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A Possible Force Mechanism Associated With the Freezing of Water In Porous Materials

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A Possible Force Mechanism Associated with the Freezing of Water in Porous Materials

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The thermodynamic equilibrium conditions for a water-ice interface in a pore of a porous medium are derived. It is found that, taking the geometry and physical dimensions of the pore into consideration, a positive pressure must develop between the ice and the solid in order for equilibrium to be maintained when the temperature at the freezing plane is depressed. A simple model utilizing this mechanism exhibits the same properties as a frost-heaving soil. The influence of air in the pores is briefly discussed.

- ●WHEN WATER is present in porous materials and is allowed to freeze, a force may be developed which is not directly related to the expansion that occurs when water changes to ice. Although many observations have been made on this phenomenon, particularly in the field of soil mechanics, a satisfactory explanation of the origin of this force has not appeared. Experiments to date indicate how the magnitude of this force depends on certain physical characteristics of the system. The following are some of the facts observed during experiments that a theory on the origin of this force must explain:
- 1. During the freezing process, the freezing plane may remain stationary while the ice phase continues to grow. When this occurs, the frozen portion is displaced relative to the unfrozen and a layer of ice, often called an ice lens is formed. The displacement may be microscopic or it may amount to several inches. This displacement occurs upwards in soil and is called frost heaving. The occurrence of heaving implies that: (a) Water is drawn from the unfrozen portion to the freezing plane by a force occurring at the freezing plane and is thus under tension; (b) The force developed at the freezing plane is capable of exerting the pressure required to displace the frozen portion relative to the unfrozen; and (c) The pressure thus developed is transmitted from the ice phase to the unfrozen solid through a mobile layer which has at least quasi-liquid properties since the ice phase can continue to grow.

2. The magnitude of the force that can be developed during the heaving process depends on the size of the pores in the solid. Generally, for a granular material, the smaller the grains the larger the force (1).

3. The magnitude of the force developed at the freezing plane can be observed in two ways: (a) If the porous solid is confined and an unlimited supply of water is available, the magnitude of the force at the freezing plane is indicated by the amount of pressure which must be applied to prevent heaving; and (b) If the porous solid is unconfined, the magnitude of the force at the freezing plane is indicated by the tension that must be applied to the water to prevent heaving (2).

Under normal conditions, a porous body will contain both water and air. During freezing the solid-water-ice-air system undergoes changes in such a direction as to attempt to maintain thermodynamic equilibrium at the freezing plane. This paper develops the conditions for thermodynamic equilibrium between a water-ice interface in a small space. The influence of air in the system, with the resulting more complicated interface conditions at the freezing plane, is briefly discussed.

Description of the System

Figure 1 shows a hypothetical cross-section of the freezing plane in the pore space of a granular material. It will be assumed that the freezing plane occupies the x-y plane and heat conduction is in the z-direction. Since the system is dynamic a temperature gradient exists in the z-direction but it will be assumed that the temperature

difference between points A, B, and C is small compared to the depression of the equilibrium temperature of the freezing plane from O deg C. This would allow, to a first approximation at least, the application of thermodynamic principles to the establishment of steady state equilibrium conditions between A, B, and C.

It is assumed that a water film exists between the solid particle and the ice. Such a film on the surface of a solid has both liquid and solid attributes. A significant and sometimes very large pressure applied normal to the film is required to cause it to fail and, in this respect, its behaviour is solid-like. In the plane of the film there is a high degree of mobility and, in this respect, its behaviour is liquid-like. Such a film existing between the ice and solid would enable pressures to be transmitted from the ice to the solid and still allow water molecules to move from the pore space at A to the ice at C.

