Module 3: "Thin Film Hydrodynamics"

Lecture 17: ""

The Lecture Contains:

Case 1 (Isothermal condition)

- Ostwald Pipening
- Bubbles (") in liquid (')
- Cappilary Condensation
- Adsorption Isotherm
- Mercury Porosimeter

Previous Next

CASE 1 (Isothermal condition)

If we increase the radius by a small amount, say $'r(r_1)'to\ 'r + dr(r_2)'$.

$$\ln\frac{p_1}{p_0} = 2\frac{\bar{V}''\gamma}{r_1 RT};\ p_1 > p_0$$

$$r_1 < r_2 \Rightarrow p'_1 > p'_2$$

That will lead to condensation.
Vice versa

If $r_1 > r_2 \Rightarrow p'_1 < p'_2$

That will lead to condensation.
Vice versa

$$r_1 > r_2 \Rightarrow p'_1 < p'_2$$

That will lead to evaporation.

$$\ln\frac{p'_2}{p_0} = 2\frac{\bar{V}''\gamma}{r_2 RT}; p'_2 > p_0$$

By similar analogy, one can show the solubility of a drop in comparison to flat surface.

$$\ln\frac{C'}{C_0} = 2\frac{\bar{V}''\gamma}{rRT}; C' > C_0 \qquad (4.21)$$

Where $\bar{V}''$ is the molar volume of crystal/drop.

Previous Next

Ostwald Ripening

This phenomenon is closely related to Kelvin equation.

As from Kelvin equation, it is clear that a smaller drop will have a higher saturation pressure in comparison to bigger drop hence the smaller one has a tendency to dissolve and bigger one to grow on expense of smaller one. So, one can conclude that smaller crystals have higher solubility.

Similar incident one notices in catalyst substrate surface where small drops of catalyst merge or agglomerate to form bigger drops and this leads to drop in surface area of catalyst.

This tendency also explains the self-stabilizing nature of a disturbed surface if it is left for a long time.

Bubbles (") in liquid (')

$$\int_{p_0}^{p''} \frac{\bar{V}' - \bar{V}''}{\bar{V}'} dp'' = \int_{\infty}^{r} d\left(\frac{2\gamma}{r}\right)$$

$$\bar{V}'' \gg \bar{V}'; \; \bar{V}'' \approx \frac{RT}{p''}$$

$$\ln\frac{p''}{p_0} = -2\frac{\bar{V}'\gamma}{rRT}$$

$$\Rightarrow p'' < p_0$$

This is also not stable equilibrium.

$$p'' = p' + \frac{2\gamma}{r};$$

So to form a bubble we reduce p', which causes cavitations.

Table 4.6

Radius of nuclei (nm)	p'/p_0	p''/p_0
1000	1.001	0.999
100	1.011	0.98
10	1.12	0.9
1	3	0.3

So it is clear that for a radius >1000 nm, equilibrium conditions do not change drastically.

Previous Next

CAPILLARY CONDENSATION

As it's was proved earlier that for condensation super saturated vapor is required.
However, in presence of small corners or pores, we can observe this phenomenon even if the vapor is under-saturated.
Suppose a pore is present
Here meniscus is assumed a part of the sphere i.e. part of a vapor bubble.

$$\ln\frac{p''}{p_0} = -2\frac{\bar{V}'\gamma}{R_c RT}\cos\theta$$

If $p'' < p_0$ bubble would be in chemical equilibrium.

So here, bulk condensation is not possible since vapor is under saturated but capillary condensation is possible.
For porous material, much of the material is absorbed by capillary condensation.
The agglomeration of suspended particles and aerosols is also explained by capillary condensation.

Consider two spherical particles in contact (Fig 4.6)

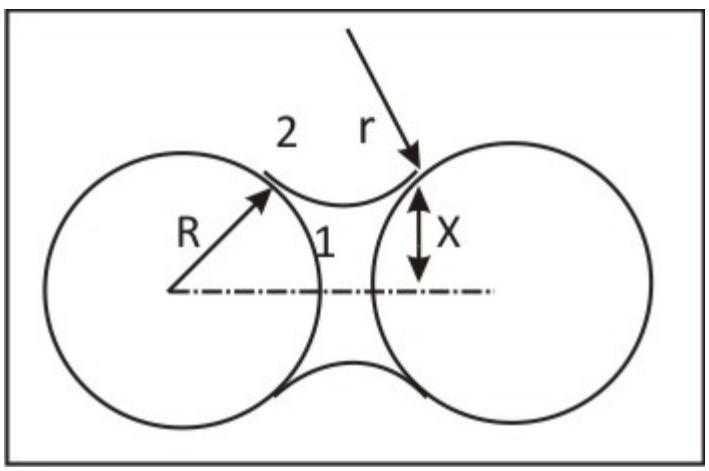

Fig:4.6:

Previous Next

Height is defined by

$$\ln\frac{p''}{p_0} = -2\frac{\bar{V}'\gamma}{R_c RT}\cos\theta \qquad (4.22)$$

Where R_c is the maximum size of the drop that will be filled up.

