INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
34100 TRIESTE (ITALY) - P.O.B. 586 - MIRAMARE - STRADA COSTIERA 11 - TELEPHONES: 224281/2/3/4/5/6
CABLE: CENTRATOM - TELEX 460392 - I

SMR/388- 22

SPRING COLLEGE IN MATERIALS SCIENCE ON 'CERAMICS AND COMPOSITE MATERIALS'

(17 April - 26 May 1989)

WETTING

P. TARAZONA
Depto de Fisica de la Materia Condensada
Universidad Autonoma de Madrid
E-28049 Madrid
Spain

These are preliminary lecture notes, intended only for distribution to participants.

WETTING

P. Tarazona
Depto de Fisica de la Materia Condensada
Universidad Autonoma de Madrid
Madrid, E-28049, Spain

Two lectures in the 1989 ICTP Spring College in Materials Science on "Ceramics and Composite Materials", covering the following subjects:

- Introduction to wetting phenomena.
- Static properties:
  - Wetting and prewetting transitions.
  - Wetting layers.
- Dynamics of wetting:
  - Contact angle hysteresis.
  - Precursor films.
  - Equilibration of wetting layers.
- Wetting in complex systems and geometries.

General references:

P.G. de Gennes, Rev. Mod. Phys. 57, 827 (1985).

D.E. Sullivan and M.M. Telo da Gama, in "Fluid Interfacial Phenomena", edited by C.A. Croxton (Wiley, New York, 1986).

S. Dietrich, "Wetting Phenomena" in " Phase transitions and Critical Phenomena", vol 12, editors C. Domb and J.L. Lebowitz (Academic 1988).

WETTING :

WHEN AND HOW DOES A LIQUID SPREAD ON A SOLID SURFACE ?

- THEORETICAL ANALISIS SINCE T. YOUNG AND LAPLACE (about 1800)
- MANY PROBLEMS OF PRACTICAL APPLICATION:
  - LUBRICATION
  - PAINTING
  - PRINTING
  - CAPILLARITY
  - ...

SINCE THE DISCOVERY OF THE "WETTING TRANSITION" IN 1977 THE MEANING OF "WETTING" HAS BEEN GENERALIZED TO: BOUNDARY EFFECTS ON FIRST ORDER PHASE TRANSITIONS

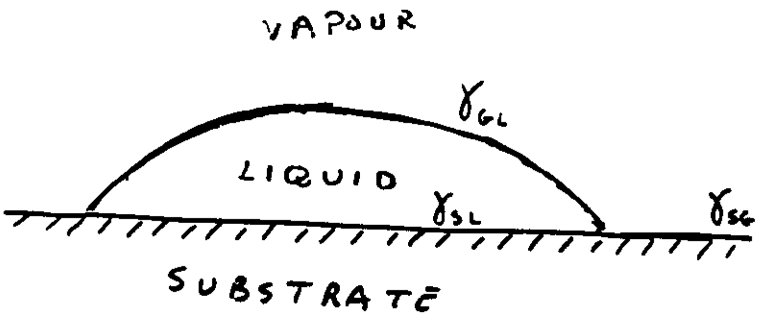
- IN THIS BROADER SENSE, THE WETTING PHENOMENA HAVE BEEN STUDIED IN
  - SEGREGATION IN SOLID ALLOYS
  - " IN MULTICOMPONENT LIQUIDS.
  - MAGNETIC DOMAINS
  - STRUCTURAL PHASE TRANSITIONS
  - LIQUID CRYSTALS
  - ...

GENERAL REFERENCES

- P.G. DE GENNES, REV. MOD. PHYS. 57, 827 (1985)
- D.E. SULLIVAN & M.M. TELO DA GAMA, in "FLUID INTERFACIAL PHENOMENA". Ed. C.A. CROXTON (WILEY, N.Y. 1986)
- S. DIETRICH, "WETTING PHENOMENA" in "PHASE TRANSITIONS AND CRITICAL PHENOMENA" VOL 12, Ed. C. DOMB & J.L. LEBOWITZ (ACADEMIC, 1988)

MICROSCOPIC DROPS (TYPICAL SIZE $R \approx 1 \mu m$)

WHAT DETERMINES THE SHAPE OF A LIQUID DROP ON A SOLID SUBSTRATE ?