The water in the unfrozen portion is continuous as described in publications dealing with soil moisture, and is capable of being placed under tension. Let this tension be p_t . If the freezing plane is curved, pressures that owe their existence to this curvature are produced in the ice immediately adjacent to the curve surface. The magnitude of this pressure is given by:

 $p_{S} = C\left(\frac{1}{r_{1}} + \frac{1}{r_{2}}\right) \tag{1}$

in which C is a constant that depends on the interfacial energy between water and ice, and r_1 and r_2 are the principal radii of curvature of the surface (3). The sign of p_S depends on the curvature; it is positive on the concave side of the surface and negative on the convex. Thus at B, $p_S = p_{Si}$ is positive, whereas at C, $p_S = p'_{Si}$ is negative. As the ice at the interface at C grows, a pressure is developed and transmitted from the ice through the film to the solid. Let the value of this pressure be p'_{Ot} . This pressure would tend to zero as B is approached.

Equilibrium Conditions1

The independent variables involved in this problem are pressure and temperature. Therefore, when discussing equilibrium, the appropriate thermodynamic function to use is the Gibb's thermodynamic potential:

g = u + pv - Ts

in which

g = thermodynamic potential in ergs per gm;

v = specific volume, in cu cm per gm;

p = pressure, in dynes per cm;

s = entropy in ergs per deg K per gm;

T = absolute temperature (deg K); and

u = internal energy in ergs per gm.

For equilibrium to exist between A, B, and C, the thermodynamic potential must be the same at these points. If a small change dg = vdp-sdT occurs, then dg_A = dg_B = dg_C when equilibrium is reestablished. In the following, changes in g are with respect to its value for T = 273.16 deg K and p = 1 atm.

First consider equilibrium conditions between A and B. If the temperature of the pore space drops by ΔT , the freezing plane will advance. As the freezing plane advances, the internal geometry of the solid requires that the surface take on a curvature as shown in Figure 1. If we assume that the water is under a tension, the change in pressure at A is equal to dp_A = pt. The change in pressure at B at equilibrium is given by p_{Si} + (pt - p_{SW}) where p_{SW} is the tension required in the water to establish

¹ The author wishes to draw attention to a very recent paper, "Resistance of Concrete to Frost at Early Ages," by T.C. Powers, presented at the RILEM Symposium on Winter Concreting, Copenhagen, February 1956, in which Mr. Powers applies the same thermodynamic principles to frost action in concrete.

naturally the same curvature in the water surface as in the ice. ²

$$p_{SW} = -p_{Si} \tag{2}$$

If the ice and water are to be in equilibrium at the freezing plane after the temperature change ΔT then

$$v_W p_t - s_W \triangle T = v_i (2 p_{Si} + p_t) - s_i \triangle T.$$

Where the subscript w refers to values for water and i to values for ice. Thus

$$\Delta T = \frac{p_t (v_W - v_i) - 2 v_i p_{Si}}{s_W - s_i}$$
 (4)

In Eq. $3 (v_W - v_i)$ and p_t are negative, $(s_W - s_i)$ is positive. Therefore, if the temperature is depressed below 273.17 deg K, a curvature must develop in the freezing plane to produce a positive p_{Si} to reestablish equilibrium. From Eq. 1 and 4, it is seen that the greater the tension

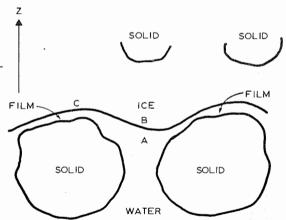


Figure 1. A hypothetical cross-section of the freezing plane in the pore space of a granular material.

 p_t , the larger is the curvature required to establish equilibrium between the ice and water for a given ΔT . The dimensions of the pores in the porous system impose a maximum value on the curvature of the interface. If the conditions are such that a surface with a larger curvature is required to establish equilibrium, the freezing plane would be able to advance to the next pore space. (In private correspondence the author has seen a discussion of this from the point of view of the kinetics of freezing prepared by Dr. B. Chalmers and his associates at Harvard University.)

The variables in Eq. 4 are potentially capable of changing in value as long as the heat flow from the freezing plane is greater than to it, i.e., ice is being formed at the freezing plane. When the condition is reached in which the heat flowing to the freezing plane exactly equals the heat flowing away, a value of ΔT , p_t and p_{si} will be associated with each pore, consistent with Eq. 4. The value of p_t will be the same for each pore.

