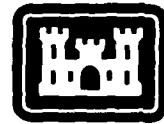


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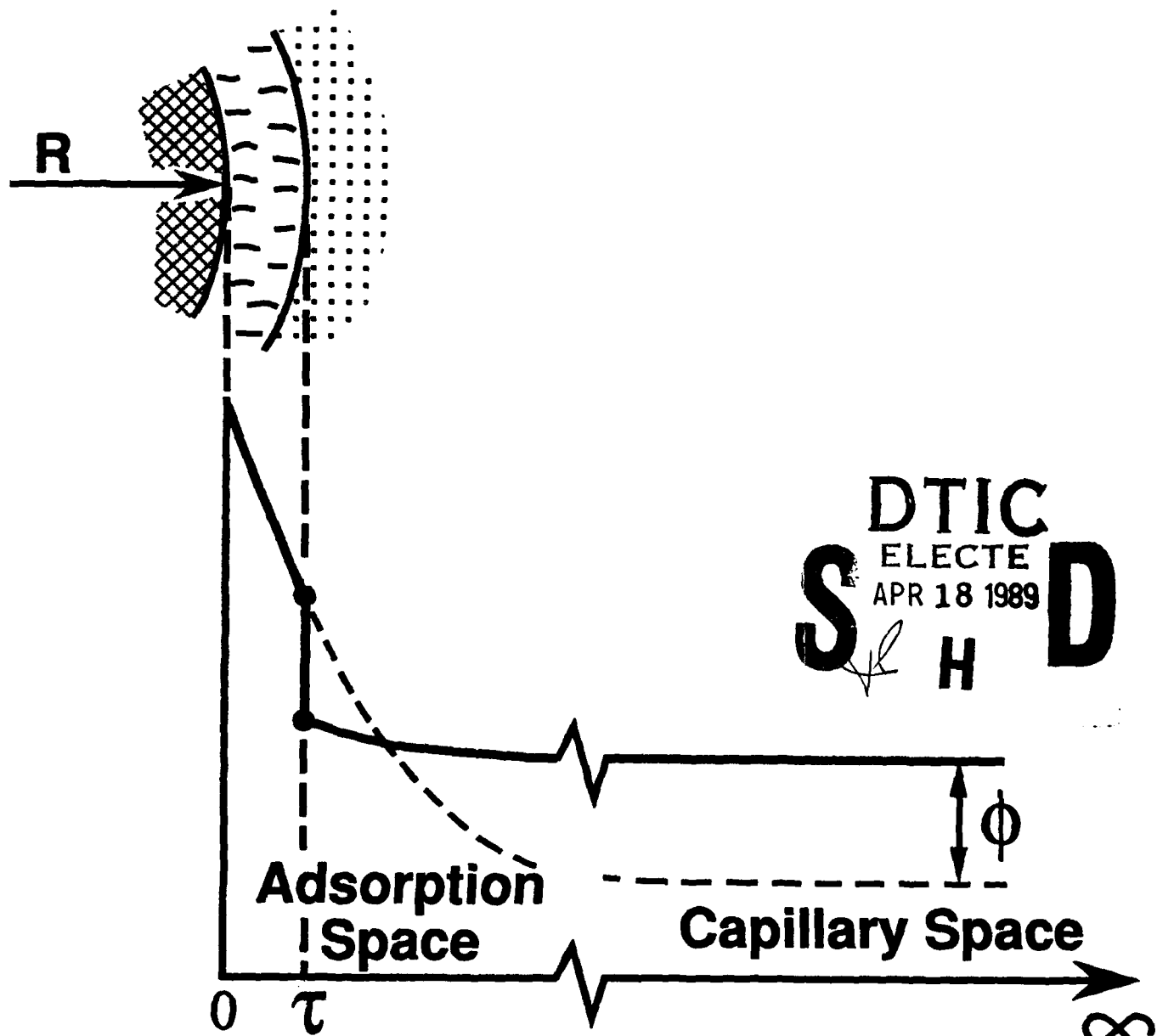
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*On the use of the ϕ -variable to describe the
state of water in porous media*



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Cover: Influence that an interface (water-ice or water-air) has upon a force field emanating from a grain that attracts liquid water more strongly than either ice or air.

