

مکانیک خاکهای غیر اشباع
(مکانیک خاکهای اشباع چند جزئی)
ترمودینامیک

Unsaturated soils
Thermodynamics

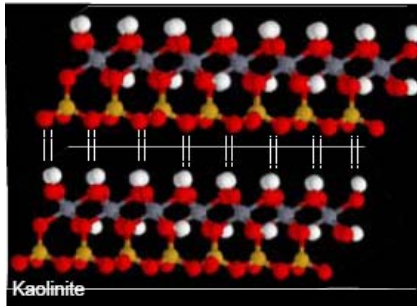
Hasan Ghasemzadeh

فهرست عناوین و فصول

- ۱- مقدمه - آشنایی - مختصری از ترمودینامیک
- ۲- رفتار فازهای مختلف در خاک غیر اشباع
- ۳- اندازه گیری در خاک غیر اشباع
- ۴- نتایج آزمایشات خاک غیر اشباع
- ۵- تنش موثر و کرنش
- ۶- تئوری های خاک غیر اشباع
- ۷- جریان در خاک غیر اشباع
- ۸- کاربرد خاک غیر اشباع در مهندسی

ترمودینامیک

علم ترمودینامیک به رابطه حرارت و دما با کار و انرژی می پردازد.



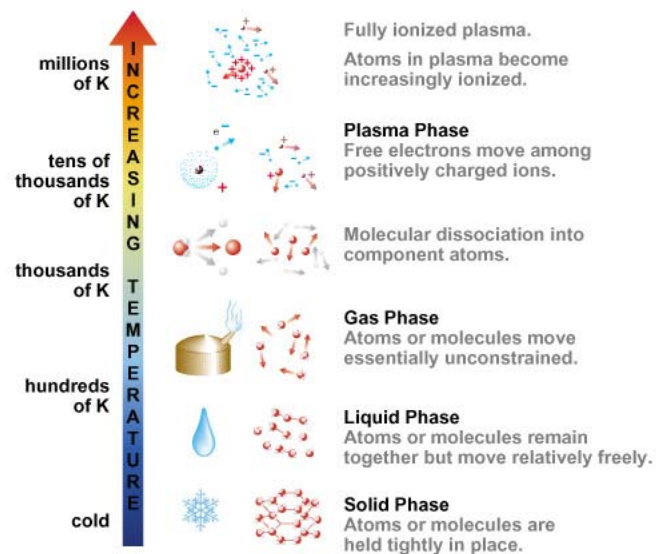
Hurricane Katrina (Cat 5)

Unsaturated Soils

3

ترمودینامیک - تعاریف

فازهای مختلف آب



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ترمودینامیک - تعاریف



Forces of Nature

Strong Force:

responsible for holding the nuclei of atoms together

Electromagnetic Force:

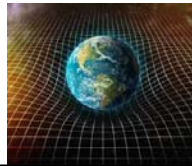
long-ranged, but much weaker than the strong force

Weak Force:

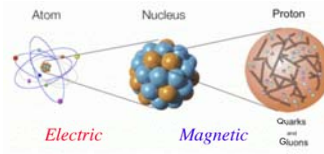
responsible for radioactive decay and neutrino interactions

Gravity Force :

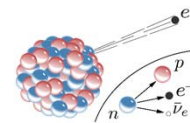
weak, but very long ranged



نیروهای طبیعت دارای شاخصه‌های می‌باشند



Electric: $F = \frac{kq_1q_2}{r^2}$
Magnetic: $\vec{F} = q\vec{v} \times \vec{B}$



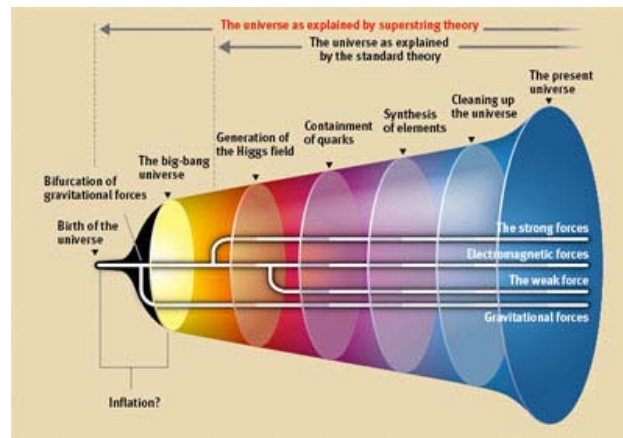
ترمودینامیک - تعاریف

Fundamental Forces

Strong		Force which holds nucleus together	Strength 1	Range (m) 10^{-15} (diameter of a medium sized nucleus)	Particle gluons, π (nucleons)
Electro-magnetic			Strength $\frac{1}{137}$	Range (m) Infinite	Particle photon mass = 0 spin = 1
Weak		neutrino interaction induces beta decay	Strength 10^{-6}	Range (m) 10^{-18} (0.1% of the diameter of a proton)	Particle Intermediate vector bosons W^+ , W^- , Z_0 , mass > 80 GeV spin = 1
Gravity			Strength 6×10^{-39}	Range (m) Infinite	Particle graviton ? mass = 0 spin = 2

ترمودینامیک - تعاریف

Forces of Nature



at high temperatures (1.4×10^{32} K) all four forces were unified into a **single force**.