If we let the pressure at B, which corresponds to the maximum curvature compatible

Consider the ice interface BC and the corresponding water interface being established in air. The pressure at B in the ice would therefore be $p_{si} = C_{ia}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$ and the pressure in the water would be $p_{sw} = -C_{wa}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$ where C_{ia} depends on the surface energy for an ice-air interface and C_{wa} on the surface energy for a waterair interface. Now, consider the ice surface replacing the air over the water surface as in Figure 1. C_{ia} and C_{wa} now become C_{wi} which depends on the surface energy between water and ice. If the surface film between the water and ice is to have the same curvature under the influence of pressure in the water only, then $p_{sw} = -C_{wi}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) = -p_{si}$. Now the pressure at A in the water must be equal to the pressure of the rest of the water in the porous solid (assuming flow is negligible) and can be controlled independent of the surface curvature whereas p_{si} existing in the ice is completely determined by the curvature. If the pressure in the water at A is changed by $p = \{p_t - p_{sw}\}$ and the curvature of the surface remains the same, an equal change in pressure must occur at B.

² The reasoning behind the expression for the change in pressure at B is as follows:

with the pore space, be p_{sim} and the tension in the water be p_t , then the freezing point depression required to freeze all the water in the pore is given by:

$$\Delta T_{\rm m} = \frac{p_{\rm t} (v_{\rm w} - v_{\rm i}) - 2 p_{\rm sim} v_{\rm i}}{s_{\rm w} - s_{\rm i}}$$
(5)

 s_w - s_i Thus the greater the tension p_t , the smaller is the freezing point depression ΔT_m required to freeze all the water in the pore.

In establishing the conditions for equilibrium between points A and C, it will be assumed that as long as the water in the pore space is not completely frozen, a water film exists between the ice and the solid. Figure 1 shows that a positive curvature developed in the ice at B results in a negative curvature at C. Let the pressure at C due to this curvature be p_{Si} as calculated from Eq. 1. In this case p_{Si} is essentially constant since the solid determines the values of r_1 and r_2 . At C the pressure p_{Ot} also exists and is transmitted from the ice through the film to the solid. Thus the change in pressure at C is $dp_C = p_{Si} + p_{Ot}$ and in order to reestablish equilibrium between A, C, and B, $dp_A = dp_B = dp_C$, $dp_B = dp_C$, $dp_B = dp_B = dp_C$. (6) Therefore,

$$p'_{ot} = 2 p_{si} + p_{t} - p'_{si}$$
 (7)

pt and p' $_{Si}$ are negative and p $_{Si}$ is positive. From Eq. 7 it is seen that depending on the values of p $_{Si}$, pt and p' $_{Si}$, a positive pressure p' $_{Ot}$ is required to establish equilibrium for a temperature depression ΔT . What Eq. 7 states is the obvious fact that at equilibrium the pressure in the ice at C must equal the pressure at B when ΔT at A equals ΔT at B.

To have a clear understanding of the conditions imposed by Eq.7, consider the case where the tension in the water is zero (p_t = 0). If the temperature in the pore is depressed by ΔT , the thermodynamic potential in the water is increased by dg_A = $-s_w$ ΔT and in the ice by dg_C = dg_B = $-s_i$ ΔT . But dg_A > dg_B = dg_C , therefore equilibrium will be upset and the ice phase will grow. To reestablish equilibrium, the pressure in the ice must be increased. This is accomplished at B by the positive curvature that develops in the freezing plane but at C this curvature is zero or negative, i.e., dg_C < dg_B . Water molecules will continue to migrate to C, therefore, until the build-up of ice at this point results in the development of the required positive pressure p'_O , the value of p'_O for p_t = 0. At equilibrium, the value of p'_O can be obtained from the condition dg_A = dg_B = dg_C . $-s_w$ Δ T = v_i (2 p_{si}) - s_i Δ T = v_i (p'_{si} + p'_O) - s_i Δ T, therefore

$$p'_{0} = 2 p_{si} - p'_{si}$$
 (8)