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On the use of the ϕ -variable to describe the state of water in porous media

Patrick B. Black

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PREFACE

This report was prepared by Dr. Patrick B. Black, Research Physical Scientist, Geochemical Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory. Funding for this research was provided by the National Science Foundation, Grant CEE-8017422, while the author was a student of R.D. Miller.

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On the Use of the ϕ -Variable to Describe the State of Water in Porous Media

PATRICK B. BLACK

INTRODUCTION

It is well known that soil water is subjected to a myriad of forces all causing different physical effects. While it might be best to take into account each separate phenomena, such a task becomes overwhelmingly cumbersome and complicated to implement. This report presents a framework to describe the bulk properties of soil water that is motivated by perceived processes taking place at the pore level. It is for two-phase soil-water systems, that is, either air-water or ice-water.

Most research on soil water has justifiably concentrated on ice-free soil. The earliest work on frozen soil meriting mention was done by Bouyoucos (1920) of Michigan State University. He discovered that water in soil does not all freeze at one temperature. Over a decade later, Schofield (1935), a soil physical chemist at Rothamstead Agricultural Experiment Station, proposed a method of determining the Gibb's free energy of liquid water in moist soils by measuring the freezing point depression. While soil scientists Edlefsen and Andersen of the University of California at Davis were developing an exhaustive analysis of the thermodynamics of soil moisture, other soil scientists were busy with laboratory measurements of freezing point depression. The unresolved ambiguities in Edlefsen and Andersen's (1943) interpretation of freezing point depression measurements, along with similar ambiguities in laboratory measurements as well, forced soil scientists to abandon studies of soil freezing.

In part, the model proposed by Edlefsen and Andersen was unsuccessful because of their unwieldy choice of framework. A more simple, direct approach is presented in this paper. What follows is a paraphrase, or direct quote, of unpublished lectures of, and personal discussions with, R.D. Miller, Emeritus Professor of Soil Physics at Cornell University. Elements have appeared in some of his publications over the years, but have not been assembled in a single paper.

DISCUSSION

If soil grains are not too small to be considered colloidal, then, if only water fills the pore space, that space can be divided between "adsorption space" and "capillary space." The basis of this distinction is the compelling reasons to believe that liquid water very close to the

grain surface experiences an adsorption force. This force may be very intense at distances of a few molecular diameters, tapering off to imperceptible levels at distances of a few tens of molecular diameters, taken to be "infinite" distance at the scale of adsorption forces. Water outside the adsorption space is then dominated by surface tension forces in the capillary space. The purpose of the following discussion is to show that under these circumstances, the variables ϕ_{aw} and ϕ_{iw} are useful to define the degree to which air or ice, respectively, would replace water in both adsorption and capillary spaces.

For discussing the state of water in soil-water systems, it is convenient to introduce the ϕ -variable, defined as the pressure difference between the water in two phases as measured in capillary space. Thus the matric pressure for ice-free soil becomes

$$\phi_{aw} = p_a(\infty) - p_w(\infty) \quad (1a)$$

where the subscripts a and w refer to soil air and soil water pressures, respectively, as they would be measured in the capillary space. Likewise, the state of water in air-free frozen soil is expressed as

$$\phi_{iw} = p_i(\infty) - p_w(\infty) \quad (1b)$$

where $p_i(\infty)$ is the ice pressure as it would be measured in the capillary space.

Imagine a rigid sheet of closely packed spheres of radius R . This sheet divides a cylinder into two chambers fitted with pistons as in Figure 1. The diagram has been drawn in such a manner to emphasize pores between grains rather than their points of contact. Two lines have been included for reference. Line RR' passes through the center of a grain and line PP' transverses through the pore. Following RR' from the grain surface, one can see that it passes through adsorption space out into capillary space. PP' , though, always remains in capillary space.

