$$T_{tp} = \frac{\left(\Delta H_m^{vaporization} - \Delta H_m^{sublimation}\right)}{R\left(\ln\frac{P_i^{liquid}}{P^\circ} - \ln\frac{P_i^{solid}}{P^\circ} - \frac{\Delta H_m^{sublimation}}{RT_i^{solid}} + \frac{\Delta H_m^{vaporization}}{RT_i^{liquid}}\right)}$$

$$= \frac{-9.95\times10^3\,\mathrm{J\,mol^{-1}}}{8.314\,\mathrm{J\,K^{-1}mol^{-1}}\times\left(\begin{array}{l}\ln\frac{10{,}000\,\mathrm{Pa}}{1\,\mathrm{Pa}} - \ln\frac{137\,\mathrm{Pa}}{1\,\mathrm{Pa}} - \frac{(30.7\times10^3+9.95\times10^3)\,\mathrm{J\,mol^{-1}}}{8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}\times 228.9\,\mathrm{K}}\\ +\frac{30.7\times10^3\,\mathrm{J\,mol^{-1}}}{8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}\times 293.15\,\mathrm{K}}\end{array}\right)}$$

$$= 278\ \mathrm{K}$$

We calculate the triple point pressure using the Clapeyron equation:

$$\ln\frac{P_f}{P_i} = -\frac{\Delta H_m^{vaporization}}{R}\left(\frac{1}{T_f} - \frac{1}{T_i}\right)$$

$$\ln\frac{P_{tp}}{101{,}325} = -\frac{30.7\times10^3\,\mathrm{J\,mol^{-1}}}{8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}}\times\left(\frac{1}{278\,\mathrm{K}} - \frac{1}{353.24\,\mathrm{K}}\right)$$

$$\ln\frac{P_{tp}}{P^\circ} = 8.6969$$

$$P_{tp} = 5.98\times10^3\,\mathrm{Pa}$$

8.7 The Vapor Pressure of a Pure Substance Depends on the Applied Pressure

Consider piston (weightless) and cylinder assembly containing water at 25℃(Figure 8.14) at which T the equilibrium vapor pressure:

$$P^* = 3.16\times10^3\ \mathrm{Pa} = 0.0316\mathrm{bar}$$

If m = 1 bar → System is in single phase liquid.(Fig 4)(Fig 14a)
If m = P^* → in the two phase gas-liquid region (Fig 14b)

If argon gas is introduced into the cylinder so that
$P_{Ar} + P_{H20} = 1$ bar (∑Partial pressures=1bar)(Fig 14c)

What is the vapor pressure of water in this case?

P = Vapor pressure of water (=Partial pressure of water in gas)
ρ = Sum of the partial pressures (Ar+ H_2O) =Total pressure

At equilibrium

$$\mu_{liquid}(T, \rho) = \mu_{gas}(T, P) \qquad (8.21)$$

(μ_{liquid} refers to water)

Differentiating this w.r.t to ρ gives,

$$\left(\frac{d\mu_{liquid}(T,\rho)}{d\rho}\right)_T = \left(\frac{d\mu_{gas}(T,P)}{dP}\right)_T\left(\frac{dP}{d\rho}\right)_T \qquad (8.22)$$

We know

$$d\mu = -S_m dT + V_m dP,$$

Then,

$$(d\mu/dP)_T = V_m,$$

Then Eq (8.22) becomes,

$$V_m^{liquid} = V_m^{gas}\left(\frac{dP}{d\rho}\right)_T \quad \text{or} \quad \left(\frac{dP}{d\rho}\right)_T = \frac{V_m^{liquid}}{V_m^{gas}} > 0 \qquad (8.23)$$