i) SURFACE TENSIONS

$$\gamma_{GL} \equiv \gamma$$

$$\gamma_{SG} - \gamma_{SL} \equiv \Delta\gamma_s$$

ii) GRAVITY

$$\sim (\rho_L - \rho_G) \cdot g$$

THE RELEVANT PARAMETER TO DECIDE WHETHER i) OR ii) IS THE DOMINANT CONTRIBUTION IS THE <u>CAPILLARY LENGTH</u>

$$\lambda \equiv \left[\frac{\gamma}{(\rho_L - \rho_G) \cdot g} \right]^{1/2} \approx 10^{-3} - 10^{-4} \text{ m}$$

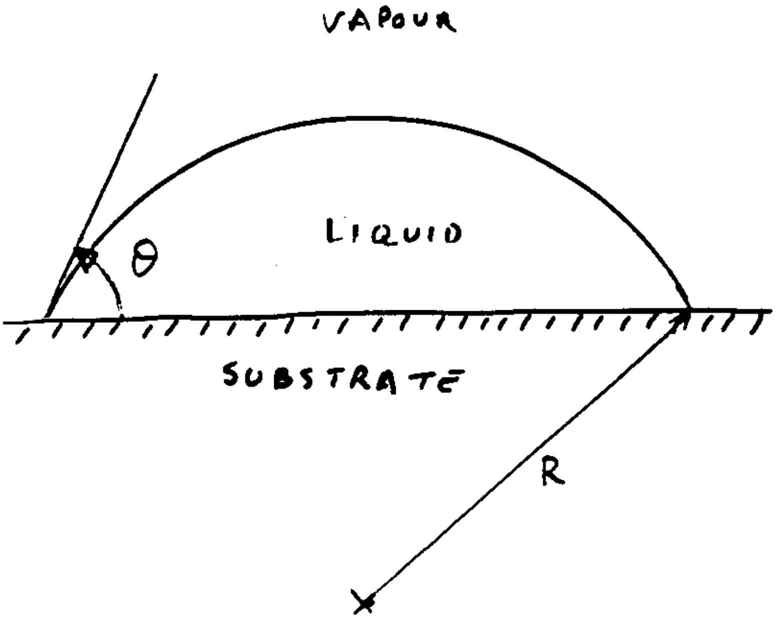
- FOR $\lambda << R$ GRAVITY IS IMPORTANT
- FOR $\lambda >> R$ GRAVITY IS IRRELEVANT

- THE ROLE OF GRAVITY (WHEN IMPORTANT) IS TO FLAT THE DROP

- THE ROLE OF SURFACE TENSION IS A MORE DELICATE BALANCE WHICH GIVE A MANY COMPLEX BEHAVIOURS

WAS STUDIED BY YOUNG AND LAPLACE, 180 YEARS AGO, WITH THE FOLLOWING CONCLUSIONS:

- THE EQUILIBRIUM SHAPE OF THE DROP IS A SPHERICAL CAP, WITH RADIUS R AND CONTACT ANGLE θ



- θ IS GIVEN BY YOUNG'S EQUATION:

$$\boxed{\gamma \cdot \cos\theta = \Delta\gamma_s = \gamma_{SG} - \gamma_{SL}}$$

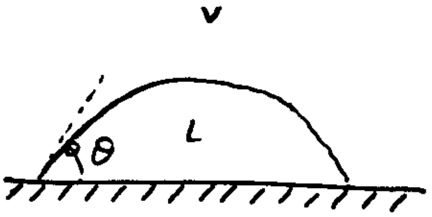
THIS MAY BE REGARDED AS A PARTICULAR FORM OF THE GENERAL WULFF CONSTRUCTION FOR THE SHAPE OF A CRYSTAL.

- THERE IS A DIFFERENCE IN PRESSURE BETWEEN THE INSIDE AND THE OUTSIDE OF THE DROP, GIVEN BY LAPLACE'S EQUATION

$$\boxed{P_L - P_G = \frac{2 \cdot \gamma}{R}}$$

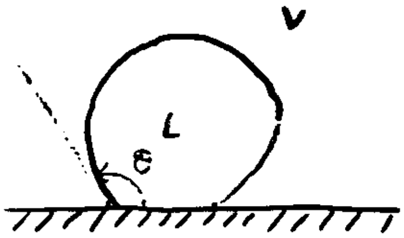
THE DROP IS DETERMINED BY THE PROPERTIES OF THE SEPARATE INTERFACES:

IF $\gamma > \Delta\gamma_s > 0$ THEN $0 < \theta < \frac{\pi}{2}$



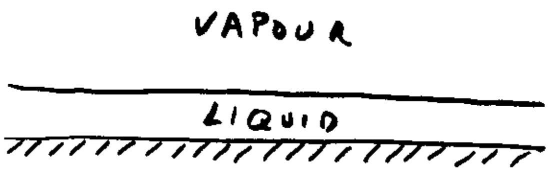
⟺ "PARTIAL WETTING"