Consider the cylinder to be filled with water held at pressure $p_w(\infty)$ by the two pistons. If, at a distance r from the grain surface, water experiences a force of magnitude $f_w(r)$ per unit volume, acting in the direction of decreasing r , then a hydrostatic pressure field will be induced

$$dp_w/dr = -f_w(r). \quad (2)$$

Upon integrating, one finds the water pressure at a distance r

$$p_w(r) = p_w(\infty) - \int_{\infty}^r f_w(\zeta) d\zeta. \quad (3)$$

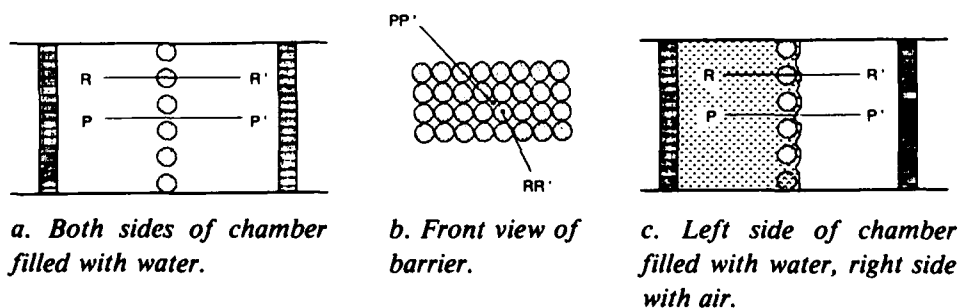


Figure 1. Phase barrier in a chamber fitted top and bottom with pistons.

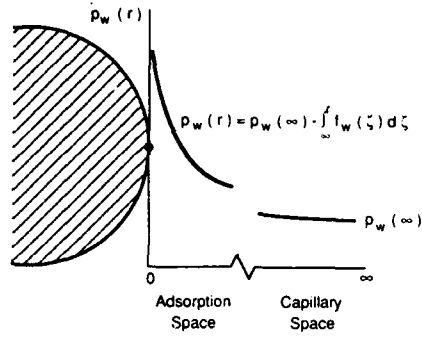


Figure 2. Adsorption force field around a grain totally surrounded by water.

By this sign convention for $f_w(r)$, $p_w(r) > p_w(\infty)$. Figure 2 diagrams the change in water pressure from the grain surface along the line RR' .

Now replace water beyond a distance τ_{aw} by air in the right-hand chamber, leaving the left-hand chamber filled with water held at the original pressure $p_w(\infty)$ as in Figure 1c. To do this without disturbing the remaining water, the air pressure $p_a(\tau_{aw})$ at the film/air interface should be less than the water pressure $p_w(\tau_{aw})$ at that interface by an amount given by Laplace's surface tension equation

$$p_a(\tau_{aw}) = p_w(\tau_{aw}) - \frac{2\sigma_{aw}}{R + \tau_{aw}} \quad (4)$$

in which σ_{aw} is the specific surface free energy of the air/water interface.

Now if air experiences an adsorption force $f_a(r)$ at all distances, then by analogy to eq 3

$$p_a(\tau_{aw}) = p_a(\infty) - \int_{\infty}^{\tau} f_a(\zeta) d\zeta. \quad (5)$$

Substituting eq 5 into eq 4, and subtracting the result from eq 3 and comparing the outcome with eq 1a, gives

$$\int_{\infty}^{\tau} [f_a(\zeta) - f_w(\zeta)] d\zeta - \frac{2\sigma_{aw}}{R + \tau_{aw}} = p_a(\infty) - p_w(\infty) = \phi_{aw} \quad (6)$$

which is to say that film thickness inside the adsorption space is a direct function of ϕ_{aw} as measured in the capillary space.