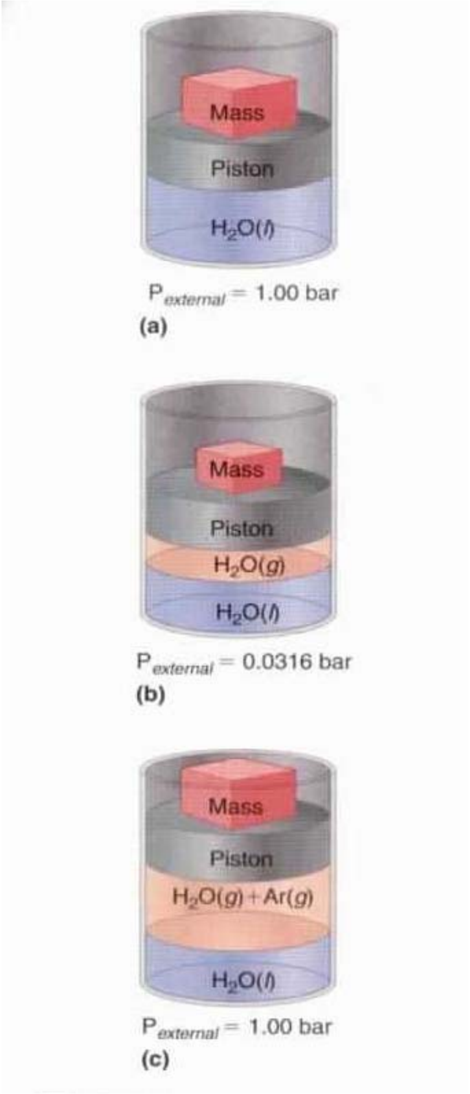

FIGURE 8.14
A piston and cylinder assembly at 298 K is shown with the contents being pure water (**a**) at a pressure greater than the vapor pressure, (**b**) at a pressure equal to the vapor pressure, and (**c**) at 1 bar for a mixture of argon and water.

⇒ Vapor pressure (P) increases as the total pressure ρ increases though the increase is small because the ratio $V_m^{liquid}/V_m^{gas} \ll 1$.

Assume IG law ($V_m^{gas} = RT/P$) is hold, Eq (8.23) becomes,

$$\frac{RT}{P}dP = V_m^{liquid}d\rho \quad \text{or} \quad RT\int_{P_0}^{P}\frac{dP'}{P'} = V_m^{liquid}\int_{P_0}^{\rho}d\rho' \qquad (8.24)$$

Integration gives,

$$RT\ln\left(\frac{P}{P_0}\right) = V_m^{liquid}(\rho - P_0) \qquad (8.25)$$

P_0 is the vapor pressure when the total pressure(ρ) is one bar.
For the specific case of water, P_0 = 0.0316bar, and V_m^{liquid} = $1.81\times10^{-5}m^3mol^{-1}$:

$$\ln\left(\frac{P}{P_0}\right) = \frac{V_m^{liquid}(\rho - P_0)}{RT}$$

$$= \frac{1.81\times10^{-5}m^3mol^{-1}\times(1-0.0316)\times10^5Pa}{8.314Jmol^{-1}K^{-1}\times298K} = 7.04\times10^{-4}$$

$$P = 1.0007P_0 \approx 0.0316\,bar$$

For an external pressure of 1 bar (ρ), the effect is negligible. However, for ρ = 100 bar, P = 0.0339bar, amounting to an increase in the vapor pressure of 7%.

8.8 Surface Tension

With no gravity, liquid droplet tends to form a sphere to maximize the number of molecules surrounded by the surface.
Interaction between the liquid molecules is attraction → Minimization of the surface-to-volume ratio is to minimize the energy.

Droplet energy vs surface?

Spherical particle $\xrightarrow{+work}$ distorted to create more surface.

$dA = \gamma d\sigma$ (8.26)

A = Helmholtz energy (=Energy/area = J/m^2 = N/m)
γ = Surface tension
σ = Surface area

Surface tension is work required to create a unit surface area (26).

For a spontaneous process @ constant T and V:

$dA < 0$

→ $dA/d\sigma = \gamma > 0$ (γ tends to decrease $d\sigma$)

→ A liquid bubble suspended in a wire frame tends to minimize the surface.

Formulation of surface tension (See Figure 8.15)

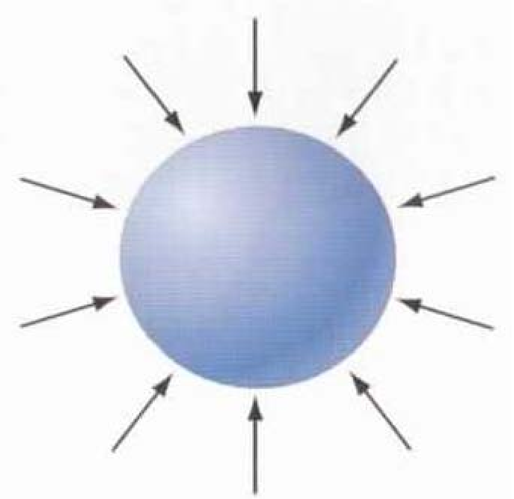

FIGURE 8.15

The forces acting on a spherical droplet that arise from surface tension.