The out of plane radius $'r' \gg$ in plane radius, hence

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{1}{R_1} = \frac{1}{r}$$

$$(R+r)^2 = R^2 + r^2 + 2Rr = R^2 + (r+x)^2$$

$$\Rightarrow r = \frac{x^2}{2R - r} \approx \frac{x^2}{2R};$$

$$p_1 < p_2$$

=> So, the net squeezing force due to pressure difference leads to force of attraction.

$$\Delta p = \frac{2\gamma}{r} = \frac{2R\gamma}{x^2}$$

$$Force: \Delta p\, \pi\, x^2 \approx 2\pi\, R\gamma$$

if contact angle θ is not zero then,

$$F = 2\pi\, R\gamma\, \cos\theta \qquad (4.23)$$

Previous Next

ADSORPTION ISOTHERM (with reference to Fig.4.7)

- 'M' represents amount adsorbed at equilibrium.
- In region '1' adsorption follows a linear path.
- In region '2', saturation has almost been reached and monolayer adsorption has occurred.
- In region '3' bulk condensation starts.
- The dotted curve represents the porous medium where most of the pores are of same radius R_c. A jump is observed at the pressure when all of these pores are filled up.

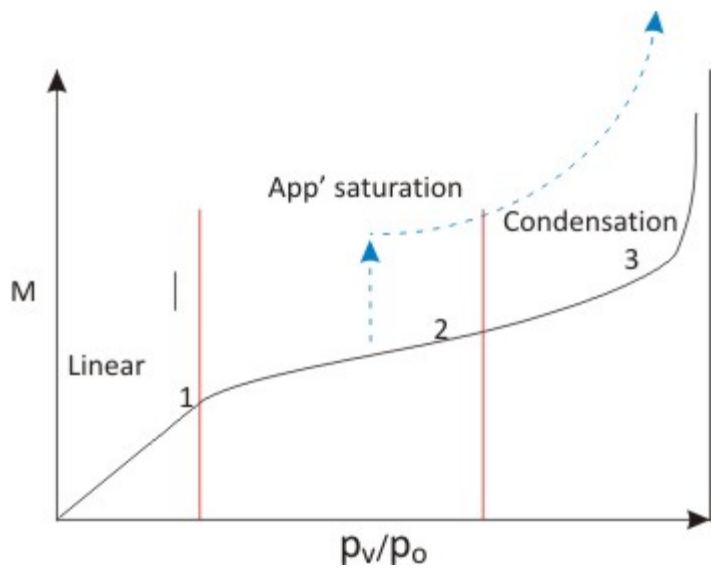

Fig:4.7: Saturation curves for non porous material(solid curve) and for material with almost constant pore radius R_c (dotted)

Hysteresis

When a filled pore is emptied, it does not follow the same path as it did during filling and a hysteresis loop is observed. If pore radius distribution is uniform then this curve also would be smooth (there won't be a sharp rise and fall)

Previous Next

Reasons

- Due to inkbottle effect, saturation pressure required for emptying is smaller than filling because the bottom radius is larger than mouth radius.
- Contact angle of advancing (filling) is greater than contact angle of receding (emptying).

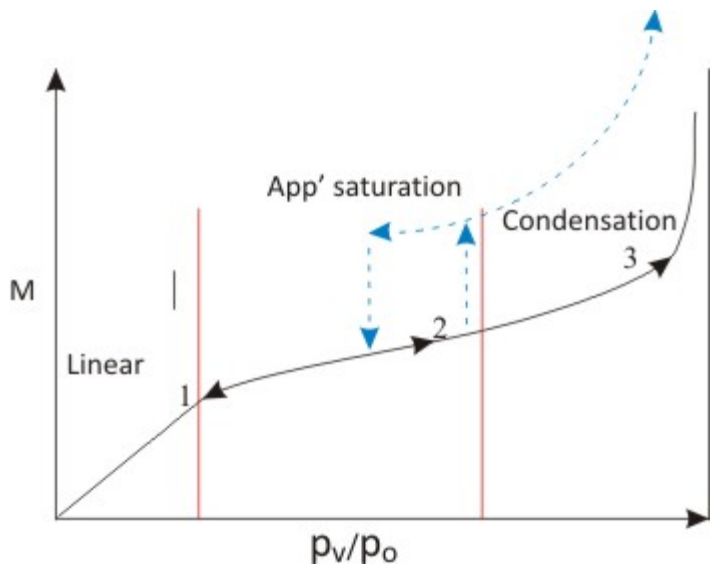

Fig:4.8: Saturation curves for non porous material(solid curve) and for material with almost constant pore radius R_c (dotted)

Mercury Porosimeter

It works on the same principle. As contact angle for mercury is $180°$, it does not fill pores by capillary condensation. To fill the pores, external pressure has to beapplied.

$$\Delta p = \frac{2\gamma|\text{Cos}\theta|}{r}$$

All pores of radius $r > \frac{2\gamma\ |\text{Cos}\theta|}{p}$ would get filled.

Previous Next

We can also get the volume distribution of pores as follows

$dV = D(r)dr;$

$\mathrm{D(r)}$: the distribution function

dV: Volume of the pores with radii $'\mathrm{r}'$ to $'\mathrm{r+dr}'$

since γ and θ are fluid properties, so from the equation $\Delta p = \frac{2\gamma\ |\mathrm{Cos}\theta|}{r}$, we can get

$pdr + rdp = 0$

$$dV = D(r)\left|-\frac{rdp}{p}\right|$$

$$D(r) = \frac{p}{r}\frac{dV}{dp} = \left[\frac{1}{r}\frac{dV}{d\ln p}\right]$$

but

$$r = \frac{2\gamma}{p}$$

$$\Rightarrow D(r) = \left[\frac{p}{2\gamma}\frac{dV}{d\ln p}\right] \qquad (4.24)$$

A graph between volume adsorbed $'\mathrm{V}'$ and $'\ln \mathrm{p}'$ would give the volume distribution function.

Previous Next