When p_t does not equal zero, p'_{ot} as given by Eq. 7 is not due alone to the pressure developed by the formation of the ice lens at C and the subsequent heaving. If the tension in the water is not satisfied by the curvature developed at B, i.e., if the term $p_t - p_{sw}$ (see footnote 2) does not equal zero, then this unbalance will contribute to p'_{ot} . If $p_t - p_{sw}$ is negative there will be a net downward pull which will result in a positive pressure contribution to p'_{ot} at C. If $p'_{ot} = p'_{o} + p'_{t}$, where p'_{t} is the contribution due to the tension in the water and p'_{o} is the actual heaving pressure, then

$$p'_{0} + p'_{t} = 2 p_{si} - p'_{si} + p_{t}$$
(9)

Eqs. 4 and 9 give the conditions which must be satisfied at A, B, and C if equilibrium is to be established when the temperature of the pore is depressed by ΔT and the

³ In establishing Eq. 6 and 7, a possible contribution to p'_{Ot} due to the tension in the film between the ice and solid at C, not balancing the tension in the water surface at B has been neglected. This component would be very difficult to calculate since the film, which must be in equilibrium with all surrounding pores, does not have the same behaviour as a liquid with regard to applied pressure. It is possible that the film over the solid can alter its thickness and thus its energy and in this way always maintain equilibrium with the forces at the periphery. This would imply that p'_{Si} would be altered accordingly.

water is under a tension
$$p_t$$
. If $p'_0 = 0$ (no overburden pressure) then
$$p'_t = 2 p_{si} - p'_{si} + p_t$$
(10)

Eqs. 4 and 10 give the conditions that must be satisfied to establish equilibrium by applying tension to the water only when the pore temperature is depressed by ΔT . A little thought soon indicates the difficulty of determining explicitly the value of p'_t , for it depends on the area over which the net downward pull of the water on the ice acts relative to the area over which p'_t acts.

Limitations Imposed on pt

The increase of pt in most problems encountered in practice is due to the drying action that results when water is drawn to the freezing plane. The distribution in pore and grain size would ensure a variation in the degree of advancement of the freezing plane through the various pores even if the temperature depression were the same in each. Initially the temperature depression may be very large so that the freezing plane could advance readily through all pores if conditions required it. As the freezing plane advances or the heat flow away from the freezing plane decreases, the temperature gradient at the freezing plane would decrease and a time would be reached when the freezing plane would be unable to advance through the smaller pores in pace with the larger. This would mean that the freezing plane would establish different stages of advancement that could exist for appreciable time (Figure 2). Such projections as A (Figure 2), would tend to act as anchors because if heaving

occurs, solid particles B and C must also lift. Not only will p'₊ be greatly increased but also the area containing A, B, and C will be unable to contribute its maximum force-developing potential to the heaving pressure.

As p_t becomes larger, the pores, depending on their size, begin to empty of water. This probably has a great influence on the rate at which equilibrium can be established. Considering these factors, it is expected that the rate of heaving and the maximum developable heavpressure will drop off rapidly when p_t reaches a value large enough to initiate the emptying of the pores.

Effect of Air

In the natural porous solid, air probably occupies a significant portion of a unit volume. Furthermore, as the water freezes, the air would be forced ahead of the freezing plane and, in time, much of the pore space at the ice-water interface would be occupied by air (Figure 3). If the air bubbles are treated on the same basis as the solid, (surface energy terms

PARTICLES

WATER

Figure 2. A hypothetical ice-water interface in a porous material.

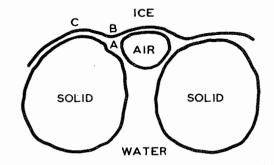


Figure 3. A hypothetical ice-air-water interface in a porous material.

being those for water-air and ice-air interfaces), the preceding discussion concerning equilibrium would still apply to points A, B, and C (Figure 3).

