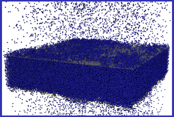
Multiphase Flow and Heat Transfer



Liquid-Vapor Interface

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Liquid-Vapor Interface

In Macroscopic view, the boundary between the bulk phases

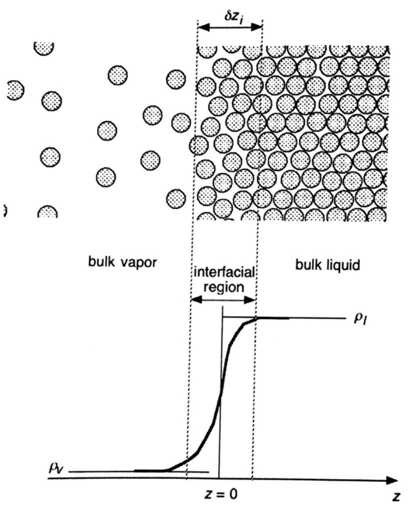
- Idealized as a surface
- Discontinuity in properties
- Net conversion of one phase into the other - Phase change

In Nanoscale view, the boundary between the bulk phases

- Actually a region
- A transition of mean molecular density exists
- This transition affects the thermo-physics and transport in this region

Easy for analysis as a surface, but Nanoscale perspective gives better understanding.

Liquid-Vapor Interface



Variation of the molecular density

Interacting Forces between Two Molecules

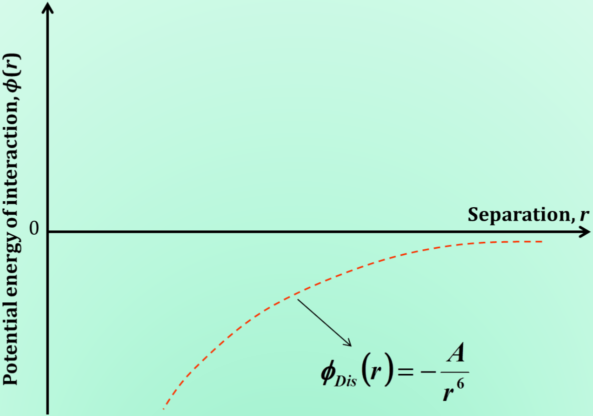
At longer range, two molecules exert attractive force.

- Dipole-dipole forces or Electrostatic forces
  - Opposite sides of the molecule have opposite charges
- Dipole-induced forces
  - Permanently charged particle induces a dipole in a nearby neutral molecule
  - Strength depends on easy of polarization
- London interactions or Dispersion forces
  - Stronger interactions allow solid and liquid states to persist to higher temperatures.
  - Non-polar molecules show similar behavior, indicating that there are some types of intermolecular interactions that cannot be attributed to simple electrostatic attractions.

$$\phi_{Dis}(r) = -\frac{A_{Dis}}{r^6}$$

Interacting Forces between Two Molecules

The potential function (ϕ) is the energy that must be input to bring two molecules from infinite distance apart to center-to-center spacing r.



A is a constant varies with the type of molecule, polarizability of the molecules.

Interacting Forces between Two Molecules

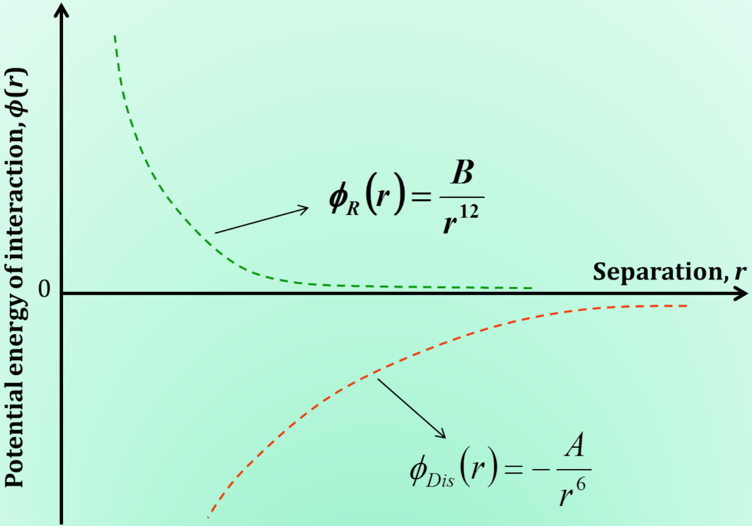
At very short range, two molecules exert a repulsive force