در دماهای بالا وحدت نیروها وجود دارد

ترمودینامیک - تعاریف

perfect gas law (a.k.a. ideal gas law)

$$PV = nRT$$

P = absolute pressure

V = volume

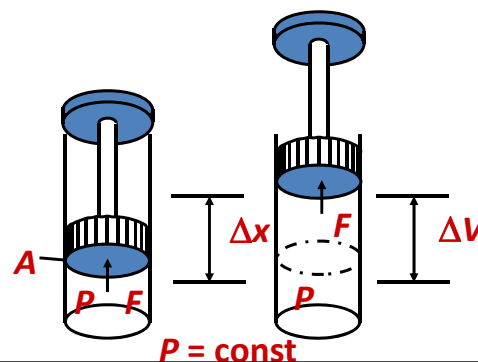
n = number of moles

R = universal gas constant $R = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

T = absolute temperature

$$\Delta W = F \Delta x$$

$$= \frac{F}{A} A \Delta x = P \Delta V$$



ترمودینامیک - تعاریف

Internal Energy, U, sum of potential energy and kinetic energy

Enthalpy, H, The amount of energy in a system capable of doing mechanical work

Entropy, S, a measure of the randomness of a system.
a measure of the unavailability of a system's energy to do work

State function a property of a system that depends only on the current state of the system, not on the way in which the system got to that state.

Pressure, P, Temperature, T, Volume, V, Internal energy, E, enthalpy, H and entropy, S, are the **state functions and path independent**.

Internal energy	$U(S,V)$
Enthalpy	$H(S,p) = U + PV$
Entropy	$dS = dq/T$

ترمودینامیک - تعاریف

Thermodynamic free energy, the total amount of energy in a physical system which can be converted to do work, in particular:

Helmholtz free energy, the amount of thermodynamic energy in a system which can be converted into work at **constant temperature**

Gibbs free energy, the amount of thermodynamic energy in a system which can be converted into work at a **constant temperature and pressure**

Helmholtz free energy	$A(T,V) = U - TS$
Gibbs free energy	$G(T,p) = U + PV - TS$

T = Temperature in Kelvins

ترمودینامیک - جداول

Table 3.3 Excess Free Energies, Enthalpies, and Entropies of Hexane (apolar), Benzene (monopolar), Diethylether (monopolar), and Ethanol (bipolar) in the Ideal Gas Phase, in Hexadecane, and in Water at Infinite Dilution.^a All Data at 25°C. Reference: Pure Liquid Organic Compound.

Phase Compound (i)	$G_{i\text{phase}}^E$ (kJ·mol ⁻¹)	=	$H_{i\text{phase}}^E$ (kJ·mol ⁻¹)	-	$T S_{i\text{phase}}^E$ (kJ·mol ⁻¹)	$S_{i\text{phase}}^E$ (J·mol ⁻¹ K ⁻¹)
Gas Phase						
Hexane	4.0	=	31.6	-	27.6	92.6
Benzene	5.3	=	33.9	-	28.6	96.0
Diethylether	0.8	=	27.1	-	26.3	88.2
Ethanol	6.3	=	42.6	-	36.3	122.0
Hexadecane						
Hexane	-0.2	=	0.6	-	0.8	2.7
Benzene	0.4	=	3.5	-	3.1	9.7
Diethylether	0.0	=	1.9	-	1.9	6.4
Ethanol	8.8	=	26.3	-	17.5	58.7
Water						
Hexane	32.3	=	-0.4	+	32.7	-109.7
Benzene	19.4	=	2.2	+	17.2	-58.4
Diethylether	12.0	=	-19.7	+	31.7	-106.3
Ethanol	3.2	=	-10.0	+	13.2	-44.3

^a Data from Abraham et al. (1990) and Lide (1995).

11

ترمودینامیک - تعاریف

Reversibility is the ability to run a process back and forth infinitely without losses.

Reversible Process E.g. Perfect Pendulum

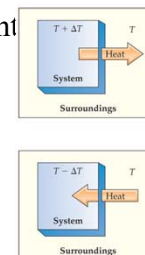
Irreversible Process E.g. Dropping a ball of clay-

All **Real** processes

Impossible Process E.g. Decrease in Entropy

Adiabatic process no heat is transferred to or from the system

Isothermal Process: A change in state occurring at constant temperature.



ترمودینامیک - قوانین

First Law of Thermodynamics

Energy can neither be created nor destroyed

$$\underset{\substack{\text{heat} \\ \text{added}}}{d q} = \underset{\substack{\text{change in} \\ \text{internal} \\ \text{energy}}}{d U} + \underset{\substack{\text{work} \\ \text{done}}}{d W}$$

$$dq = C_v dT + PdV$$

For adiabatic process

$$0 = C_v dT + PdV$$

ترمودینامیک - قوانین

• Definitions:

- coefficient of isobaric thermal expansion $\alpha_P = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$ ضریب انبساط حجمی
- isothermal compressibility $\beta_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$ قابلیت تراکم پذیری هم‌دما
- isentropic compressibility $\beta_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S$ قابلیت تراکم پذیری آدیباتیک
- heat capacity at constant pressure $c_p \equiv \left(\frac{\partial Q_{rev}}{\partial T} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p$ حرارت مخصوص در فشار ثابت
- heat capacity at constant volume $c_v \equiv \left(\frac{\partial Q_{rev}}{\partial T} \right)_v = T \left(\frac{\partial S}{\partial T} \right)_v$ حرارت مخصوص در حجم ثابت

ترمودینامیک - قوانین

Second Law of Thermodynamics

Naturally occurring processes are directional & irreversible

The entropy of the universe does not change for reversible processes and increases for spontaneous processes.