The volume and pressure of the air in the bubble can change with time. The maximum pressure that could be developed in the air bubble would depend on the water tension pt, the volume of air, and the minimum radius of curvature of the water-air interface compatible with the pore size. The air bubble would begin to contribute to the heaving pressure when its radius exceeded the minimum compatible with the pore for, if the air is to pass into the next pore, its pressure must increase until it over-

comes the capillary forces associated with the water in the constriction between the pores. The expansion that occurs when water changes to ice is a mechanism by which the pressure in the air bubble can be increased.

Under normal conditions it is possible that all the interfaces at the freezing plane are either air-ice or solid-film-ice. Since the interface energy associated with ice and water is probably much less than that associated with air and water (evidence to date indiciates that it is less by a factor of 10) the forces associated with a system containing air should be somewhat larger than with one not containing air.

Air bubbles and columns that occurred in an ice lens formed in a water-saturated clay-silt specinien, are shown in Figure 4 (magnified 16 times). Of particular interest is the shape of the bubbles and the fact that they occur in rows orientated in the direction of freezing, similar to those formed when water freezes in bulk. The air bubbles are not resolved to the naked eye but appear as striations in the ice. The occurrence of rows of bubbles with no solid particles in the immediate vicinity would indicate that certain sites must act as nucleating centers for air and, as the lens grows, parcels of air are removed from these collection centers.

DISCUSSION

In the preceding section, the conditions were derived which must be satisfied if ice and water are to be in equilibrium in a small space for a given temperature depression and water tension. In practice, only one of the variables involved, p_t , can be measured directly. To estimate the value of the remaining independent variables.

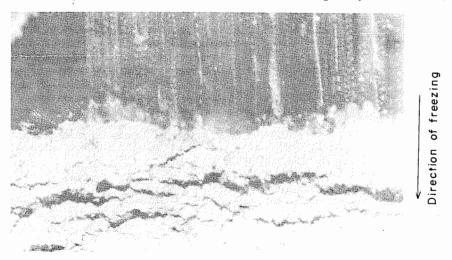


Figure 4. Air bubbles and columns photographed in an ice lens formed in a clay-silt soil (magnification 16 x).

assumptions must be made regarding the curvatures associated with the pore and solid, the energy of the ice-water interface, and the temperature depression at the freezing plane in each pore. The nature of these assumptions would ensuue that the final values arrived at would be no more than "educated guesses." The heaving pressure, which can be measured in practice, is the sum of pressures in the ice integrated over their respective pore and solid areas. Thus it would appear impractical at this stage to bridge the gap between theory and observation, i.e., to attempt to calculate possible heaving pressures from theoretical considerations only.

Perhaps the greatest use of the preceding theoretical considerations is in gaining a better understanding of the mechanism of frost heaving, the factors involved, and their possible relationships to each other in a practical problem. For instance, consider the very simple system of spheres of radius r_1 (Figure 5). Let the minimum radius compatible with the pore space formed be r_2 . The number of spheres per unit area, equal to the number of pores per unit area is proportional to 1. From Eq. 1:

 \mathbf{r}

(11)

$$p_{sim} = \frac{2C}{r_2}$$
$$p'_{si} = -\frac{2C'}{r_1}$$

If we assume a constant temperature depression ΔT in each pore consistent with water tension p_t , then the contribution at equilibrium to the heaving pressure by the ice in the pore = $p_{si} + p_t$ and by the ice above the sphere = $2 p_{si} + p_t$ and by the ice above the sphere = $2 p_{si} + p_t$ - p_{si} . Total maximum heaving pressure P_0 would be given approximately by an equation of the following form:

$$P_0 \prec \frac{1}{r_1^2} \left\{ (p_{Si} + p_t) \ \gamma \ r_2^2 + (2 \ p_{Si} + p_t - p'_{Si}) \ \beta \ r_1^2 \right\}$$
Therefore.