IF $0 > \Delta\gamma_s > -\gamma$ THEN $\frac{\pi}{2} < \theta < \pi$



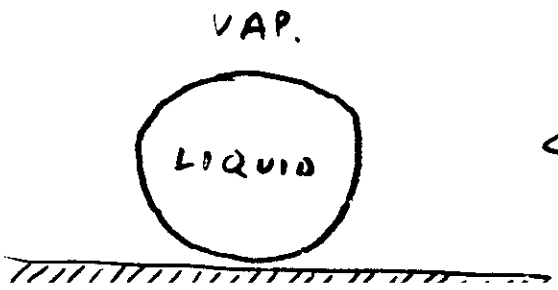
⟺ "PARTIAL DRYING"

IF $\Delta\gamma_s = \gamma$ THEN $\theta = 0$



⟺ "COMPLETE WETTING"

F $\Delta\gamma_s = -\gamma$ THEN $\theta = \pi$

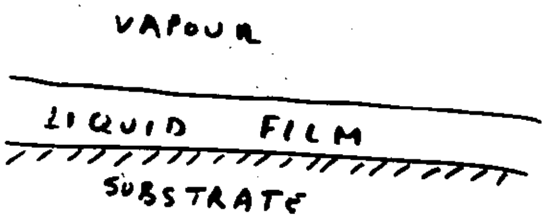


⟺ "COMPLETE DRYING

- AT FIRST GLANCE THE COMPLETE WETTING (OR DRYING) CASE M APPEAR AS A VERY UNLIKELY SITUATION, BEING THE RESULT OF TWO INDEPENDENT QUANTITIES, $\gamma \equiv \gamma_{LV}$ AND $\Delta\gamma_s \equiv \gamma_{SV} - \gamma_{SL}$ BECOMING EQUAL.

- HOWEVER, γ IS AN UPPER BOUND FOR THE POSSIBLE VAL OF $\Delta\gamma$, BECAUSE THE EQUILIBRIUM STRUCTURE OF THE S INTERFACE HAS TO GIVE THE MINIMUN GRAND-POTENTIAL ENER OVER ALL THE POSSIBLE MACROSCOPIC CONFIGURATIONS

IF A VAPOUR IS AT <u>COEXISTENCE</u> WITH A LIQUID THE IS ALWAYS A POSSIBLE CONFIGURATION OF THE SV INTER LIKE



WITH SURFACE TENSION $\gamma_{SL} + \gamma_{LV}$ SO THAT

$$\boxed{\gamma_{LV} + \gamma_{SL} \geq \gamma_{SV}} \Longleftrightarrow \boxed{\gamma \geq \Delta\gamma_s}$$

THUS, <u>ALL</u> THE POSSIBLE SITUATIONS WHICH WOULD LEAD $\Delta\gamma_s > \gamma$ ARE <u>LOCKED</u> IN THE <u>COMPLETE WETTING</u> VALUE $\Delta\gamma_s = \gamma$.

FOLLOWING A PARALLEL ARGUMENT WE MAY ALSO GET THAT THE COMPLETE DRYING VALUE $\Delta\gamma_s = -\gamma$ IS A LOWER BOUND FOR $\Delta\gamma_s$.

TO VALIDATE THE UPPER BOUND $\gamma_{SV} \leq \gamma_{SL} + \gamma_{LV}$ THE SYSTEM HAS TO DEVELOP A THICK (MACROSCOPIC) WETTING LAYER OF LIQUID ALL OVER THE SOLID SUBSTRATE, THIS MAY BE A VERY SLOW PROCESS SO THAT IN MANY PRACTICAL SITUATIONS ONE MAY HAVE NON-EQUILIBRIUM BUT WELL DEFINED SURFACE FREE ENERGIES FOR THE SV INTERFACE γ_{SO} DIFFERENT FROM THE EQUILIBRIUM VALUE γ_{SV}.

IT IS USUAL TO DEFINE A SPREADING COEFFICIENT

$$\boxed{S \equiv \gamma_{SO} - \gamma_{SL} - \gamma}$$

WHICH MAY BE POSITIVE OR NEGATIVE CONTRARY TO ITS EQUILIBRIUM VALUE $\gamma_{SV} - \gamma_{SL} - \gamma = \Delta\gamma_S - \gamma \leq 0$.

