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# Let's learn "thermodynamics of frozen soil"

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# Background

- Frost heaving
  - Ground surface is often lifted during soil freezes
  - Soil water moves from unfrozen region to the freezing front that ice is growing in soil
  - even on the condition that the ground surface is fixed mechanically
- Why does soil water move to the freezing front against the pressure on the freezing front?

# Background (cont.)

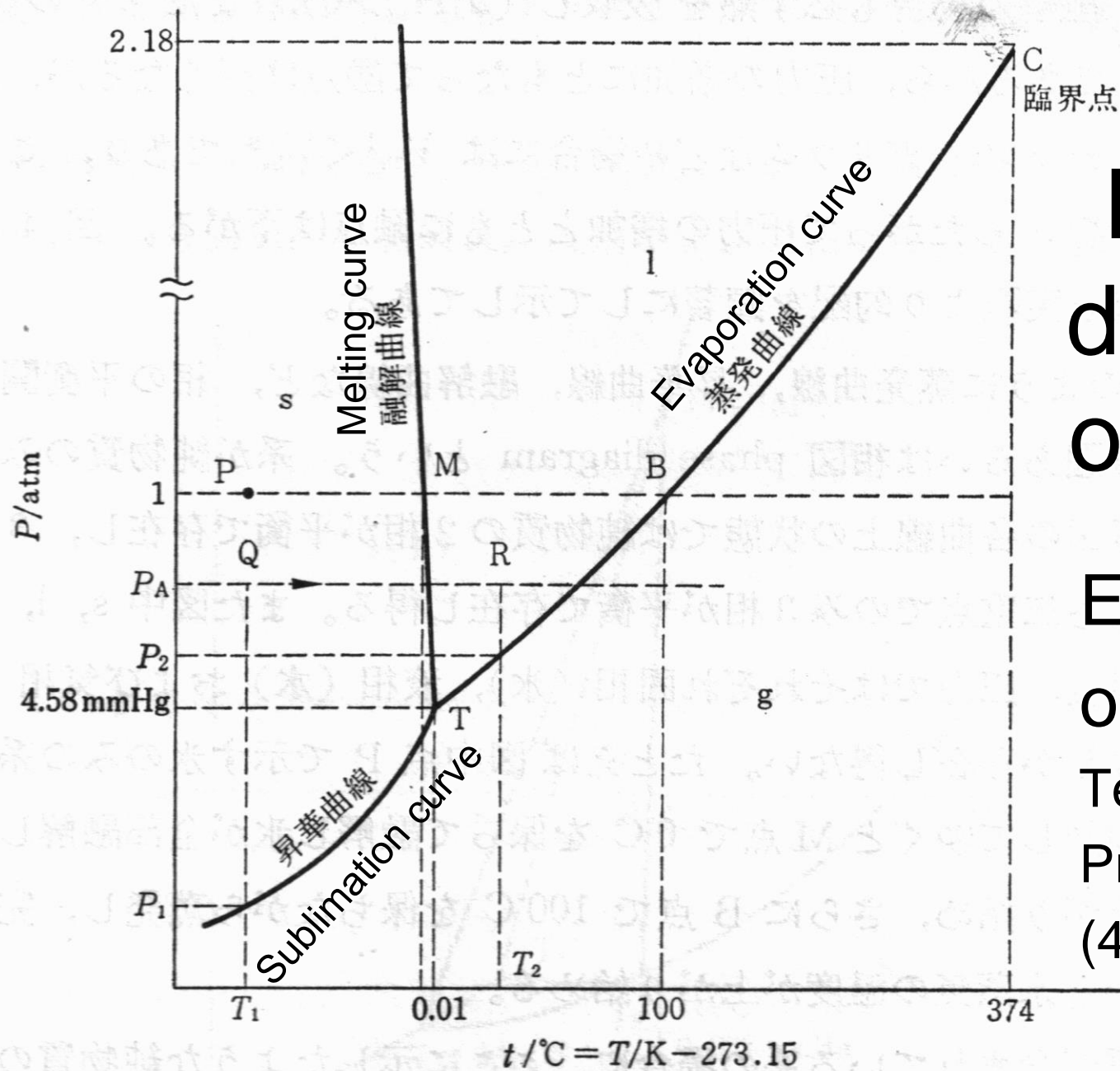
- Although many researchers have tried to explain the movement of water during frost heaving, a clear answer has not been given from the viewpoint of soil physics
- In order to understand the phenomenon, I believe thermodynamics of unfrozen soil water is important

# Background (cont.2)

- However, young generation are not interested in this classic thermodynamic theory of soil water.
- Therefore, I try to recall thermodynamics of frozen soil and chemical potential of unfrozen water based on the paper that I wrote in 1993.

