \rho \psi_r \theta_{sat} = \rho \Lambda \theta_{sat}. \tag{6}
\]

In any nonreversible (real) system some finite force needs to be applied to overcome friction. Work performed during the real system displacement \( dz \) in Fig. 1 requires force \(-2\pi r \gamma + F_f\), thus using (3) work per unit volume from dryness to saturation is

\[
w_n = (-2\pi r \gamma + F_f)(l/V_b) = (\rho \psi_r + F_f/A)(V_w/V_b) = (\rho \psi_r + P_f)\theta_{sat} \tag{7}
\]

where \( P_f \) is a positive pressure increment to overcome friction. Now we find from (4) and (5)

\[
q_n = \rho(\psi_r + \Lambda)\theta_{sat} - (\rho \psi_r + P_f)\theta_{sat} = (-P_f + \rho \Lambda)\theta_{sat} \tag{8}
\]

In spontaneous absorption of water no restriction is placed on water entering the soil. Thus in Fig. 1 zero net force is applied. An equivalent way to say this is that \( P_f \) is taken to offset \(-2\pi r \gamma \) exactly. Setting \( P_f = -\rho \psi_r \) accomplishes this and \( q \) for the spontaneous process becomes

\[
q_s = \rho(\psi_r + \Lambda)\theta_{sat} - (\rho \psi_r - \rho \psi_r)\theta_{sat} = \rho(\psi_r + \Lambda)\theta_{sat}. \tag{9}
\]

According to theory (Edlefsen and Anderson, 1943) \( \Lambda = -T(\partial \psi/\partial T) < 0 \), implying that when an increment of water is added to soil at constant temperature, the minimum heat evolved is \(-\rho \Lambda \theta_{sat}\).
Wetting in Coupled Flow Theory

In 1958 deVries presented and extended the theoretical approach of Philip and deVries (1957) to simultaneous heat and moisture transfer. The extension was primarily in the energy equation and one of the extensions was to include a heat of wetting term on the left hand side. The final forms deVries came up with are not very useful for the type of analysis intended here. However, the deVries heat flux and heat content per unit volume expressions (his equations (10) and (11)) contain all the information of the final equations in a more usable form. The heat content equation of deVries (1958) is

\[
\Delta E = C_d(T - T_0) + L_0 \rho_l \theta_v + (c_p \rho_l \theta_v + c_l \rho_l \theta_l)(T - T_0) - \rho_l \int_0^{\theta_l} W d\theta \tag{10}
\]

where \(C_d\) is heat capacity of dry soil, \(L_0\) is latent heat of water vapor, subscript \(v\) is for vapor, subscript \(l\) is for liquid, and \(W\) is differential heat of wetting. Using this to find the energy change in passing from dry to saturated capillary soil we find

\[
\Delta E = (C_d + c_l \rho_l \theta_{sat})(T - T_0) - \rho_l \int_0^{\theta_l} W d\theta \tag{11}
\]

since \(\theta_v\) is near at dryness and exactly zero at saturation. According to deVries (1958), referencing Edlefsen and Anderson (1943),

\[
W = -\rho_l(\psi - T \frac{\partial \psi}{\partial T}) \tag{12}
\]

Using the \(\theta - \psi\) relationship of the capillary tube model and equation (12)

\[-\rho_l \int_0^{\theta_{sat}} W d\theta = \rho_l(\psi_r - T \frac{\partial \psi_r}{\partial T})\theta_{sat} \tag{13}\]

and we identify

\[-T \frac{\partial \psi_r}{\partial T} = \Lambda. \tag{14}\]