Suppose a spherical shell with thickness dr.

Area of inner surface $\sigma = 4\pi r^2$

$d\sigma/dr = 8\pi r$ or $d\sigma = 8\pi r dr$ (8.27)

Work done in the expansion = Area x surface tension = $8\pi r dr \gamma$

→ Force (normal to the surface) = (work/distance)

$F = 8\pi r dr \gamma / dr = 8\pi r \gamma$ (8.28)

The net effect of force is to generate a pressure differential across the droplet surface.

Inward force = Pressure at outer surface + surface tension

Outward force = Pressure at the inner surface

(Note : Pressure acts normal to the surface)

At equilibrium,

$$4\pi r^2 P_{outer} + 8\pi r \gamma = 4\pi r^2 P_{inner}$$

$$\rightarrow P_{inner} - P_{outer} = \frac{2\gamma}{r} \qquad (8.29)$$

Note inner = Concave side, Outer = Convex side

Note: $(P_{inner} - P_{outer}) \rightarrow 0$ as $r \rightarrow \infty$

⇒ Pressure differential exists only for a curved surface!!!

Note: The higher pressure is always the concave side of the interface!!! (Figure 8.15)

See Table 8.5 (Surface tension of liquids)

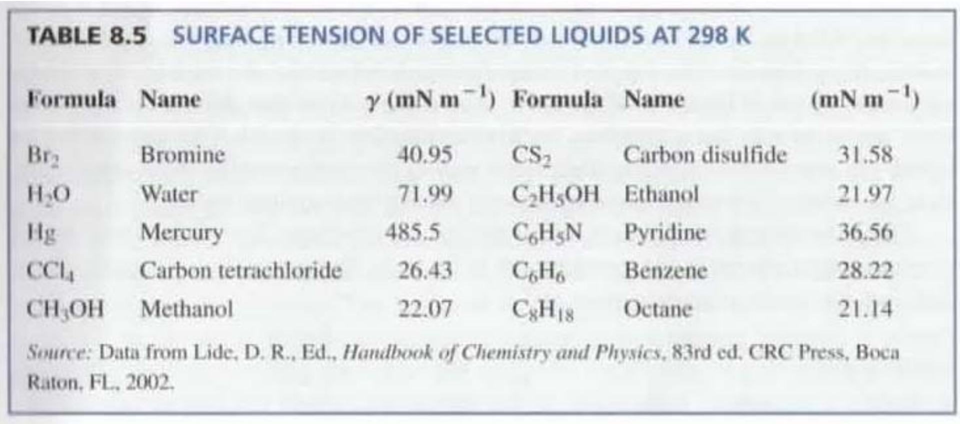

TABLE 8.5 SURFACE TENSION OF SELECTED LIQUIDS AT 298 K

Formula	Name	γ (mN m^{-1})	Formula	Name	(mN m^{-1})
Br_2	Bromine	40.95	CS_2	Carbon disulfide	31.58
H_2O	Water	71.99	C_2H_5OH	Ethanol	21.97
Hg	Mercury	485.5	C_6H_5N	Pyridine	36.56
CCl_4	Carbon tetrachloride	26.43	C_6H_6	Benzene	28.22
CH_3OH	Methanol	22.07	C_8H_{18}	Octane	21.14

Source: Data from Lide, D. R., Ed., *Handbook of Chemistry and Physics*, 83rd ed. CRC Press, Boca Raton, FL, 2002.

Application of Eq (8.29)

Bubble stability (Foam coarsening)

Two air filled bubble with radius R_1 and R_2 ($R_1 > R_2$) (Figure 8.16)

Assume surface tension of the two bubbles are the same.

External pressure is the same.