- Interference of the electron orbits of one molecule with those of the other.
- The energy required to bring two molecules from infinite distance apart to center-to-center spacing, r

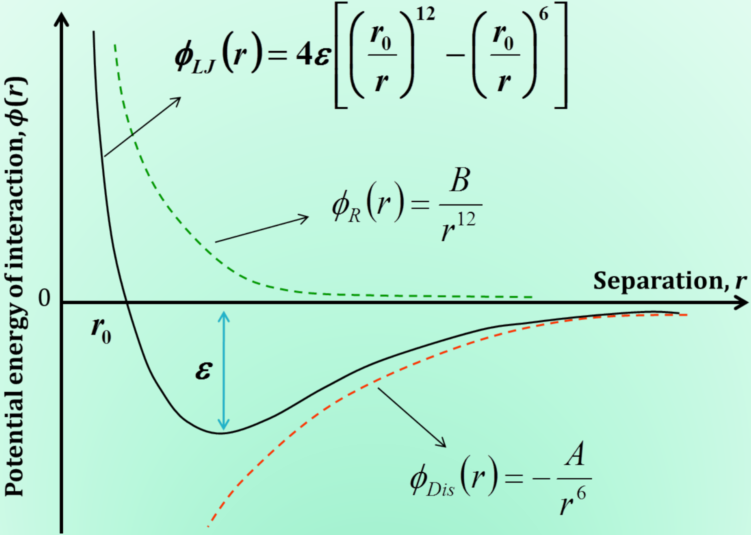
$$\phi_R(r) = \frac{B}{r^k}, 9 \leq k \leq 15$$

where B is a constant depending on the type of molecule.

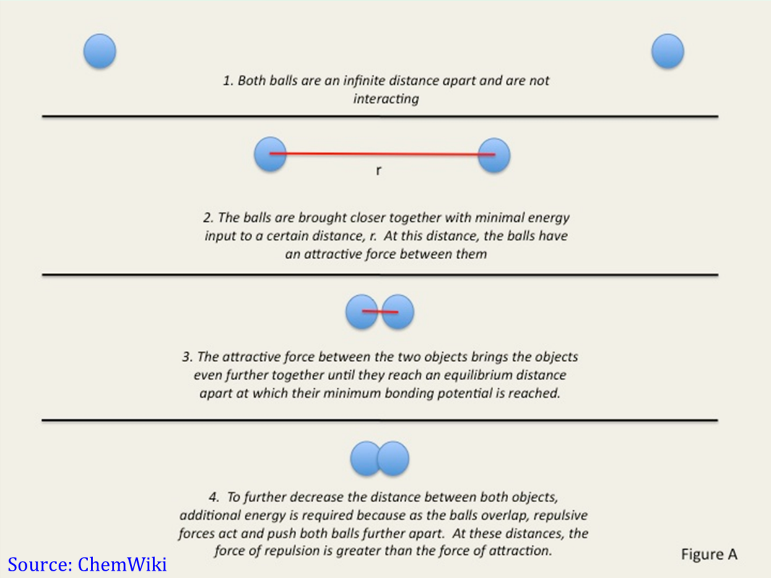
Interacting Forces between Two Molecules



Lennard-Jones 6-12 Potential



Liquid-Vapor Interfacial Region (Nanoscale)



1. Both balls are an infinite distance apart and are not interacting

2. The balls are brought closer together with minimal energy input to a certain distance, r. At this distance, the balls have an attractive force between them