The heat flux density expression of deVries

\[
J_q = -\lambda_s \nabla T + L_0 J_v + c_p(T - T_0)J_v + c_l(T - T_0)J_l \tag{15}
\]

with \(\lambda_s\) the thermal conductivity is now applied to the wetting portion of the capillary of Fig. 1. Water entering the capillary is all in liquid phase at
the left end and water flux at the right end is zero. There is no temperature gradient and we take the entire system initially to be at the reference temperature \( T_0 \). Also, all water entering the left end of the wetting portion is at the reference temperature. With these conditions this equation (15) says that the heat, \( q \) of (1), transported to the wetted portion of the tube while it fills with water is zero. Note also that the formulation of (15) implicitly makes the tube insulated so that no heat passes through its walls. For simplicity we take the tube walls to be massless. Also, no work is included in the deVries formulation, so \( w = 0 \). Applying equation (1) leads to equating (11), with (13) substituted, to the sum of heat and work, \( q + w \), found just above as zero:

\[
\Delta E = c_l \rho_l \theta_{sat}(T - T_0) + \rho_l (\psi + \Lambda) \theta_{sat} = 0
\]  

(16)

and inspection reveals that this result is independent of \( \psi \) at the inflow.

The independence is because \( w \) on the right of (1) has no corresponding term in the deVries (1958) formulation. The \( q \) on the right of (1) is given by (15) in deVries (1958) but it is incomplete because it only provides for heat flowing from one infinitesimal soil element to the next. There is no provision in the deVries equations for either water or energy to be inserted directly into a soil element through source terms in the equations. If heat of wetting considerations are included at all in a formulation, then complete omission of work terms and omission of the energy source term is rather confounding. The classic heat of wetting experiment cannot be simulated by a model that does not include the energy and work source terms just mentioned.

Additional terms are thus needed to complete the coupled flow theory in accordance with (1). New source terms are needed for \( w \) and \( q \) and an additional term needs to be added to (15). These terms are

\[
w = \rho_l \psi_x S_{lx} + w_x
\]  

(17)

\[
q = \rho_l c_l (T_x - T) S_{lx} + q_x
\]  

(18)

\[
J_q^+ = (\psi + \Lambda) J_l
\]  

(19)

where subscript \( x \) indicates something entering the volume element directly from outside the soil rather than being transported in from the adjacent soil element. In (17) \( w_x \) is work not included in \( \psi \), perhaps shaft work or electrical work. In (18) \( q_x \) is conducted heat entering perpendicular to the flow direction and \( S_{lx} \) is water introduced directly into the volume element.
from outside the soil. Adding these terms in for the same conditions stated for (16) and where also \( w_x = 0 \) and \( T_x = T = T_0 \) leads to
\[
\Delta E = \rho_l (\psi_r + \Lambda) \theta_{sat} = \rho_l \psi_x S_{lx} + q_x. \tag{20}
\]
In (20) the added term of (19) did not play a part since \( S_{lx} \) is directly introduced.

For reversible saturation \( \psi_x = \psi_r \) and \( S_{lx} = \theta_{sat} \) so
\[
q_x = \rho \Lambda \theta_{sat} \tag{21}
\]
as in (6) while for spontaneous absorption of water \( \psi_x = 0 \) and
\[
q_x = \rho_l (\psi + \Lambda) \theta_{sat} \tag{22}
\]
as in (9). In equations (6), (8), (9), (21), and (22) it should be noted that \( q \) is less than zero because the initial sign convention for \( q \) was that positive \( q \) corresponds to heat flowing into the soil. Since \( q \) in these equations is negative, heat is evolved from wetting and flows out of the soil element to a heat sink at constant temperature when water at \( \psi = 0 \) is freely added to the soil. This corresponds exactly to the classic experimental procedure for determining heat of wetting.

**Conclusion**

Heat of wetting is included in the deVries (1958) formulation in incomplete form. Because of this incompleteness additional terms are needed in order to model the classic heat of wetting experiment. One such term, the heat generated by frictional flow of water, is noted by deVries as generally of small magnitude. In the water-soil system heat of wetting also is usually a fairly small effect. Nevertheless, it seems that an analysis such as this one is necessary for completeness.

The deVries (1958) formulation has very recently been used in several papers without mention of any modification with respect to the heat of wetting term. Some of these papers are: Cahill and Parlange (1998), Janssen et al. (1999), and Nassar and Horton (1992). Salzmann et al. (2000) use, without citation, the same approach, but omit heat of wetting.

Models should be written to include proper terms for \( w \), both external and convected with flow, and for any source of external \( q \). Then comparison of model results with and without the terms suggested here should be made.
References