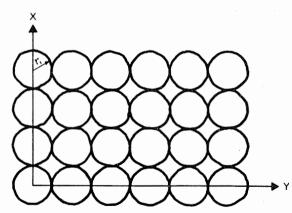


Figure 5. A hypothetical spherical particle arrangement for a porous material.

Y and B constants.

From Eq. 11 derived on the basis of a very simple model, it is seen that the maximum possible equilibrium heaving pressure increases with decreasing particle and pore size. Eq. 11 also indicates that the heaving pressure required to establish equilibrium can be reduced to zero by a sufficiently large water tension. If $p_t = 0$, the heaving can be stopped by applying the pressure P_0 . This system has the same behavior as is observed in practice. Eq. 11 also indicates that if there is a correlation between pore size and particle size, a factor obtained from the particle-size distribution curve, which is a measure of the term $\frac{\Sigma}{r} \frac{n_r}{r}$ where n_r is the number of particles per unit area of radius r, might be of value as a measure of susceptibility of a material to frost action.

 $P_{O} \prec \left(\frac{2C}{r_{2}} + p_{t}\right) \left(\gamma \frac{r_{2}^{9}}{r_{1}^{2}} + \beta\right) + \left(\frac{2C}{r_{2}} + \frac{2C'}{r_{1}}\right) - \beta$

Finally, the following points should be emphasized with regard to the presented theory. The source of the force potential, which results in frost heaving and the movement of water through the porous materials, is a temperature depression existing at the freezing plane. This temperature depression raises the thermodynamic potential of the water above that of the ice. If the temperature depression remains constant, the ice must raise its thermodynamic potential to be in equilibrium with the water. This can be done by increasing its internal pressure at the freezing plane. In the pore space, this increase in pressure can be established through the development of a positive curvature in the ice surface; this fact is implicit in the derivations of Eq. 4. If the curvature required for equilibrium is too great, the ice will propagate through the pore.

For equilibrium conditions over the remaining freezing surface, i.e., above the solid particles, it has been assumed for simplicity in this presentation that the particles be spheres. This assumption is not necessary for p'i, the internal ice pressure due to the curvature at the solid-ice interface, can have any value including zero (a flat surface). Equilibrium conditions still require that a positive pressure be built up in the ice above the solid (the pressure at B, Figure 1, must be equal to the pressure at C), and this fact is obvious when p'i is made zero in Eq.7. Therefore, any granular material has a potential for heaving, the first and most important requirement being that a temperature depression exist at the freezing plane. If the granular material is very fine, it will be more susceptible to frost heaving because the pore size requires that significant temperature depressions be established at the freezing plane before the ice will propagate through the pore. If the granular material is very coarse, the contribution to heaving from the pore space portion of the freezing plane will be very small. Also, since the ice readily propagates through the pore, by the time the termperature depression at the solid-film-ice interface is of a value to ensure an appreciable contribution to the heaving pressure, the particle will likely be "frozen

in" (Figure 2). If the extraction of heat is rapid enough or the boundary conditions are such that water can migrate to the solid-film-ice interface before the ice has propagated through the pore, then there is a possibility that heaving will occur even in a gravel.

As yet the boundary conditions which exist in a porous material, and to which any thermodynamic relation must be subject, are not adequately known. The theory indicates that the following three variables are involved:

- 1. The temperature depression at the freezing plane,
- 2. The pressure existing in the ice, and
- 3. The pressure existing in the water.

Further carefully planned experiments are required to bring out the relationships that actually exist between these three variables in any particular situation.

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Discussion

WARREN L. LAWTON, Technical Development Branch, Civil Aeronautics Administration, Indianapolis—The writer is of the opinion that the water causing frost heaving is being moved up under the ice by a positive pressure. There is no physical property that would produce a negative pressure in soil water greater than atmospheric pressure. The forces that affect the flow of water in soil are cohesion, adhesion, surface tension, and viscosity. It should be remembered that these fundamental properties can be varied by temperature, vapor pressure, interface conditions, salt content, and many other factors.