S WILL BE ASSOCIATED TO PROCESSES ON "DRY" SOLID SURFACES, WHILE THE EQUILIBRIUM VALUE WILL BE ASSOCIATED TO "MOIST" SURFACES IN WHICH THE LOCAL THERMODYNAMICAL EQUILIBRIUM BETWEEN THE COEXISTING VAPOUR AND LIQUID HAS BEEN ACHIEVED.

S IS THE CRUCIAL PARAMETER TO DETERMINE THE DYNAMICS OF WETTING

- FOR WATER ON METALLIC OXIDES S MAY BE AS LARGE AS 300 erg/cm^2
- FOR ORGANIC LIQUIDS ON OXIDES $S \sim 60$ erg/cm^2

EXPERIMENTAL DETERMINATION OF THE WETTING BEHAVIOUR

— IN PRINCIPLE, THE EVALUATION OF θ WILL ONLY REQUIRE MEASUREMENTS ON THE THREE INDEPENDENT INTERFACES FOR γ_{LV}, γ_{SV} AND γ_{SL} WHICH MAY BE DONE AWAY FROM THE MORE COMPLEX THREE-PHASES LINE.

— HOWEVER, IT IS EASY TO MEASURE γ_{LV} BUT NOT γ_{SV} OR γ_{SL} SO THAT IN PRACTICE IT IS EASIER TO MEASURE θ AND TO GET FROM IT INFORMATION ON $\Delta\gamma_S$.

— THE CONTACT ANGLE θ MAY BE MEASURED BY:

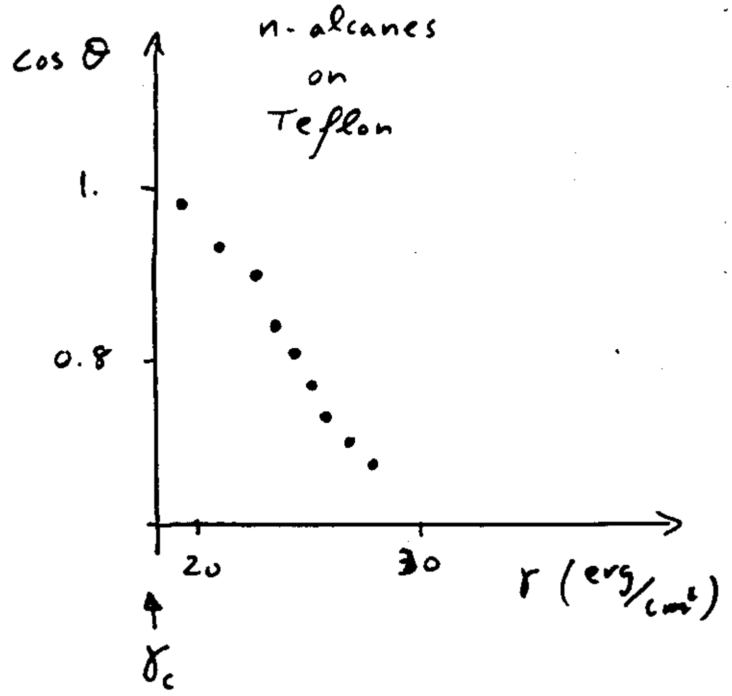
i) DIRECT PHOTOGRAPH
ii) REFLECTION OR REFRACTION BY THE LIQUID | FOR LARGE VALUES OF θ
iii) INTERFERENCE OF LIGHT || FOR SMALL θ
iv) CAPILLARY RISE $h = \frac{\lambda^2 \cos\theta}{R}$

= ALTHOUGH IT MAY APPEAR AS A SIMPLE QUANTITY TO MEASURE, IT IS IN FACT QUITE DIFFICULT TO GET GOOD, REPRODUCIBLE RESULTS BECAUSE OF:

i) CONTAMINATION OR POOR CHARACTERIZATION OF THE SAMPLES

ii) CONTACT ANGLE <u>HYSTERESIS</u> DUE TO THE PINNING OF THE INTERFACE AT CHEMICAL OR TOPOLOGICAL DEFECTS ON THE SURFACE

BY EXTENSIVE STUDIES OF THE CONTACT ANGLE OF A SERIES OF HOMOLOGOUS LIQUIDS (LIKE THE n-ALKANES) ON THE SAME SOLID SUBSTRATE AT ROOM TEMPERATURE, ZISMAN ET. AL. (1950) OBSERVED THAT EACH SOLID HAS A "CRITICAL" γ_c, SO THAT IT IS COMPLETLY WET BY ANY LIQUID WITH $\gamma \leq \gamma_c$