Apply Eq (8.29) to each bubble :

$$P_1 - P_{outer} = \frac{2\gamma}{R_1} \qquad (A)$$

$$P_2 - P_{outer} = \frac{2\gamma}{R_2} \qquad (B)$$

(A) - (B)

$$P_1 - P_2 = 2\gamma\left(\frac{1}{R_1} - \frac{1}{R_2}\right) \qquad (8.30)$$

Since $R_1 > R_2 \rightarrow P_1 < P_2$

⇒ Air will flow from bubble 2 to bubble 1 until the smaller bubble disappears.
(This process is called "Coarsening" in foam and "Ostwald ripening" in crystal)

Biologically relevant issue
= Stability of lung tissue

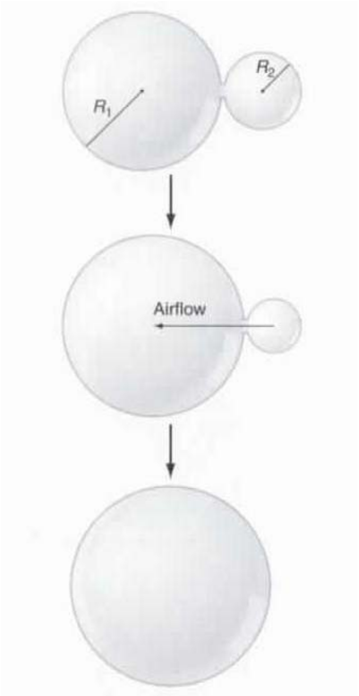

FIGURE 8.16

Two bubbles with unequal radii R_1 and R_2 make contact (top). Because the pressure within a bubble varies inversely with the bubble radius, air flows from the smaller into the larger bubble until a single large bubble remains (bottom).

Lung tissue = a small water-lined air-filled chamber called "alveoli". If two air-filled alveoli are interconnected, smaller one will collapse and the larger one would expand because

$$P_{smaller} > P_{larger}$$

Due to the surface tension of water that lines the alveoli will collapse, leaving a ever diminishing number of alveoli of increasing size⇒ Collapse of lung

Capillary rise and capillary depression
= A consequency of pressure difference across a curved surface.

If $\gamma_{\text{liquid}} < \gamma_{\text{solid}}$ → Liquid will wet the surface(Fig 8.17a) (capillary rise)
If $\gamma_{\text{liquid}} > \gamma_{\text{solid}}$ → Capillary depression (Fig 8.17b)

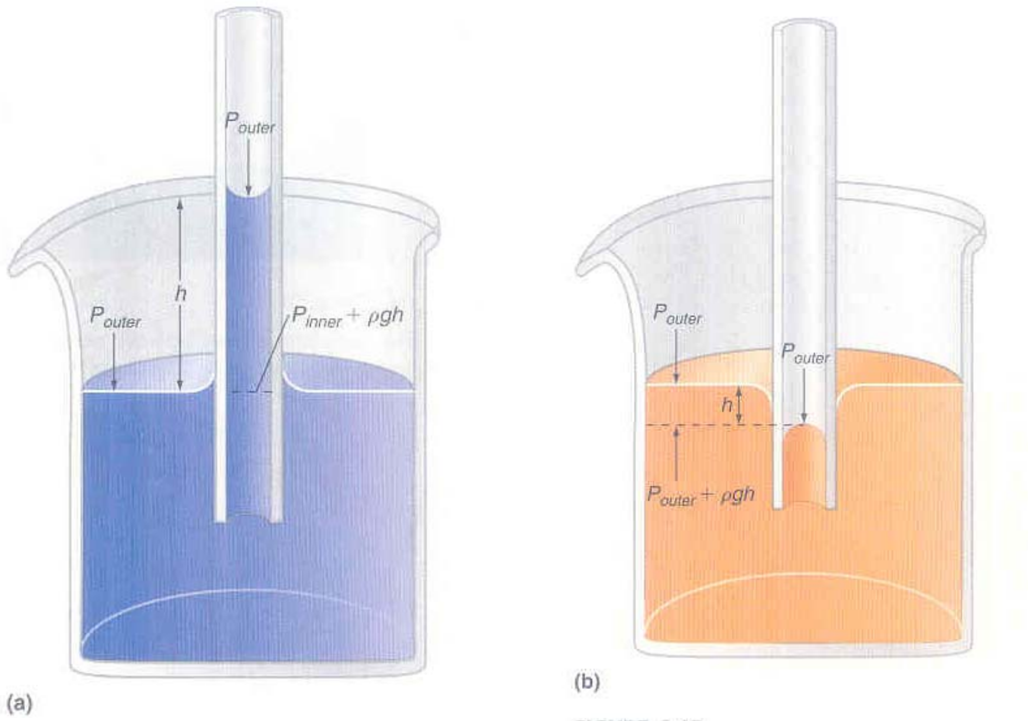

FIGURE 8.17

(a) If the liquid wets the interior wall of the capillary, a capillary rise is observed. The combination Pyrex–water exhibits this behavior. **(b)** If the liquid does not wet the capillary surface, a capillary depression is observed. The combination Pyrex–mercury exhibits this behavior.