Implicit in the above is that air did not displace water from the narrowest part of the pore traversed by PP' in Figure 1c. If the magnitude of ϕ_{aw} is not too large, the interface in capillary space also satisfies Laplace's equation

$$p_a - p_w = 2\sigma_{aw}/\bar{r}_{aw} = \phi_{aw} \quad (7)$$

where $1/\bar{r}_{aw}$ is mean (Gaussian) radius of curvature of the interface, previously taken to be positive if the center of curvature was on the air side of the interface. That is, the combined volumes of adsorbed water and capillary water to the right of the plane that contains the centers of the barrier in Figure 1c are a function of ϕ_{aw} only when $\phi_{aw} > 0$.

If $f_i(r)$ is an adsorption force experienced by ice, also on a volumetric basis, and if water had been replaced by ice beyond the distance τ_{iw} , exactly the same arguments hold, and by analogy to eq 6

$$\int_{\infty}^{\tau} [f_i(\zeta) - f_w(\zeta)] d\zeta - \frac{2\sigma_{iw}}{R + \tau_{iw}} = p_i(\infty) - p_w(\infty) = \phi_{iw}. \quad (8)$$

Thus, unfrozen water to the right of the plane of symmetry for the sheet of grains in Figure 1c is a function of ϕ_{iw} only when $\phi_{iw} > 0$. This is true if the specific surface energy of the ice/water interface, σ_{iw} , is independent of crystallographic orientation of the interface.

Next, the influence of temperature in determining the stipulated equilibrium at the ice/water interface is determined.

Suppose that both pistons exert the same pressure, p_0 , on the contents of the chamber. Further, suppose that the water is pure and the right half of the chamber contains a modest quantity of ice in capillary space (see Fig. 1c). Under such conditions, if u_0 is standard atmospheric pressure (101.3 kPa), then the equilibrium temperature T_0 is 273.15 K or, by definition, 0°C. Reversible extraction of heat, with pressures on each chamber half held constant, will produce no change in temperature until ice begins to form at the fringe of adsorption space, with a correspondingly slight penetration of the capillary space adjoining the pore necks.

Mechanical equilibrium must then be maintained by either increasing the pressure on the ice-containing half or decreasing pressure on the water-containing half, or adjusting both sides simultaneously. In general, these perturbations in confining pressure must be accompanied by a perturbation in equilibrium temperature.

If water and ice in capillary space are pure and incompressible phases with molar volumes V_w and V_i , molar entropies S_w and S_i , and molar Gibbs free energies G_w and G_i , perturbation from the initial equilibrium state to a new one involves equal incremental changes of G for both phases

$$dG_w = dG_i \quad (9)$$

or

$$\begin{aligned} [\partial G_w / \partial p(\infty)_w] dp(\infty)_w + (\partial G_w / \partial T) dT \\ = [\partial G_i / \partial p(\infty)_i] dp(\infty)_i + (\partial G_i / \partial T) dT. \end{aligned} \quad (10)$$

Using the identities

$$\begin{aligned} [\partial G_w / \partial p(\infty)_w] &= -V_w, & [\partial G_i / \partial p(\infty)_i] &= -V_i \\ (\partial G_w / \partial T) &= S_w, & (\partial G_i / \partial T) &= S_i \end{aligned}$$

and the definition for molar heat of fusion

$$\Delta H_{wi} = [S_w - S_i] T_0$$

and eq 10 becomes

$$V_w dp(\infty)_w - V_i dp(\infty)_i = (S_w - S_i) dT = \frac{\Delta H_{wi}}{T_0} dT. \quad (11)$$

Next, define pressures for water and ice in the capillary space with reference to atmospheric pressure

$$u_w = p(\infty)_w - p_0, \quad u_i = p(\infty)_i - p_0$$

and temperatures in terms of the Celsius scale

$$\theta = (T - T_0).$$

Upon substitution of these definitions into eq 11 and integration of the result, the equation describing ice/water equilibrium for small perturbations becomes

$$u_w - \frac{u_i}{\gamma_i} = \frac{h}{T_0} \theta \quad (12)$$

where the specific gravity of ice, γ_i , and the volumetric latent heat of fusion, h , are defined

$$\gamma_i = V_i/V_w, \quad h = (\Delta H_{wi}/V_w).$$

Equation 12 can be expressed in terms of the ϕ -variable by the use of eq 1b to obtain

$$\phi_{iw} = (\gamma_i - 1)u_w - \gamma_i(h/T_0)\theta. \quad (13)$$

The state of water in an ice-water soil system, ϕ_{iw} , is now a function of u_w and θ only, and the piston on the ice-containing right half of the chamber in Figure 1c can be replaced by a rigid wall. While eq 13 was developed with respect to water and ice in capillary space at equilibrium, it equally applies to adsorption space at equilibrium.