Reversible (ideal) $\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} = 0$

Irreversible (real, spontaneous) $\Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} > 0$

First and second Law combination

$$dU = TdS - PdV$$

ترمودینامیک - قوانین

Third Law of Thermodynamics

As a system approaches absolute zero of temperature, all processes cease and the entropy of the system approaches a minimum value

$$U \rightarrow U_{\min} \Rightarrow S \rightarrow 0$$

or

$$T \rightarrow 0 \Rightarrow S \rightarrow S_{\min}$$

a temperature of absolute zero is not possible

ترمودینامیک شیمیایی

Chemical Thermodynamics Thermodynamics of Solutions

- **Phases:** Part of a system that is chemically and physically homogeneous, bounded by a distinct interface with other phases and physically separable from other phases.
- **Components:** Smallest number of chemical entities necessary to describe the composition of every phase in the system.
- **Solutions:** Homogeneous mixture of two or more chemical components in which their concentrations may be freely varied within certain limits.

Unsaturated Soils

17

ترمودینامیک شیمیایی

Chemical Thermodynamics

Mole Fractions

$$x_A \equiv \frac{n_A}{\sum n} = \frac{n_A}{(n_A + n_B + n_c + \dots)}$$

where x_A is called the “mole fraction” of component A in some phase.

If the same component is used in more than one phase,
Then we can define the mole fraction of component
 A in phase i as x_A^i

For a simple binary system, $x_A + x_B = 1$

Unsaturated Soils

18

ترمودینامیک شیمیایی

Chemical Thermodynamics

Raoult's law(1888)

when a dilute liquid solution of a volatile solvent and a nonelectrolyte solute is equilibrated with a gas phase:

$$p_A = x_A p_A^*$$

p_A partial pressure of the solvent in the gas phase

p_A^* saturation vapor pressure of the pure solvent
(star stands for pure material)

x_A mole fraction of component A in the solution

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19

ترمودینامیک-پتانسیل شیمیایی

Chemical potential

chemical potential, μ , the partial molar Gibbs free energy variation.

$$\mu_A \equiv \left(\frac{\partial G_A}{\partial x_A} \right)_{P,T,x_B,x_C} \quad \text{direction of reaction}$$

standard state a reference state from which to calculate differences in chemical potential (25°C and 1 bar).

Fugacity is a measure of chemical potential $f = \exp(\mu / k_B T)$

Boltzmann constant $K_B = 1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$

For gases, ideal behavior is assumed, so a compound's fugacity is equal to its partial pressure: $f_{ig} = p_i$

As a result, fugacity is given in units of pressure, often Pa.

Pressure (and therefore f) is easy to measure, unlike μ

Unsaturated Soils

20

ترمودینامیک-تانسیل شیمیایی

Partial Molar Gibbs Free Energy

$$dG = VdP - SdT + \sum_i \mu_i dx_i$$

$$\sum_i \mu_i dx_i = \mu_A dx_A + \mu_B dx_B + \mu_C dx_C + \dots + \mu_n dx_n$$

This equation demonstrates that changes in Gibbs free energy are dependent on:

- changes in the **chemical potential**, μ , through the concentration of the components expressed as mole fractions of the various phases in the system
- changes in **molar volume** of the system through dP
- changes in **molar entropy** of the system through dT

- Chemical potential is analogous to gravitational or electrical potentials:
the most stable state is the one where the overall potential is lowest.
- At equilibrium the chemical potentials for any specific component in ALL phases must be equal.

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21

ترمودینامیک-تانسیل شیمیایی

For pure solid (s) or liquid (L), the fugacity is:

$$f_{il}^* = \gamma_{il} p_{il}^* \quad f_{is}^* = \gamma_{is} p_{is}^*$$

Where γ describes the non ideal behavior resulting from molecule-molecule interactions. For pure solid or liquid, γ is assumed to equal one.

In a mixture (i.e. aqueous solution):

$$f_{il} = x_{il} (f_{il}^*) = x_{il} (\gamma_{il} p_{il}^*)$$

aqueous solutions of organic chemicals are usually not ideal. $\gamma \neq 1$

Activity coefficients: γ_{il}

solute =>	hexane	benzene	diethylether	ethanol
solvent ↓				
n-hexadecane	~1	~1	~1	35
CHCl ₃	1.8	0.8	0.3	4.5
ethanol	12	5.4	n.a.	1
water	460,000	2500	130	3.6

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22

ترمودینامیک-پتانسیل شیمیایی

Activity coefficient and chemical potential

$$\mu_{il} = \mu_{il}^* + RT \ln \left[\frac{f_{il}}{p_{il}^*} \right]$$

chemical potential in solution

chemical potential of pure liquid (ideal)

fugacity relative to ideal

activity coefficient

mole fraction

$$\mu_{il} = \mu_{il}^* + RT \ln \gamma_{il} x_{il}$$

Unsaturated Soils

23

ترمودینامیک-پتانسیل شیمیایی

Chemical reaction

$$aA + bB + \dots \rightleftharpoons cC + dD + \dots$$

reactants products

Stoichiometry coefficient

$$aA + bB + \dots \rightleftharpoons cC + dD + \dots$$

activity coefficients

Equilibrium constant $K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$

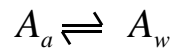
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24