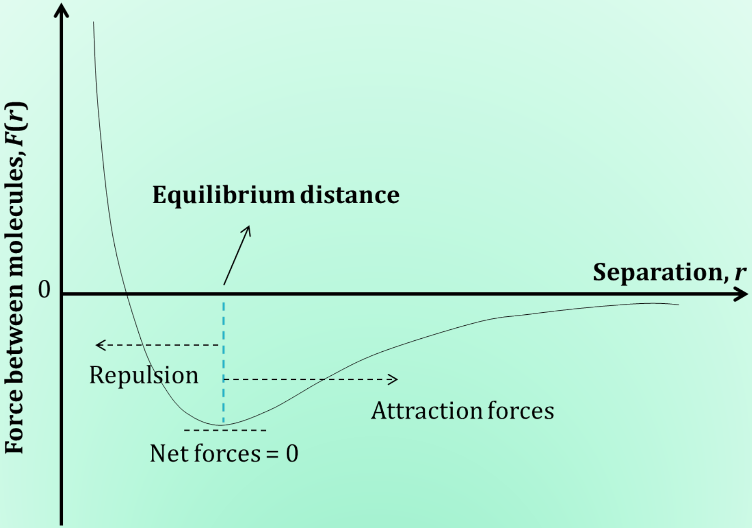
3. The attractive force between the two objects brings the objects even further together until they reach an equilibrium distance apart at which their minimum bonding potential is reached.

4. To further decrease the distance between both objects, additional energy is required because as the balls overlap, repulsive forces act and push both balls further apart. At these distances, the force of repulsion is greater than the force of attraction.

Figure A

Source: ChemWiki

Interacting Forces between Two Molecules



Lennard-Jones 6-12 Potential

$$\phi_{LJ}(r) = 4\varepsilon\left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^{6}\right]$$

- To bring two molecules that are initially very far apart into closer proximity, we must remove energy - **Condensation**
- If two molecules are close enough to feel attractive forces, but not so close that repulsive forces come into play, then energy must be supplied to increase the spacing of the molecules - **Vaporization**

Lennard-Jones 6-12 Potential

$$\phi_{LJ}(r) = 4\varepsilon\left[\left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^{6}\right]$$

ε is the depth of potential well (J):

$$\phi_{LJ} = -\varepsilon\big|_{r=2^{1/6}r_0}$$

- Energy that must be input for one molecule to escape the attractive pull of another.
- In a two-phase system, escape of molecules from a liquid phase into a vapor phase at the interface is more probable if the translational kinetic energy is larger than ε.

r_0 is the distance at which potential energy is zero (nm).

Maxwell-Boltzmann Distribution

The number of molecules with seed in the interval c to $c + dc$:

$$dN_c = 4\pi N \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} c^2 e^{\frac{-mc^2}{2k_B T}} dc$$

N is the number of molecules
c is the speed of the molecule, m/s
m is the mass of the molecule, kg
k_B is the Boltzmann constant, 1.38×10^{-23} $\mathrm{m^2 kg/s^2\ K}$
T is the absolute temperature, K

Maxwell-Boltzmann Distribution

We are interested in knowing the number of molecules that would have kinetic energy more that the minimum potential (depth of the potential well).

Convert speed distribution to kinetic energy of a molecule:

$$K = \frac{1}{2}mc^2$$

$$c = \sqrt{\frac{2K}{m}} \qquad dc = \frac{1}{\sqrt{2mK}}dK$$

$$dN_K = 2\pi N \left(\frac{1}{\pi k_B T}\right)^{\frac{3}{2}} K^{\frac{1}{2}} e^{\frac{-K}{k_B T}} dK$$

Maxwell-Boltzmann Distribution

The number of molecules in the gas with energies above ε:

$$N_{>\varepsilon} = \int_{\varepsilon}^{\infty} dN_K$$

The fraction of molecules with energies above ε is:

$$\boxed{\frac{N_{>\varepsilon}}{N} = \left(\frac{4\varepsilon}{\pi k_B T}\right)^{\frac{1}{2}} e^{-\frac{\varepsilon}{k_B T}} + \mathsf{erfc}\left(\sqrt{\frac{\varepsilon}{k_B T}}\right)}$$

$$\mathsf{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt$$

Error function term can be neglected if $\varepsilon \gg k_B T$.