# Content

1. Phase diagram of water
2. Chemical potential
3. Water potential of soil
4. Thermodynamics of soil water
5. Matric potential in frozen soil



# Phase diagram of water

## Environment on Mars

Temp =  $-63^{\circ}\text{C}$

Press =  $6\text{ hPa}$   
( $4.5\text{ mmHg}$ )

図 4.4 水の状態図の略図

# Chemical potential

The first law of TD

$$dU = dQ + dW \dots \textcircled{1}$$

Only volumetric work

$$dW = -PdV \dots \textcircled{2}$$

The second law

$$dQ = TdS \dots \textcircled{3}$$

From  $\textcircled{1}\textcircled{2}\textcircled{3}$

$$dU = TdS - PdV \dots \textcircled{4}$$

Gibbs free energy (GFE)

$$G = U + PV - TS \dots \textcircled{5}$$

$$dG = VdP - SdT \dots \textcircled{6}$$

Chemical potential

= GFE per unit mol.

$$G / n \equiv \mu \dots \textcircled{7}$$

$$d\mu = v dP - s dT \dots \textcircled{8}$$

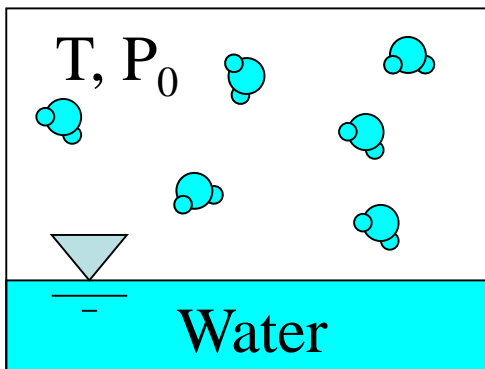
# Equilibrium of adsorbed water and vapor at constant temp

The difference between Vapor-A and Vapor-B(C) = Work required  $P_s \rightarrow P_0$

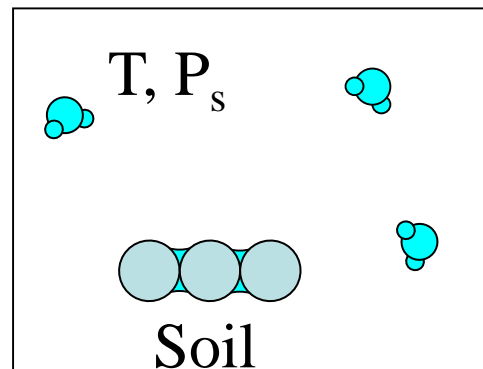
$$\mu_0 - \mu_s = \int_{P_s}^{P_0} v dP = \int_{P_s}^{P_0} \frac{RT}{P} dP = -RT \ln\left(\frac{P_s}{P_0}\right) > 0$$

$$PV = nRT \quad v = \frac{V}{n} = \frac{RT}{P}$$

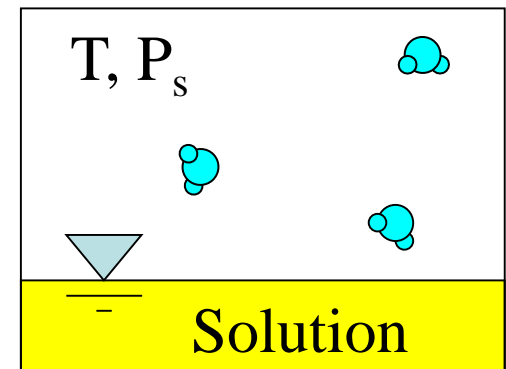
**P:** Vapor press.   **v:** specific volume  
**R:** Gas constant   **T:** Abs. Temp  
 **$P_s/P_0$ :** Relative Humidity



(A) vapor-pure water



(B) vapor-soil water



(C) vapor-solution




# Chemical potential of absorbed water

$$\mu_s(T) = \mu_0(T) + RT \ln\left(\frac{P_s}{P_0}\right)$$

Unit of energy

- Per Mol. J/mol
- Per Mass J/kg
- Per Volume J/m<sup>3</sup> = Pa
- Per weight J/gw = m


$$\Delta\mu_s(T) = \frac{RT}{M} \ln\left(\frac{P_s}{P_0}\right)$$

Using below:

$$R = 8.314 \text{ (J/mol/K)}$$

$$T = 293.15 \text{ K (20°C)}$$

$$M = 18 \times 10^{-3} \text{ (kg/mol}_g\text{)}$$

$$\Delta\mu_s(T) = 3.12 \times 10^5 \log\left(\frac{P_s}{P_0}\right)$$

# Relative humidity and Potential of absorbed water

$$\Delta\mu_s(T) = 3.12 \times 10^5 \log\left(\frac{P_s}{P_0}\right)$$

RH	Potential of absorbed water 20 °C				
$P_s/P_0$	J/kg	Pa	cmH <sub>2</sub> O	pF	
1	0	0	0	$\infty$	
0.99999	-1	1000	10.2	1	
0.99993	-10	10000	102	2	
0.99926	-100	100000	1020	3	
0.99264	-1000	1000000	10200	4	
0.92877	-10000	10000000	102000	5	
0.8	-30214	30214000	308185	5.5	

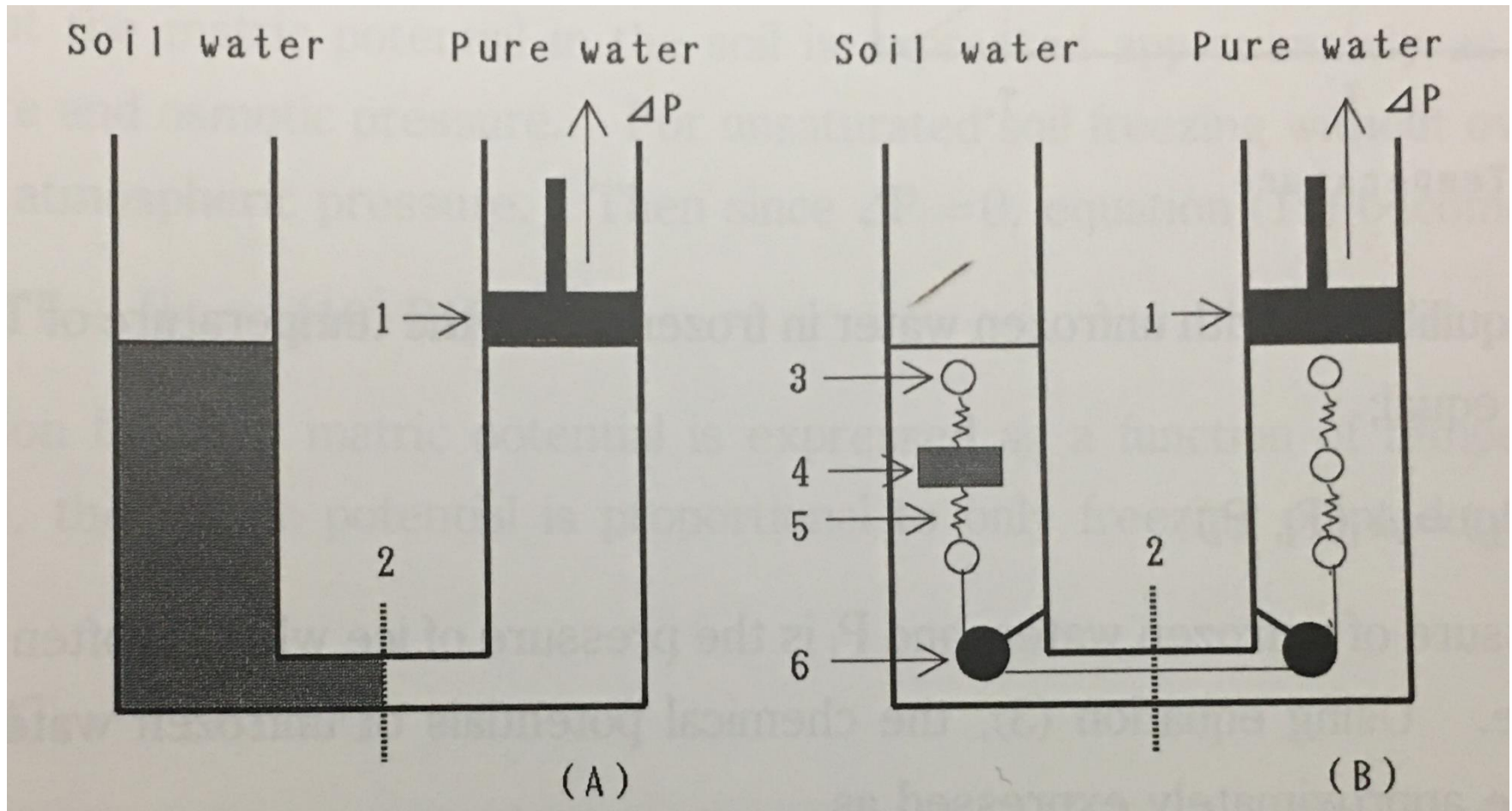
- pF is used conventionally

$$pF = \log|cmH_2O|$$

# Thermodynamics of soil water

$$d\mu = v dP - s dT$$

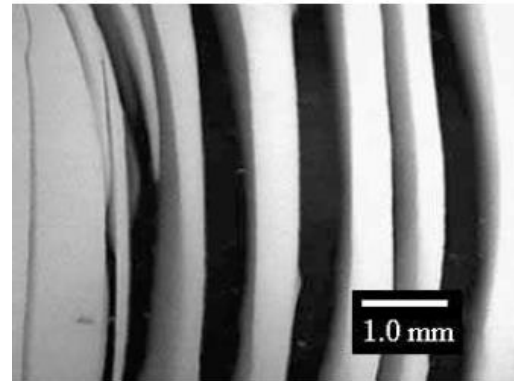
# Mechanical model of Equilibrium between soil water and pure water



# Frozen soil



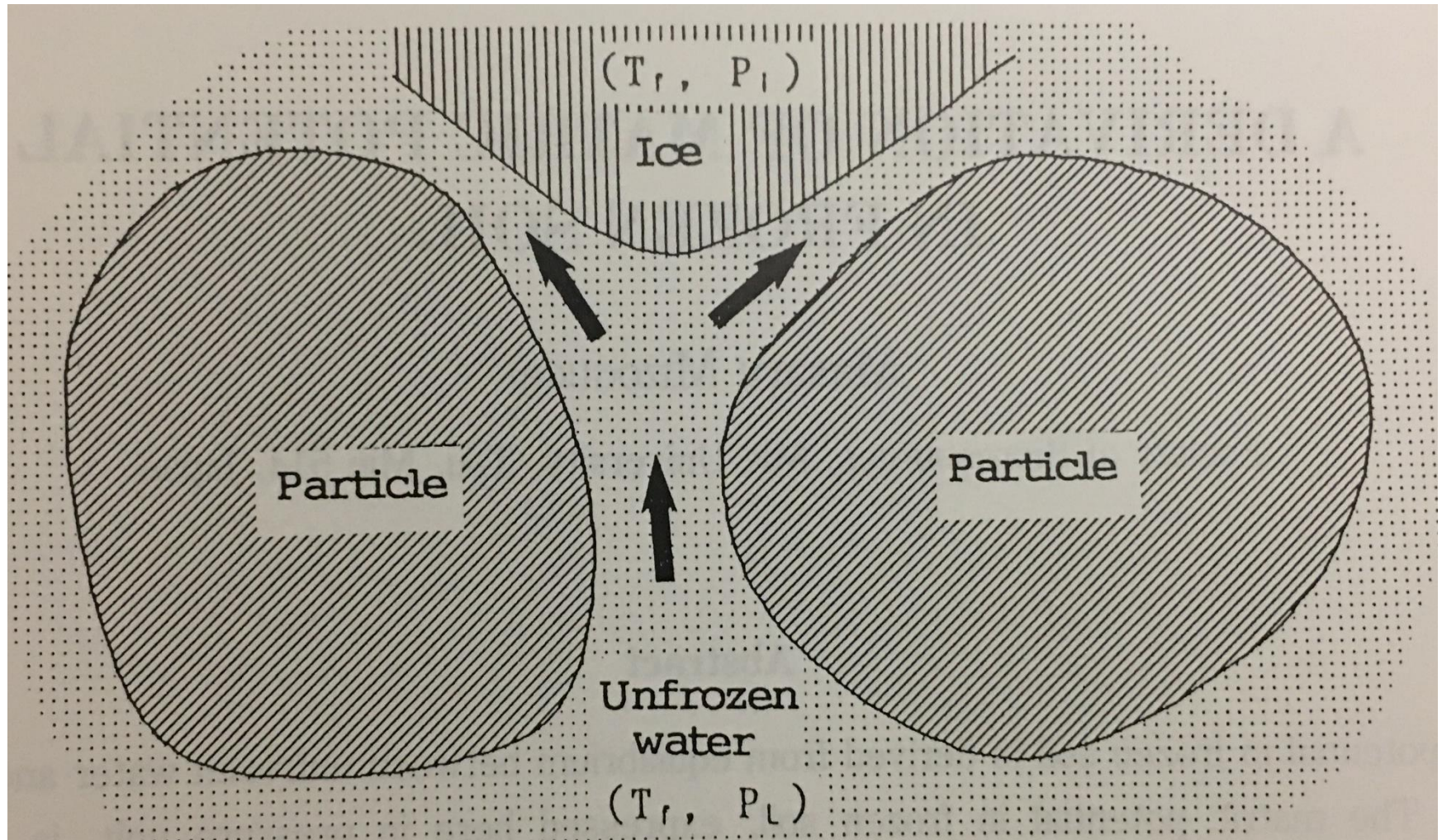
Ice needle( by Watanabe)