ترمودینامیک-تانسیل شیمیایی

Phase transfer processes

Consider a chemical (A) equilibrating between air and water:



$$\mu_{Aa} = \mu_{AL}^* + RT \ln \gamma_{Aa} x_{Aa}$$

$$\mu_{Aw} = \mu_{AL}^* + RT \ln \gamma_{Aw} x_{Aw}$$

Note: still using
pure liquid as
reference state

At equilibrium, μ is equal in the two phases

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25

ترمودینامیک-تانسیل شیمیایی

After some rearranging you get:

$$\ln \frac{x_{Aa}}{x_{Aw}} = - \frac{RT \ln \gamma_{Aa} - RT \ln \gamma_{Aw}}{RT}$$

$$\frac{x_{Aa}}{x_{Aw}} = e^{- \frac{RT \ln \gamma_{Aa} - RT \ln \gamma_{Aw}}{RT}}$$

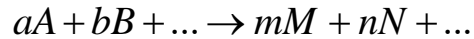
$$K'_{Aaw} = e^{- \frac{\Delta G}{RT}} = e^{- \frac{\Delta H - T\Delta S}{RT}}$$

entropic and enthalpic terms

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26

Chemical reaction



$$\Delta G_r = \Delta G_r^0 + RT \ln \left(\frac{[M]^m [N]^n \dots}{[A]^a [B]^b \dots} \right)$$

Standard free energies of formation $\Delta G_r^0 = \sum G_{products}^0 - \sum G_{reactants}^0$

At thermodynamic equilibrium $\Delta G_r = 0$ and so

$$\Delta G_r^0 = -RT \ln K$$

ΔG^0 can be looked up in tables,
Or calculated

Where K = equilibrium constant

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27

ترمودینامیک-تانسیل شیمیایی

Equilibrium is related to kinetics



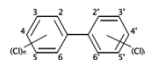
$$-\frac{dA}{dt} = k_1[A] - k_{-1}[B] = \frac{dB}{dt}$$

At equilibrium, there is no change in concentrations:

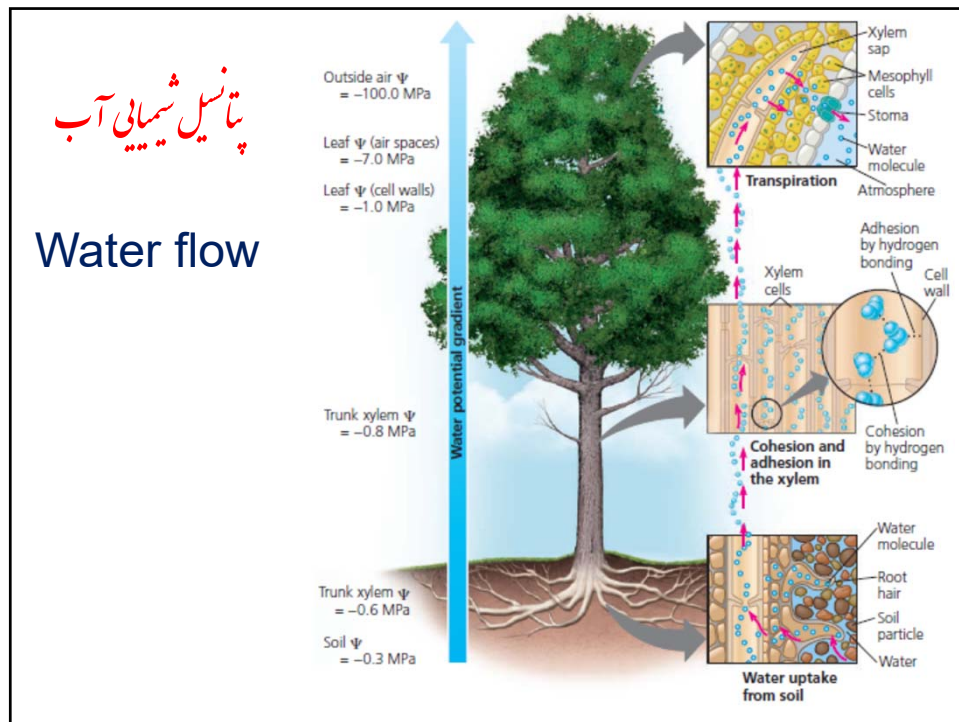
$$-\frac{dA}{dt} = \frac{dB}{dt} = 0 \quad \text{thus} \quad k_1[A] = k_{-1}[B]$$

$$\frac{[B]}{[A]} = \frac{k_1}{k_{-1}} = K_{eq}$$

Example: sorption of PCBs to organic matter. K_{eq} is large, implying that sorption is fast and desorption is slow



PCBs: polychlorinated biphenyls



پتانسیل ترمودینامیک آب

$$\Psi_{\text{soil}} > \Psi_{\text{root}} > \Psi_{\text{stem}} > \Psi_{\text{leaf}} > \Psi_{\text{air}}$$

$$\begin{array}{ccccccccc} \Psi_{\text{soil}} & & \Psi_{\text{root}} & & \Psi_{\text{stem}} & & \Psi_{\text{leaf}} & & \Psi_{\text{air}} \\ -2 & & -6 & & -10 & & -12 & & -50 \end{array}$$



Water flows from high to low water potential

What is water potential?