At equilibrium, the free energies of both phases are uniform throughout the system, inside or outside of force fields. If conditions were considered at an interface in adsorption space instead of capillary space, perturbations of pressure created by the pistons must be equal in magnitude but opposite in sign to perturbations in potential energy (per unit volume) at the interface. This would be manifested by a change in interface position within the adsorption space in the sense of eq 3. Thus at equilibrium, eq 13, which involves only temperature and pressures on the phases in capillary space, also defines, perfectly well, conditions for thermo-mechanical equilibrium throughout the system.

So far no attempt has been made to quantify the properties of the adsorption force field emanating from the grain surface. There has been an implicit assumption, though, made about the magnitudes of $f_w(r)$, $f_a(r)$ and $f_i(r)$: the magnitude of $f_w(r)$ is larger than either of the other two. This results in water being more strongly attracted to the grain than are either ice or air. In other words, ice or air will always be held at some distance from the grain surface with a film of water interspersed. It is not an unreasonable assumption—Beskow (1935) proposed it for the case of ice and water—and it might further be true that $f_i(r)$ and $f_a(r)$ are in fact negligibly small when compared to $f_w(r)$.

The most appealing model for a long range force $f_w(r)$ near a soil grain is based upon the Gouy-Chapman theory of a diffused electrical double layer at the grain/water interface. There is evidence that such double layers exist on the surfaces of soil grains immersed in water. And it emerges as a virtual body force that would be perceived only in a space in which significant concentrations of ions can exist. Such a double layer would act on liquid water only and $f_i(r)$ and $f_a(r)$ would be zero (i.e., ice and air phases would not contain significant quantities of solutes).

If $f_i(r)$ and $f_a(r)$ were indeed zero, both phases would actually be devoid of anisotropic stresses at equilibrium. This point has been a sticky one for many who instinctively feel that if a body of ice (or an ice lens) were pressed against an array of grains and their adsorbed films, with ice necessarily bridging gaps between grains, stresses in the ice must be highly anisotropic. More careful thought reveals that this vision is not correct, owing to the compensating effect of fluctuating interfacial curvature: concave opposite grains and convex opposite pores. Thus, ice pressure, like air pressure, would be uniform at such an interface.

Some (Vignes and Dijkema 1974, Vignes-Alder 1977, Takagi 1980) insist that film water must be a very special form of H₂O. Such special water is simultaneously capable of support-

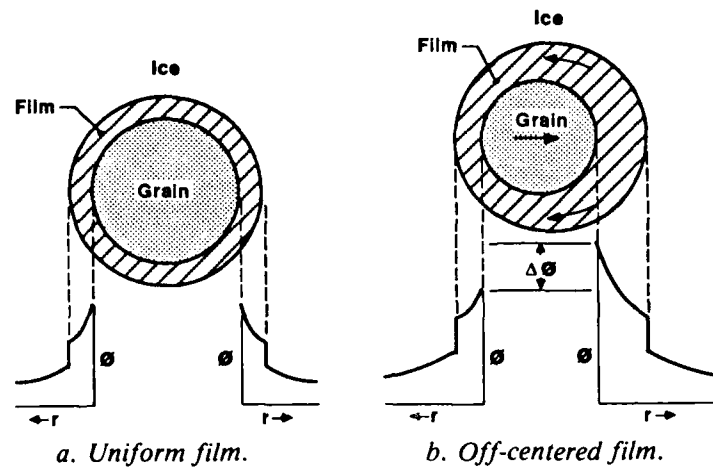


Figure 3. Grain-film system encased in ice.

ting large normal stresses as if the film were loaded solid, while at the same time responding as a fluid by transmitting water laterally, even adsorbing water from a low pressure reservoir while forming an ice lens at high pressure. This anomaly is readily understood as an artifact, attributable to the action of the adsorption force.