SUBSTRATE	γ_c (erg/cm²)
Nylon	46
P. VINYL CHLORIDE	39
P. ETHYLENE	31
PV F_2	2[illegible]
PV F_4	[illegible]

"THEORETICAL INTERPRETATION" IF THE DOMINANT CONTRIBUTION TO THE FREE ENERGY COMES FROM VAN DER WAALS DISPERSION FORCES $\Delta\gamma_s \simeq V_{SL} - \gamma$ AND $\gamma \simeq \frac{1}{2} V_{LL}$, WHERE V_{ij} REPRESENTS THE VAN DER WAALS INTERACTIONS BETWEEN THE PHASES i AND j ACROSS AN INTERFACE

$$V_{ij} = k\,\alpha_i\,\alpha_j$$

α_i = POLARIZABILITY OF PHASE

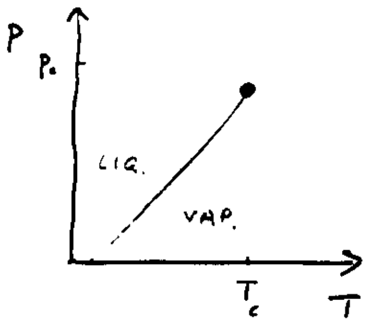
$k \simeq$ CONSTANT

$$\cos\theta = \frac{\Delta\gamma_s}{\gamma} = \frac{V_{SL}}{\gamma} - 1 = \frac{2\alpha_S}{\alpha_L} - 1$$

$$1 = \cos\theta_c = \frac{2\alpha_S}{\alpha_{Lc}} - 1 \Rightarrow \alpha_S = \alpha_{Lc} \Longrightarrow \boxed{\gamma_c = \frac{1}{2} k\,\alpha_S^2}$$

INDEPENDEN OF THE

THE LIQUID - VAPOUR COEXISTENCE ENDS IN A CRITICAL POINT WHERE THE DIFFERENCE BETWEEN LIQUID AND VAPOUR DISAPPEARS



- AS $T \to T_c$ FOLLOWING THE COEXISTENCE LINE THE SURFACE TENSION VANISHES AS:

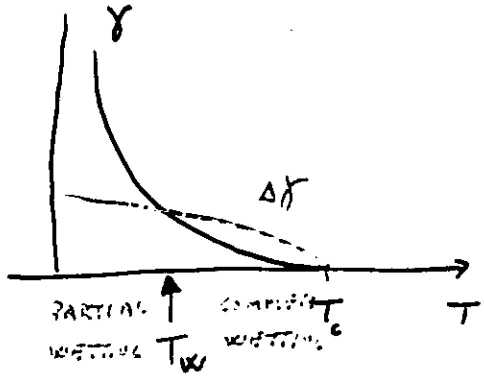
$$\gamma \sim (T_c - T)^{\mu} \quad , \quad \mu = (d-1)\,\nu = 1.26 \quad (\text{FOR } d=3)$$

- THE DIFFERENCE $\Delta\gamma_s = \gamma_{sv} - \gamma_{sl}$ SHOULD ASLO VANISH. CAHN PROPOSED THAT

$$|\Delta\gamma_s| \sim \rho_L - \rho_V \sim (T_c - T)^{\beta} \qquad \beta = 0.32$$

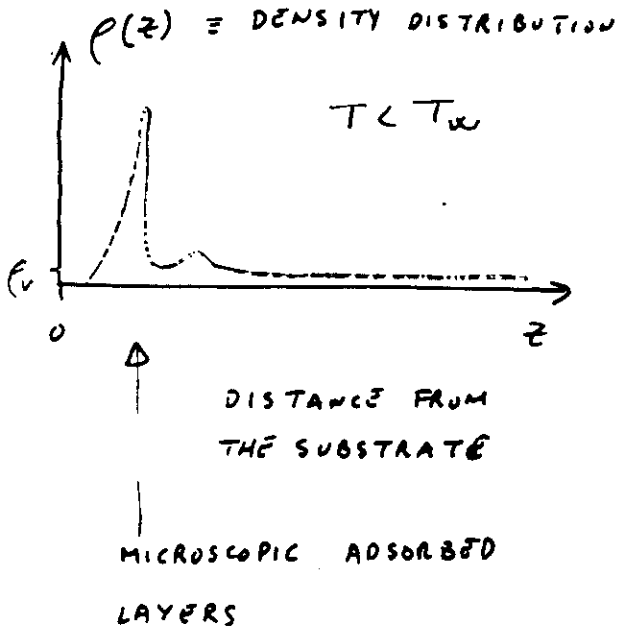
[IN FACT $|\Delta\gamma_s| \sim (T_c - T)^{\beta_1}$ WITH β_1 BEING A SURFACE CRITICAL EXPONENT $\beta_1 \simeq 0.81$]