These forces are all present in soil masses in the field. As the soil mass goes through cycles of wetting and drying or freezing and thawing, each force produces its own phenomenon.

Cohesion tends to pull the water out of the voids and off of the soil particles and return the water to the water table. This force is limited to a negative value of 14.7 psi for water, a tensile strength for ice, and a positive value for vapor pressure.

Adhesion tends to hold the water to the particle of soil. Its value depends upon the molecules that compose both the surface and the inside of the soil particle. It also depends upon the distance between the water molecule and soil particle. The water affected by adhesion is drawn toward the soil particle and produces a positive pressure on the water between it and the soil particle.

Surface tension tends to move the water around until it is uniform over everything. It will produce a positive or negative force in the water depending upon the pore shape and vapor pressure.

Viscosity only affects the moving water and limits the quantity that can be moved per second.

Now let us consider the frost action. If water is removed from the surface of a soil particle, the water in its new state must have a greater cohesion than the adhesion of water to the soil particle, or it will return to the soil. This means that the cohesion of ice is greater than the adhesion of the water. Since the freezing occurs on one side of the particle before it does on the other side, the surface tension and thickness of the water film will be changed at this point. Both the surface tension and adhesion will tend to drive the water from the rest of the particle over this depleted area until equilibrium is again established. If the forces tending to move the water are greater than the weight of the ice, the ice is lifted. Then a new cycle starts and the ice crystal continues to grow.

Since there is a water interface between the water on this particle and surrounding particles, water is moved from all particles to replenish the water removed by freezing. The same surface tension and adhesion is the force that moves the water from one particle to another. The speed and quantity of water that moves depends upon the viscosity and capillary size. As long as the water is brought to the freezing plane, the ice crystal continues to grow. Should the water move too slowly or stop, the freezing plane will move deeper into the soil. In all of this, it is assumed that there is enough heat transfer to cause freezing.

Freezing temperatures can and often do exist below the point of frost heaving. If this water is moving and is not frozen under these conditions, something must reduce the freezing point of the water. There are two possible causes, dissolved salts and increased hydrostatic pressure. Since there is no evidence of salt crystals being formed, the reduced freezing point is caused by an increase in hydrostatic pressure. This pressure can only be produced by surface tension and adhesion. Cohesion produces a negative force which would elevate the freezing point of water.

LORNE W. GOLD, Closure—Mr. Lawton's discussion does bring up two points upon which I would like to comment although, generally, I would conclude that we do not differ very much in our mental picture of what is happening at the freezing plane.

Can water support a tension greater than 14.7 psi? You certainly cannot grasp water and place it in tension in a testing machine like you would a piece of steel, still, the energy of interaction between water molecules is of such an order that it requires a very large tension to pull them apart. When water exists in a fine pore system or on a surface, then the forces associated with the interaction energy of the molecules play a major role in determining the behavior of the water. In such a system, the intermolecular forces can become effective in a way they never could in larger hydraulic systems. It is possible for water to withstand considerable tensions under such conditions. On page 179 of Dorsey's book: "Properties of Ordinary Water Substance" reference is made to a number of papers describing experiments in which water was subject to tensions of over 10 atmospheres.

In referring to the depression of the freezing point of water Mr. Lawton states: "There are two possible causes; dissolved salts and increased hydrostatic pressure." I would like to point out that in deducing the change in freezing point with pressure, it is not necessary that the pressure be the same on both the liquid and the solid and this must be recognized in making calculations. For example, if water is under a positive pressure greater than atmospheric and ice forms from this water but is subject to atmospheric pressure, the freezing point of ice and water is actually greater than 32 deg F. Edlefsen and Andreson in their paper: "Thermodynamics of Soil Moisture," Hilgardia, Vol. 15, No. 2, February 1943, bring this point out quite clearly in Section 30.