پتانسیل ترمودینامیک آب

مطابق تعریف کمیسیون انجمن بین المللی علوم خاک (۱۹۶۳)
پتانسیل کل: مقدار کاری که باید روی مقدار واحد آب خالص در استخر آب صورت پذیرد تا در شرایط بازگشت پذیر و همدمای آب به یک نقطه مشخص از خاک منتقل شود. استخر در تراز مشخص و با دمای و فشار گاز مساوی با نقطه مزبور در خاک می باشد.

توجه: آب خالص ماده (H_2O) می باشد در صورتیکه آب در خاک محلولی است که مواد دیگری نیز در آن حل شده اند.

پتانسیل ترمودینامیک آب

در حالت کلی تر پتانسیل ترمودینامیکی کل آب بصورت زیر می تواند تعریف شود:
 مقدار انرژی پتانسیل آب در خاک نسبت به آب خالص در شرایط مرجع

شرایط مرجع: استخر آب خالص با تراز و دما و فشار مشخص می باشد.
 پتانسیل ترمودینامیکی تمایل جابجایی آب تحت نیروهای ثقلی و شیمیایی و فشارهای مکانیکی را نشان می دهد

پتانسیل ترمودینامیک آب

$$\psi_t = \psi_m + \psi_o + \psi_g + \psi_p + \psi_T + \psi_v$$

ψ_t Total thermodynamics potential

ψ_m Matric potential

ψ_o Osmotic potential

ψ_g gravity potential

ψ_p Pressure potential

ψ_T Thermal potential

ψ_v Humidity potential

$$\psi_t^w = \psi_m^w + \psi_o^w + \psi_g^w + \psi_p^w + \psi_T^w + \psi_v^w \quad \text{جزء آب}$$

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33

پتانسیل ترمودینامیک آب

مطابق تعریف کمیسیون انجمن بین المللی علوم خاک (۱۹۶۳)
پتانسیل ماتریسی: مقدار کاری که باید روی حجم واحد آب خالص (آب به عنوان یک جزء) در استخر آب صورت پذیرد تا در شرایط بازگشت پذیر و همدمای آب به یک نقطه مشخص از خاک منتقل شود. استخر در تراز و با دما و فشار گاز مساوی با نقطه مزبور در خاک می باشد.

توجه: آب در استخر و در خاک دارای ترکیب یکسان می باشد.

نیروهای مؤثر نیروی موئینگی و نیروی جذب آب به دانه های خاک می باشد.

$$\psi_m = \psi_{cap} + \psi_{ads}$$

ψ_{cap} capillary potential

ψ_{ads} Adsorption potential

Liquids and Surface Tension

Surface tension is the amount of energy required to stretch or increase the surface of a liquid by a unit area.

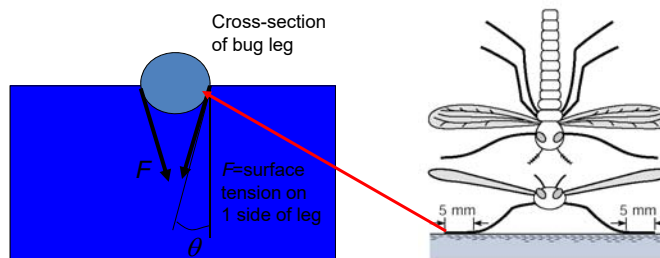


Strong intermolecular forces ➔ High surface tension

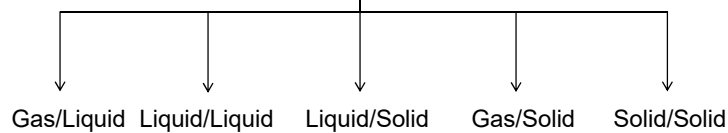
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35 11.3

Liquids and Surface Tension



Interfaces



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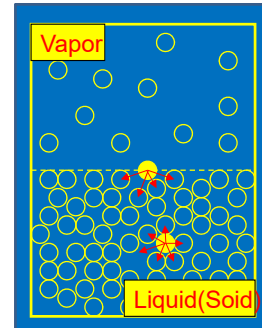
36

Liquids and Surface Tension

Interfacial tension γ_{ij} - force/unit length (N/m) arises from the imbalance of forces on molecules at liquid-gas interface

Interfacial energy = free energy necessary to increase by one unit area of contact between two different phases i, j

$$\Delta G/\Delta A = \gamma_{ij}$$



- Below surface, forces act equally in all directions
- At surface, some forces are missing, pulls molecules down and together, like membrane exerting *tension* on the *surface*
- If interface is curved, higher pressure will exist on concave side
- Pressure increase is balanced by surface tension, σ
- $\sigma = \gamma_{ij} = 0.073 \text{ N/m}$ (@ 20°C)