Fig 8.17 here.

In either cases, there is a pressure differential across the gas-liquid interface since the interface is curved.

Assumption
Liquid-gas interface is tangent to the interior wall of the capillary.
→ Radius of interface curvature = capillary radius

Pressure difference across the curved interface

$$P_{inner} - P_{outer} = \frac{2\gamma}{r}$$

This pressure difference is balanced with gravity force :

$$\frac{2\gamma}{r}(\uparrow) = \rho g h(\downarrow)$$

or $$h = \frac{2\gamma}{\rho g r} \qquad (31)$$

Capillary rise is proportional to surface tension and inversely to capillary radius. (Surface tension of liquid is simply determined by this method, where that of solid from contact angle measurements)

In the above we assumed either (1) or (2):
(1) Liquid completely wets interior surface (does not fill the core, a)
(2) Liquid is completely non-wetting (does fill the core, b)
In reality, it is intermediate (See Figure 8.18).
→ liquid surface is characterized by contact angle(Θ)
Complete wetting Θ = 0
Complete non-wetting Θ = 180°

For intermediate cases (Gamma=gamma*cosΘ)

$$P_{inner} = P_{outer} + \frac{2\gamma\cos\Theta}{r}, \qquad h = \frac{2\gamma\cos\Theta}{\rho g r}$$

(8.32)

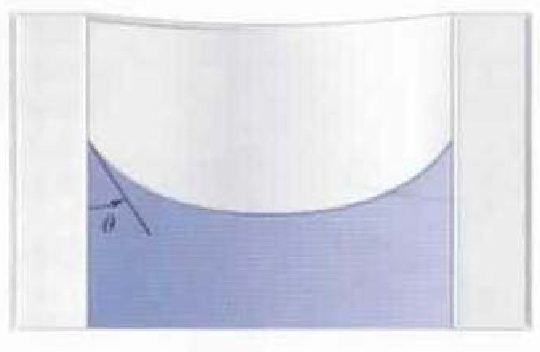

FIGURE 8.18

For cases intermediate between wetting and nonwetting, the contact angle θ lies in the range $0° < \theta < 180°$.

8.9 Chemistry in Supercritical Fluids

SCF near critical point ($T_r=T/T_c=1.0-1.1$, $P_r=P/P_c=1-2$) shows favorable properties of liquid and gas.

That is, high density of SCF (as compared with gas) → high solid (reactant) solubility...... (A)
Low density of SCF (as compared with liquid) → high diffusivity of reactant.....(B)
(A) + (B) → High mass transfer and high reactivity

Examples of Applications

►Supercritical CO_2 (Pc=73bar, Tc=304K, easily attainable condition) replaces toxic solvent for dry cleaning industry.

►Many hydrogen bonds in supercritical H_2O (Pc=220bar, Tc=647K) are destroyed →Dielectric constant changes from 80 (normal) to 5. At low end of the +range, supercritical water acts as nonpolar solvent and is effective in dissolving organic materials.

8.10 Liquid Crystal Display

Three states of matter: solid, liquid, gas

Crystalline solid = Perfectly ordered (See Figure 8.20)
Liquid = Randomly oriented (molecules)
Liquid crystal= There is some order in liquid state.
(The degree of order is between solid and liquid)