Equilibrium Vapor Pressure

- Molecules having energies above the threshold value (ε) increase rapidly with temperature.
- This determines chemical reaction rates and the equilibrium conditions in two-phase systems.
- Even at low temperatures some fraction of the molecules in the liquid will have sufficient energy to escape the cohesive forces of other liquid molecules at the liquid-vapor interface.
- The fraction capable of escaping in this manner will increase rapidly with temperature.

Vapor Pressure & Latent Heat of Vaporization

- A liquid with a small cohesive energy will have a higher vapor pressure than one with a large cohesive energy.
- In general, cohesive energy $\propto \varepsilon$ (Lennard-Jones potential).
- $H_{lv} \cong$ cohesive energy of the liquid
- At same temperature, a liquid with a high H_{lv} should have a lower vapor pressure than a liquid with a smaller H_{lv}.

- At 20°C, Water:

$$P_{\text{sat}} = 2.34 \text{ kPa and } H_{lv} = 2454 \text{ kJ/kg}$$

- At 20°C, Saturated refrigerant-134a:

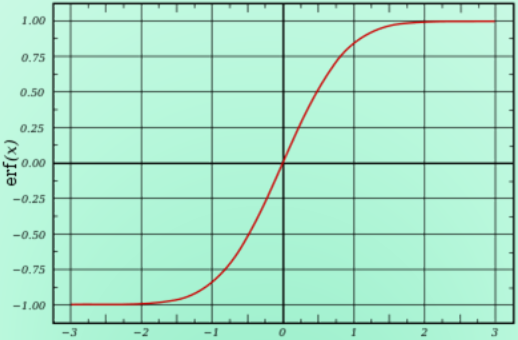
$$P_{\text{sat}} = 572.1 \text{ kPa and } H_{lv} = 182.3 \text{ kJ/kg}$$

Problem

For saturated nitrogen at 77 K, estimate the fraction of the molecules that have translational kinetic energies larger than, $\varepsilon = 1.31 \times 10^{-21}$ J.

$$\frac{N_{>\varepsilon}}{N} = \left(\frac{4\varepsilon}{\pi k_B T}\right)^{\frac{1}{2}} e^{-\frac{\varepsilon}{k_B T}} + \mathrm{erfc}\left(\sqrt{\frac{\varepsilon}{k_B T}}\right)$$

$$k_B = 1.38 \times 10^{-23}\ \mathrm{m^2 kg/s^2\ K}$$



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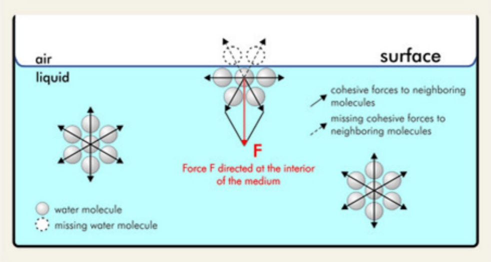
$$\frac{\varepsilon}{k_B T} = 1.23$$

$$\boxed{\frac{N_{>\varepsilon}}{N} = \left(\frac{4 \times 1.23}{\pi}\right)^{\frac{1}{2}} e^{-1.23} + \mathsf{erfc}\left(\sqrt{1.23}\right) = 0.483}$$

Thus, the Boltzmann distribution predicts that almost half the molecules have translation energy values greater than $\varepsilon = 1.31 \times 10^{-21}$ J.

Surface Tension

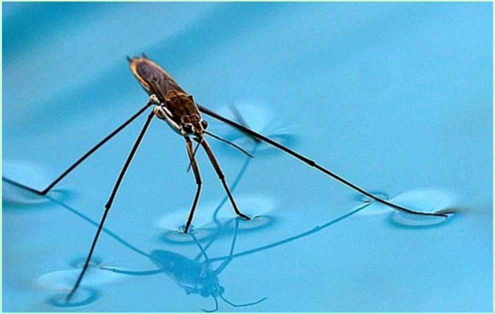
The net attractive force causes the liquid surface to contract inwards until repulsion from other surrounding molecules start dominating.