Unsaturated Soils

37

Surface tension of various liquids in <u>dyn</u> /cm against air			1 dyn	= 10 ⁻⁵ N
Mixture %'s are by weight				
Liquid	Temperature °C	Surface tension, γ		
Acetic acid	20	27.6		
Acetic acid (40.1%) + Water	30	40.68		
Acetic acid (10.0%) + Water	30	54.56		
Acetone	20	23.7		
Diethyl ether	20	17.0		
Ethanol	20	22.27		
Ethanol (40%) + Water	25	29.63		
Ethanol (11.1%) + Water	25	46.03		
Glycerol	20	63		
n-Hexane	20	18.4		
Hydrochloric acid 17.7M aqueous solution	20	65.95		
Isopropanol	20	21.7		
Mercury	15	487		
Methanol	20	22.6		
n-Octane	20	21.8		
Sodium chloride 6.0M aqueous solution	20	82.55		
Sucrose (55%) + water	20	76.45		
Water	0	75.64		
Water	25	71.97		
Water	50	67.91		
Water	100	58.85		

Unsaturated Soils

38

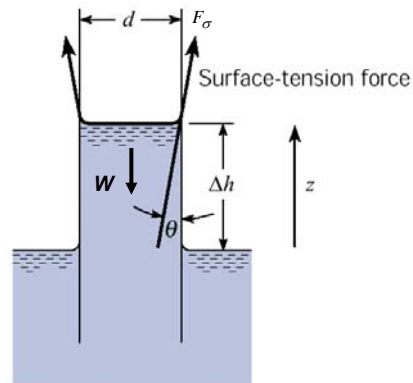
Capillary Rise

$$F_{\sigma,z} - W = 0$$

$$\sigma \pi d \cos \theta - \gamma (\Delta h) \left(\frac{\pi}{4} d^2 \right) = 0$$

$$\Delta h = \frac{4\sigma \cos \theta}{\gamma d}$$

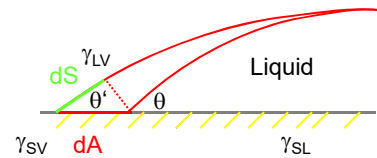
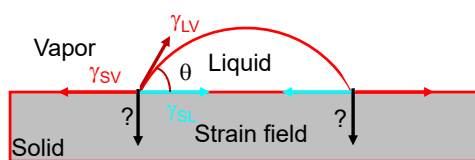
$$d = 2r \quad \Delta h = \frac{2\sigma \cos \theta}{\gamma r}$$



Unsaturated Soils

39

Young equation (homogeneous, smooth, rigid solids)



Horizontal balance of forces:

Young equation

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$

$$dG^S = (dG^S)_{SV} + (dG^S)_{SL} + (dG^S)_{LV}$$

$$dG^S = dA (\gamma_{SL} - \gamma_{SV}) + dA \gamma_{LV} \cos (\theta')$$

At equilibrium:

$$dG^S / dA = 0 \Rightarrow$$

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta$$

Vertical balance of forces: $\gamma_{LV} \sin \theta = ?$

Hard solids - no visible effect but the stress is there

If $\gamma_{SV} - \gamma_{SL} > \gamma_{LV} \cos \theta$ then $\cos \theta = 1$

Unsaturated Soils

40

Some liquid-solid contact angles¹

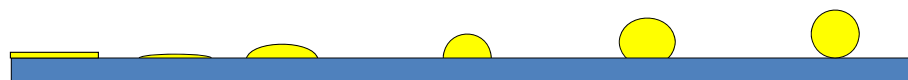
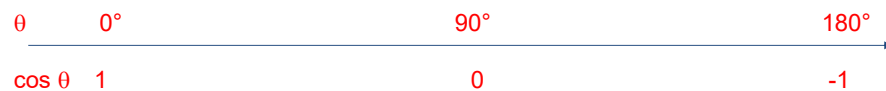
Liquid	Solid	Contact angle
water	soda-lime glass lead glass fused quartz soda-lime glass lead glass fused quartz soda-lime glass lead glass fused quartz	0°
soda-lime glass		
lead glass		
fused quartz		
ethanol		
diethyl ether		
carbon tetrachloride		
glycerol		
acetic acid		
water	paraffin wax	107°
	silver	90°
	soda-lime glass	29°
methyl iodide	lead glass	30°
	fused quartz	33°
mercury	soda-lime glass	140°

Unsaturated Soils

41

Wettability

Contact angle:



Spreading	Complete wett.	Partial wetting	$\gamma_{SL} = \gamma_{SV}$	Negligible wett.	Non-wett.
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- θ depends on chemical constitution of both S and L

- 1) **hard solids** - covalent, ionic, metallic => high energy surfaces $\gamma_{SO} \sim 500$ to 5000 ergs/cm^2
- 2) **weak molecular crystals** - vdW, H bonds => low energy surfaces $\gamma_{SO} \sim 50 \text{ ergs/cm}^2$

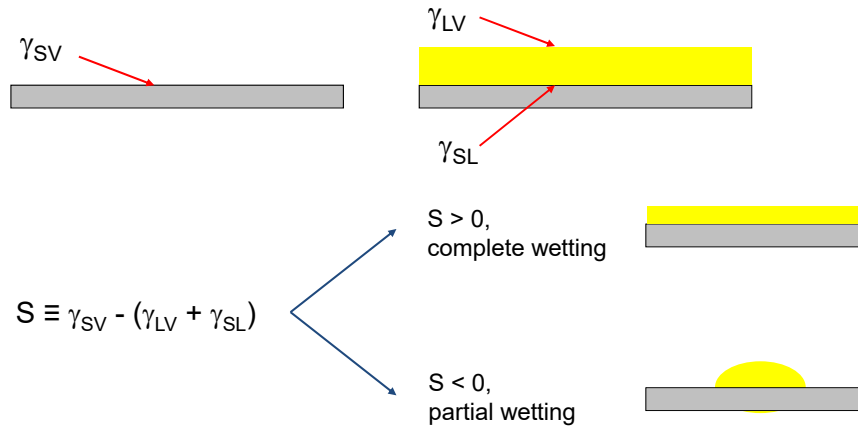
It is difficult to clean the floor if liquids with contact angle $\approx 0^\circ$ spill, like petrol, kerosene, benzene, contact angle exactly 180° : Water with specially prepared Teflon