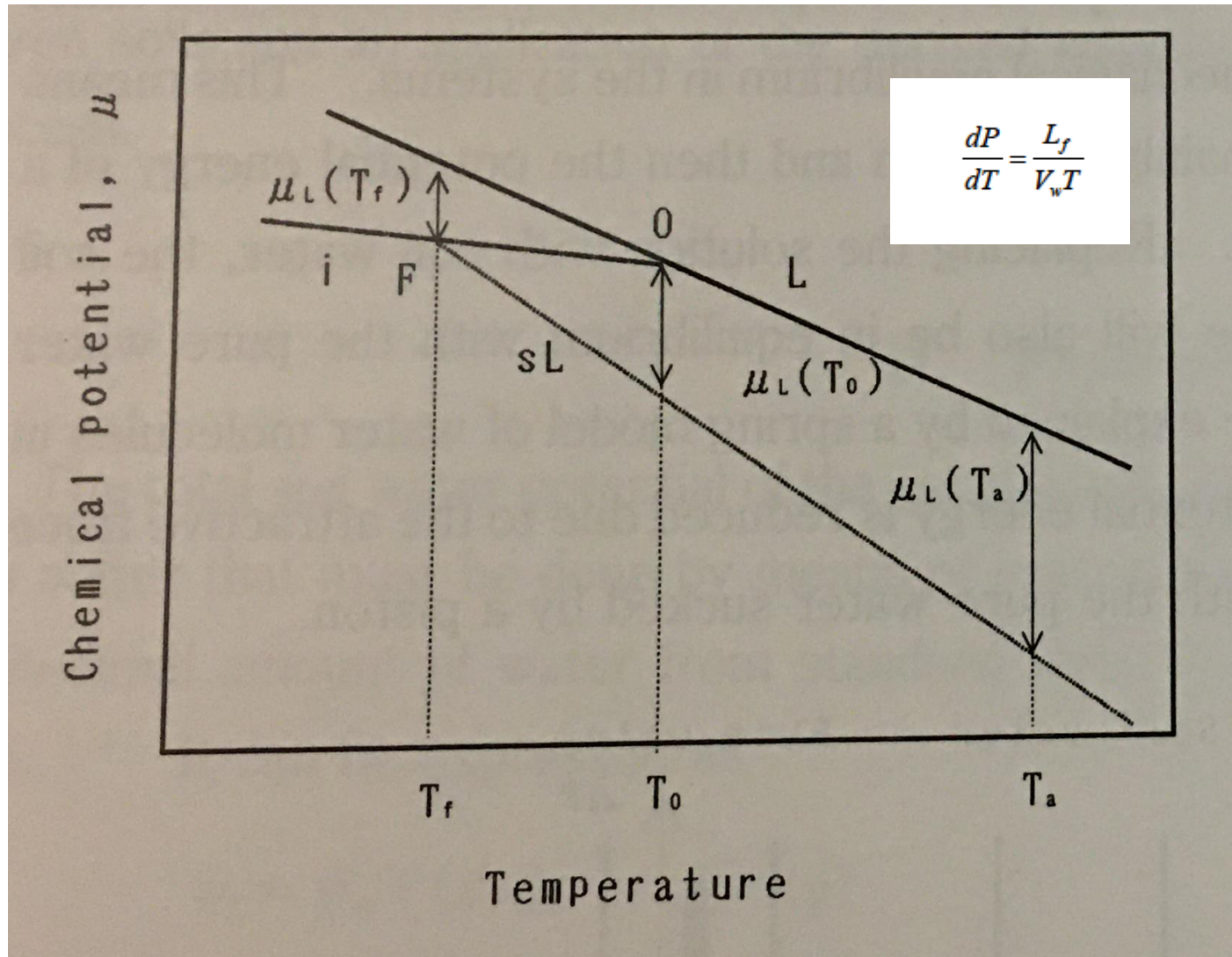
Ice lens in glass beads (by Muto)



# Equilibrium between ice and unfrozen water in frozen soil



# Chemical potentials of pure and ice



# Challenge

- Let's try to understand “thermodynamics of frozen soil” reading a paper of chemical potential of unfrozen water based on the paper that I wrote in 1993



# Conclusion

- In order to understand frozen soil, thermodynamics of unfrozen soil water is important.
- Let's learn "thermodynamics" again !