- If there are no external forces, spherical interface is formed.
- Intermolecular attraction - Interfacial Tension.

Surface Tension

Practically, the phenomenon is comparable to a thin layer surrounding the liquid and making it hard to dip an object in and to pull it out of the liquid.



Water strider

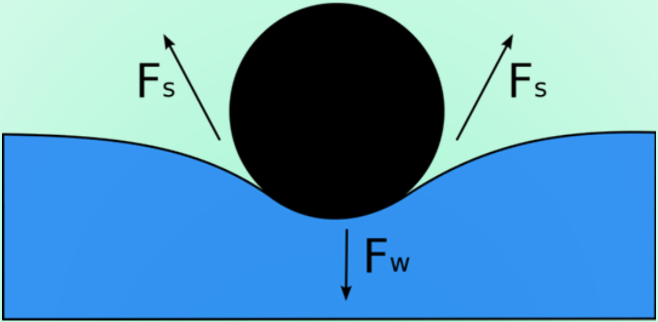
Surface Tension

Practically, the phenomenon is comparable to a thin layer surrounding the liquid and making it hard to dip an object in and to pull it out of the liquid.

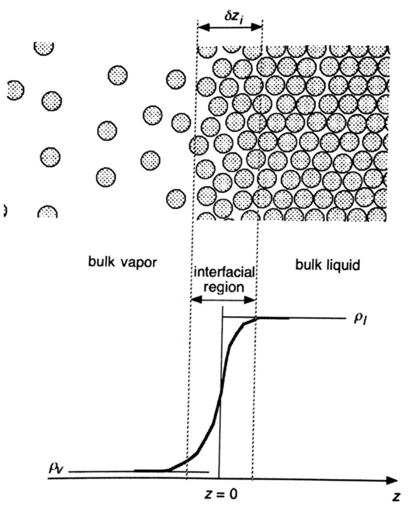
Green Basilisk Lizard - The Jesus Christ Lizard

Surface Tension

- Against force (F) work has to be performed to move something through this layer or to expand its surface.
- Hence, σ is the amount of force (Nm) necessary to expand the surface (m^2) of a liquid by one unit.



Van der Waals (Molecular) Theory of Capillarity



Variation of the molecular density

Normal to the Interface

- The mean spacing of the molecules in the liquid near the interface is greater than in the bulk liquid.
- The repulsive force varies more rapidly with spacing than the longer-range attractive forces.
- In the direction normal to the interface, this combination of effects would produce a force imbalance that would draw the molecules towards the bulk liquid.
- The mean spacing of the molecules in the direction normal to the interface could decrease slightly to establish a balance between long-range attractive forces and repulsion from close neighboring molecules.

Parallel to the Interface

- In the directions parallel to the interface, however, the decrease in repulsion force between molecules produced by the increases spacing does not create a force imbalance because of the radial symmetry of the force interactions.
- Consequently, there is no impetus to decrease the mean spacing in this direction.
- The decrease in repulsive forces between immediate neighbors, with littel change in the longer-range attractive forces may thus produce a net tension force among molecules in the interface region acting equally in all directions parallel to the interface.

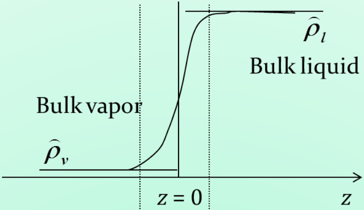
Van der Waals (Molecular) Theory of Capillarity

- **Postulate:** Postulate: The mean properties vary continuously across the transition region between the bulk phases. Mean molar density,

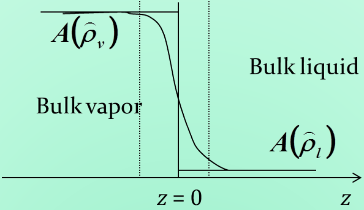
$$\hat{\rho} = \frac{\rho_n}{N_A}$$

- On the liquid side of the interfacial region, ρ is lower that that in the bulk liquid.
- Energy per molecule in the interfacial region $>$ in bulk liquid.
- The system has an additional free energy per unit area of interface due to the presence of the interface.
- Interfacial tension is due to the excess interfacial free energy per unit area.