Unsaturated Soils

$$1 \text{ erg} = 10^{-7} \text{ joule}$$

Spreading coefficient (spreading power)

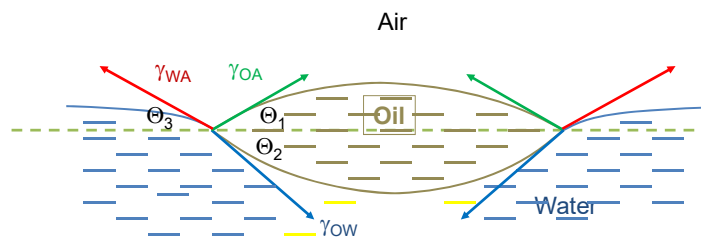
S = free energy difference between a bare solid, directly in contact with the vapour and a solid covered by a flat, thick liquid layer



Unsaturated Soils

43

Wetting of liquid surfaces




- When an oil does not wet water, a tiny drop of oil has the shape of a lens
- Force balance for both horizontal and vertical direction
- The initial shape may change with time if the oil is able to spread and/or if the two liquids are to some extent mutually soluble

Unsaturated Soils

44

Benzene-Water system




Air
Oil
Water

$$S = \gamma_{WA} - (\gamma_{OW} + \gamma_{OA})$$

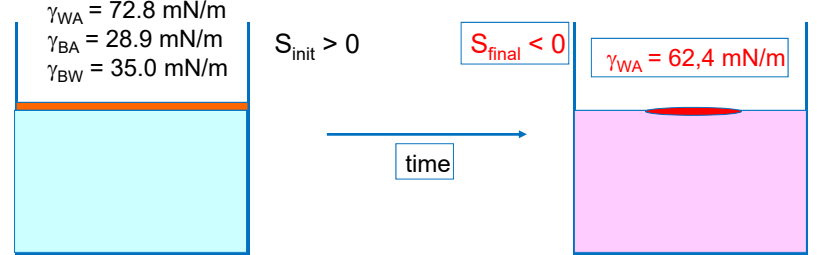
$S > 0$ the oil spreads into a thin film (complete wetting)
 $S < 0$ lens with finite size (partial wetting)

Example: adding a drop of benzene to the surface of water

$\gamma_{WA} = 72.8 \text{ mN/m}$
 $\gamma_{BA} = 28.9 \text{ mN/m}$
 $\gamma_{BW} = 35.0 \text{ mN/m}$

$S_{\text{init}} > 0$


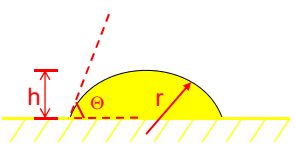
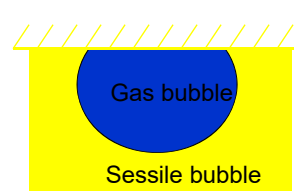
$S_{\text{final}} < 0$
 $\gamma_{WA} = 62.4 \text{ mN/m}$



time

Unsaturated Soils 45

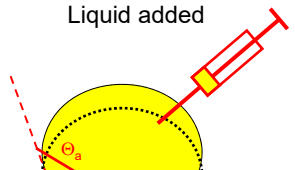
Experimental Methods for contact angle measurements

Spherical shape: $\tan \theta/2 = h/r$

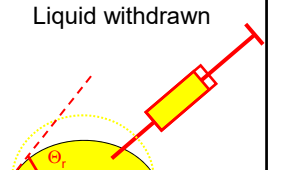
- Photograph of the drop => either by direct measurement of the contact angle
- or calculating it from drop profile

Liquid added



θ_a

Liquid withdrawn



θ_r

Use of a micrometer syringe: swell (shrink) the drop / bubble => receding & advancing angle

Unsaturated Soils 46

Contact angle hysteresis

Young eq. predicts *single* value for *intrinsic* c. a. but

Range of stable *apparent* c. a. can be measured experimentally:

=> **hysteresis**, $H \equiv \theta_a - \theta_r$

maximum - **advancing**

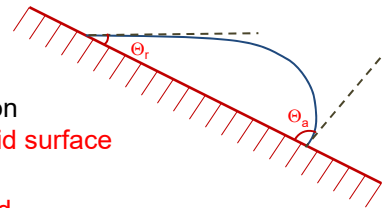
minimum - **receding**

Hysteresis

Roughness

Chemical contamination
or heterogeneity of **solid surface**

Solutes in the **liquid**
(surfactants, polymers)
may deposit a film on solid surface