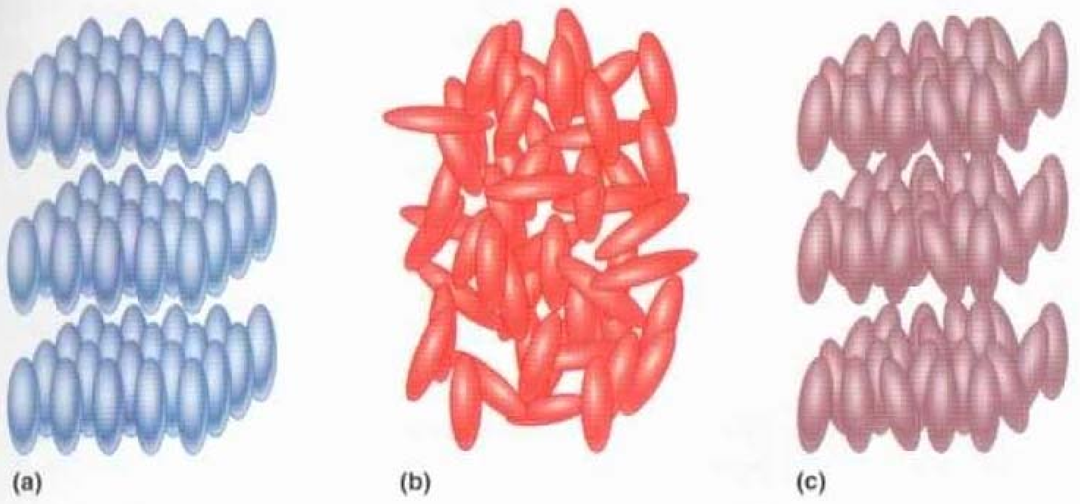

FIGURE 8.20

Solid **(a)** liquid **(b)** and liquid crystal **(c)** phases are shown.

Why liquid crystals have some order in liquid state?

They are rod-like shape having polar groups (Figure 8.19).
Rod-like structure = Rigid = No chain coiling or folding
Polar groups = Strong intermolecular interactions

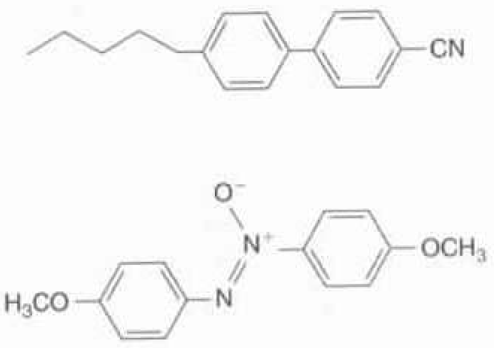

FIGURE 8.19

Liquid crystals are generally formed from polar organic molecules with a rod-like shape.

Types of LC

-Nematic (1D order, used for LCD)

TN (Twisted nematic, Twist angle=90°, Figure 8.21),
STN (Twist angle > 90°)
-Smectic (2D order), and
-Cholesteric (Periodic)

►TN phase consists of parallel planes in which the angle of preferred orientation increases as the number of layer increases.
►Light incident on TN is partially reflected, and partially transmitted from a number of layers.
►A maximum reflection occurs if the angle of incidence and spacing between layers make constructive interference in the light reflected from successive layers. This occurs only in a narrow range of wavelength.
►So, the film is colored with the color determined by the wave length. Red=633, Green=516, Blue=488nm.
►As temperature changes, layer spacing, and therefore color of the reflected light changes.

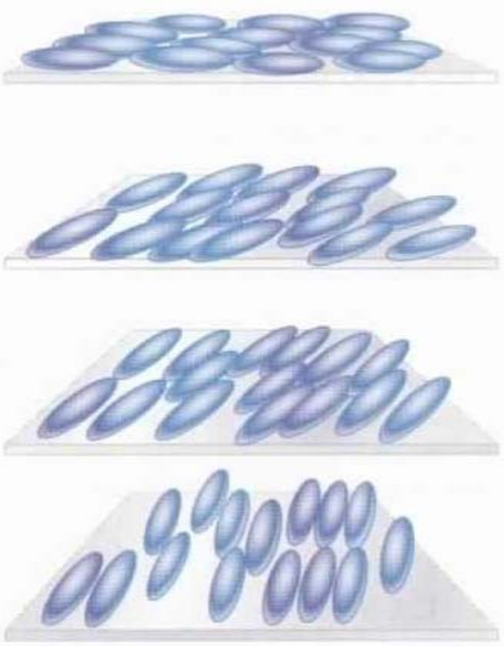

FIGURE 8.21
In a twisted nematic phase, the direction of preferential orientation of the rod-like molecules increases in a well-defined manner from one plane to the next.

Operating principle (Figure 8.22)

TN LC is sandwiched between two transparent conducting electrodes. Film thickness is such that the orientational direction rotates by a total of 90° through the film.

Ambient light is incident on an upper polarizing filter that allows only