Van der Waals (Molecular) Theory of Capillarity



Variation of mean molar density



Variation of the volumetric free energy

Van der Waals (Molecular) Theory of Capillarity

The interface surface is so chosen that the mass in the interfacial region with a distributed density profile is the same as would exist in the region with a discontinuous density step change at $z = 0$.

$$\int_{-\infty}^{0} (\hat{\rho} - \hat{\rho}_v) dz + \int_{0}^{\infty} (\hat{\rho} - \hat{\rho}_l) dz = 0$$

Van der Waals (Molecular) Theory of Capillarity

$$\boxed{\sigma = \int_{-\infty}^{0} \left[A - A(\hat{\rho}_v)\right] dz + \int_{0}^{\infty} \left[A - \psi(\hat{A}_l)\right] dz}$$

A is the Helmholtz free energy per unit volume

the max. work a system can do at constant $V \& T$.

- Apply a system held at constant T with a V that encompasses the interfacial region over a unit area of the interface.
- Equilibrium corresponds to a minimum in volumetric free energy (A).
- σ is the property nothing but this equilibrium free energy.

Van der Waals (Molecular) Theory of Capillarity

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- Apply a system held at constant T with a V that encompasses the interfacial region over a unit area of the interface.
- Equilibrium corresponds to a minimum in volumetric free energy (A).
- σ is the property nothing but this equilibrium free energy.

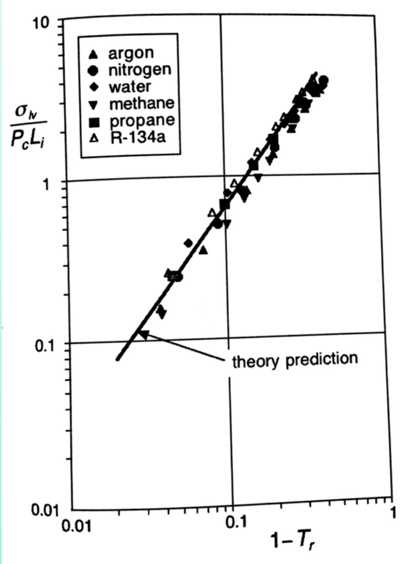
Dimensionless Surface Tension

Modified Redlich-Kwong model for dimensionless σ:

$$\frac{\sigma_{lv}}{P_c L_i} = 14.65 \left(1 - \frac{T}{T_c}\right)^{1.33}$$

L_i is a characteristic length associated with the size of the interfacial region:

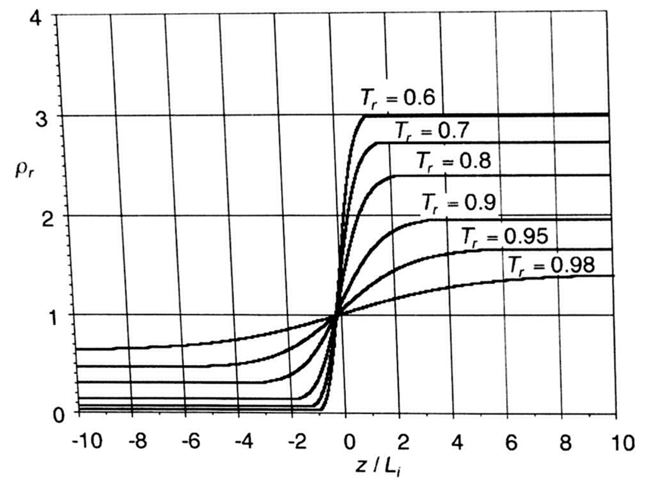
$$L_i = \left(\frac{k_B T_c}{P_c}\right)^{\frac{1}{3}}$$