Unsaturated Soils

47

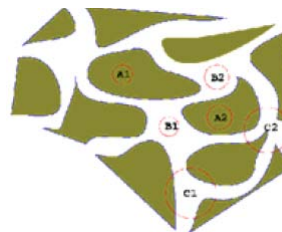
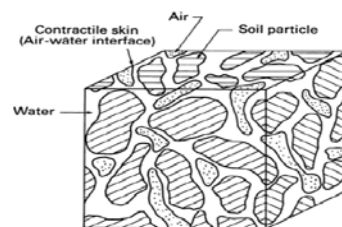
پتانسیل ترمودینامیک آب

پتانسیل ماتریسی: در اشل میکروسکوپی تعریف شده است و ما بیشتر به اشل ماکروسکوپی
علاقه مند هستیم

معمولاً یک المان پایه نماینده کل خاک در نظر گرفته می شود و پتانسیل ماتریسی
میکروسکوپی متوسط روی آن به عنوان پتانسیل ماتریسی ماکروسکوپی در نظر گرفته
می شود.

REV: Representative Elementary Volume

المان پایه نماینده



پتانسیل ترمودینامیک آب

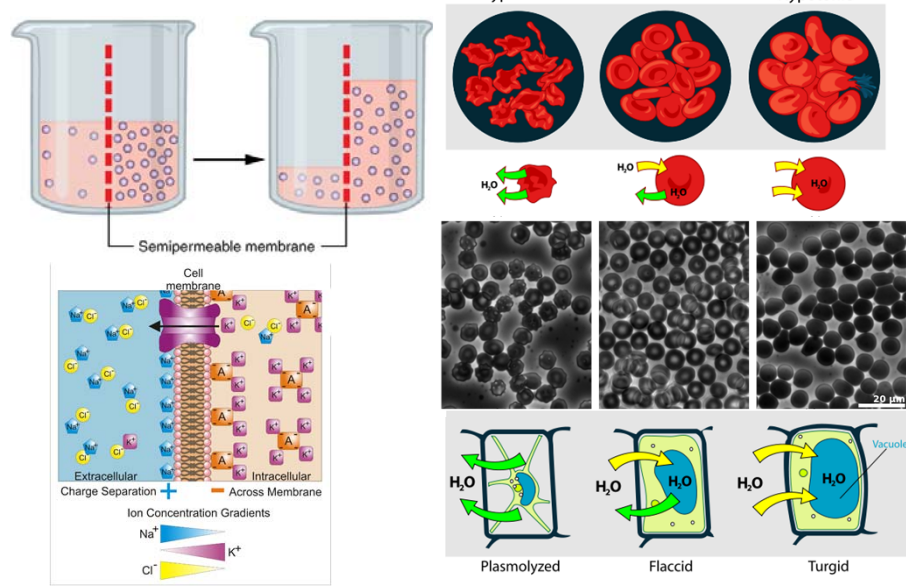
پتانسیل اسمزی:

آب در خاک یک محلول می باشد که مواد غیر محلول نیز در آن وجود دارد این مواد بر روی کشش سطحی آب و همچنین بر روی نیروهای جذب مولکولهای آب به دانه های خاک اثر می گذارند

بنابر این تعریف پتانسیل اسمزی مانند پتانسیل ماتریسی بوده با این تفاوت که آب در خاک بصورت یک محلول (دارای چند جزء) می باشد. پتانسیل برای جزء آب است و برای محلول اگر پتانسیل بخواهیم باید پتانسیل تک تک اجزا را حساب کرده با هم جمع کنیم.

پتانسیل ترمودینامیک آب

Osmotic Pressure



پتانسیل ترمودینامیک آب

Osmotic Pressure

Van't Hoff (1890)

Reverse Osmosis

$$P_{os} = RT(C_2 - C_1)$$

Unsaturated Soils

51

پتانسیل ترمودینامیک آب

پتانسیل جاذبه:

تغییرات انرژی جنبشی بعلاوه اختلاف ارتفاع استخر و نقطه مورد نظر در خاک می باشد.

در صورتیکه این انرژی بر واحد جرم آب حساب شود برابر است با $z - z_0$

در صورتیکه این انرژی بر واحد حجم آب حساب شود برابر است با

$$\rho_w g(z - z_0)$$

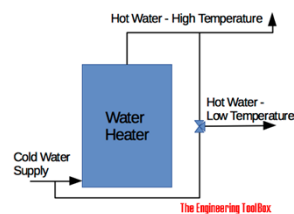
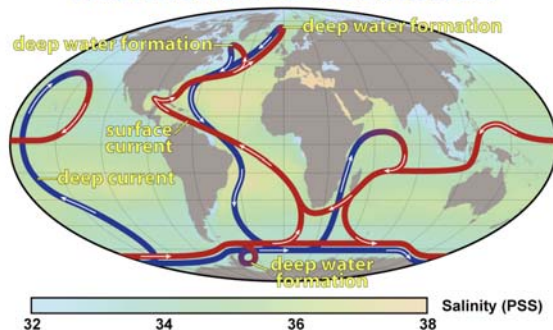
جرم حجمی آب ρ_w

پتانسیل ترمودینامیک آب

پتانسیل حرارتی:

تغییرات انرژی جنبشی باعث اختلاف درجه حرارت استخر و نقطه مورد نظر در خاک

Thermohaline Circulation



Thermohaline circulation (THC) is driven by global density gradients created by surface heat and freshwater fluxes