Figure 3a represents a grain of soil surrounded by a film of exaggerated but constant thickness embedded in a block of isothermal ice. Under such conditions, the water potential is constant around the grain at the ice/water interface and nothing exciting happens. If the grain is forced off-center, the resulting variation in film thickness will cause a corresponding variation in film potential at the ice/water interface analogous to eq 5. This causes a mechanical imbalance between the thick and thin extremes in the film, as in Figure 3b. Water now flows from the high-potential, thick side to the lower-potential, thin side, causing the grain to be recentered. This phenomenon is analogous to what would happen if the center of mass of the earth was somehow forced off-center, with the oceans being the film.

Now, if the ice is subjected to a temperature gradient, it too will cause a similar variation in film thickness according to eq 13 and 8. Film water will again move, this time from the thick, warm side to the thin, cooler side, attempting to reestablish equilibrium. Unlike the previous example, though, the ensuing grain movement does not result in mechanical equilibrium. Instead, the grain is simply moved up the temperature gradient, all the time surrounded by a nonuniform film thickness. This movement was observed by Romkens and Miller (1973).

The perceived anomaly of the adsorbed film being able to imbibe low pressure capillary water and still support ice at high pressure is seen to be a consequence of the adsorption force and not ascribable to special properties of water. If pressure is maintained constant on the ice in Figure 4, then as heat is reversibly removed, water is taken out of adsorption and capillary space and frozen. The thinner film creates a larger potential difference between location A beneath high pressure ice and location B in low pressure capillary water. With the ice pressure maintained constant, mechanical equilibrium is achieved by the flow of water from B to A just as in Figure 3b. This time the grains remain stationary and a thicker lens of ice is created.

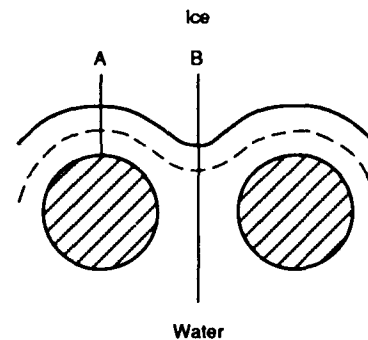


Figure 4. Equilibrium configuration of ice/water interface in an isothermal system (solid line is equilibrium configuration; dashed line is unstable configuration just after reversible heat extraction.)

SUMMARY

The effect that soil has on determining physical behavior of water was explained in terms of a general force field emanating from the grain surface subject to two constraints. First, this force field attracts water more strongly than either ice or air. Second, this force field quickly dissipates in strength with distance from the grain surface, approaching the properties of bulk water. The first constraint causes a film of water to always be present on the grain surface, separating air or ice from the grain. The second condition presents a useful scheme to classify soil water as being controlled either by the force field (adsorption space) or by the bulk properties of water in the pore (capillary space).

The ϕ -variable was introduced as the pressure difference between two phases of water in capillary space. It was shown that this variable controls microscopic interfaces between the two pore constituents. Through a thermodynamic argument, it was also shown that the ϕ -variable, expressed as a function of temperature and pressures on the phases in capillary space, defines perfectly well conditions for thermo-mechanical equilibrium throughout the system.

Lastly, it was shown that the nonuniform thickness of film surrounding grains was responsible for the apparent anomaly of water beneath high pressure ice imbibing low pressure capillary water.

While this thermodynamically based explanation of the behavior of water in soil is neither the first nor the most rigorous (Edelfsen and Andersen 1943, Bolt 1976, Sposito 1984), it is intrinsically simple and explains (perhaps qualitatively at best) the known macroscopic behavior of soil-water systems. As Feynman explains, thermodynamics is a rather difficult and complex subject to apply, in part because there are so many different ways to describe the same thing (Feynman et al. 1963).

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