Interface Properties

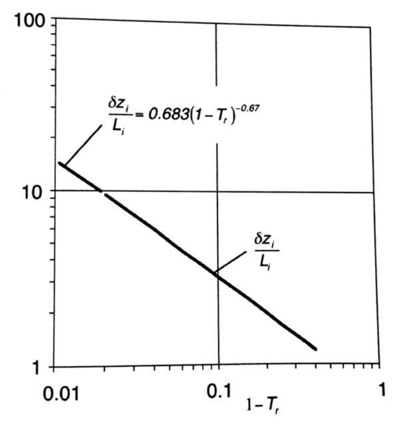
$$\rho_r = \frac{\rho}{\rho_c}$$

$$T_r = \frac{T}{T_c}$$



Reduced density profiles across the interfacial region predicted at various reduced temperatures

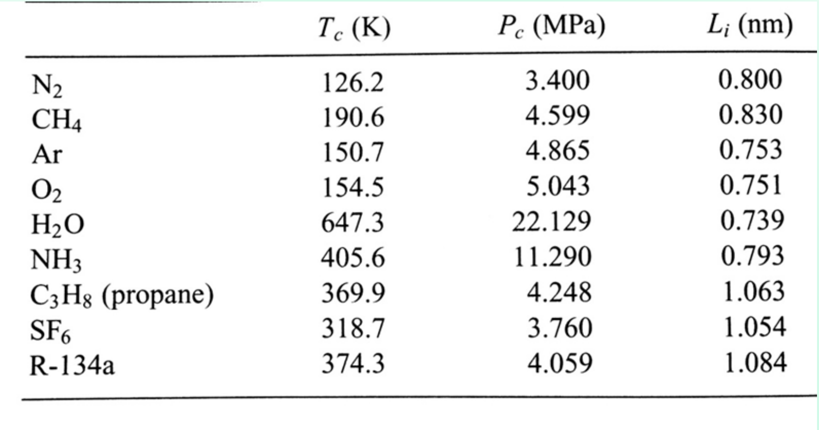
Dimensionless Interfacial Thickness



Dimensionless interfacial thickness:

$$\frac{\delta z_i}{L_i} = 0.683\left(1-\frac{T}{T_c}\right)^{-.67}$$

Characteristic Length



	T_c (K)	P_c (MPa)	L_i (nm)
N_2	126.2	3.400	0.800
CH_4	190.6	4.599	0.830
Ar	150.7	4.865	0.753
O_2	154.5	5.043	0.751
H_2O	647.3	22.129	0.739
NH_3	405.6	11.290	0.793
C_3H_8 (propane)	369.9	4.248	1.063
SF_6	318.7	3.760	1.054
R-134a	374.3	4.059	1.084

$$L_i = \left(\frac{k_B T_c}{P_c}\right)^{\frac{1}{3}}$$

Problem

For water at atmospheric pressure, estimate the surface tension and the interfacial region thickness. $T_c = 647.3$ K, $P_c = 22.1$ MPa and $L_i = 0.739$ nm.

$$\frac{\sigma_{lv}}{P_c L_i} = 14.65 \left(1 - \frac{T}{T_c}\right)^{1.33}$$

$$L_i = \left(\frac{k_B T_c}{P_c}\right)^{\frac{1}{3}}$$

$$k_B = 1.38 \times 10^{-23} \text{ m}^2\text{kg/s}^2 \text{ K.}$$

$$\frac{\delta z_i}{L_i} = 0.683 \left(1 - \frac{T}{T_c}\right)^{-.67}$$

Problem: Solution

For water at atmospheric pressure, estimate the surface tension and the interfacial region thickness. $T_c = 647.3$ K, $P_c = 22.1$ MPa and $L_i = 0.739$ nm.

At $T = 300$ K

$$\sigma_{lv} = 0.105 \text{ N/m}$$
$$\delta z_i = 0.766 \text{ nm}$$

At $T = 373.14$ K

$$\sigma_{lv} = 0.07635 \text{ N/m}$$
$$\delta z_i = 0.898 \text{ nm}$$

Actual value, $\sigma = 0.0712$ N/m at T = 303.2 K

$\sigma = 0.0589$ N/m at T = 373.14 K

The effective diameter of a water molecule = 0.28 nm.