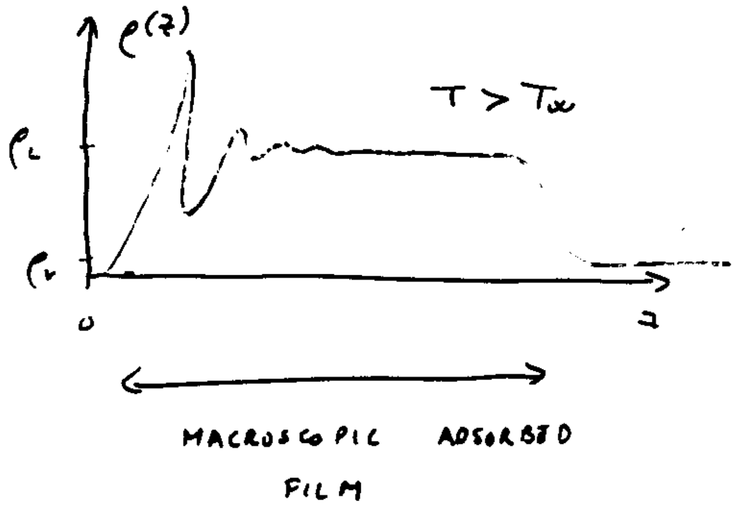
SO THAT AS $T \to T_c$, $\gamma \to 0$ FASTER THAN $|\Delta\gamma|$ WHICH IMPLIES THAT IN THE NEIGHBOURHOOD OF THE CRITICAL POINT, ANY SUBSTRATE WILL BE COMPLETELY WET (OR COMPLETELY DRY).



IF A SUBSTRATE IS PARTIALLY WET AT LOW T. THERE SHOULD BE A WETTING TEMPERATURE, T_W, AT WHICH THERE IS A WETTING TRANSITION FROM PARTIAL TO COMPLETE WETTING.

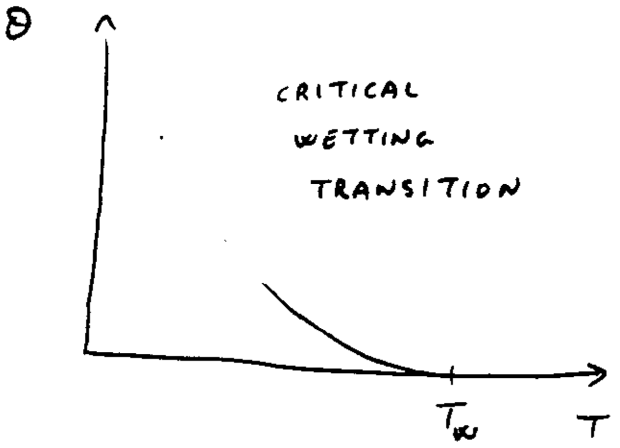
AT MICROSCOPIC LEVEL THERE IS A DRAMATIC CHANGE IN THE STRUCTURE OF THE VAPOUR - SUBSTRATE INTERFACE :

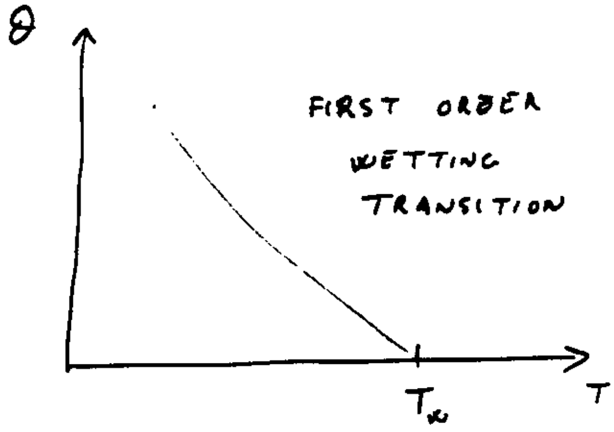




FROM THIS POINT OF VIEW, IT IS CLEAR THAT THE WETTING TRANSITION IS A <u>SURFACE PHASE TRANSITION</u>

FROM EARLY THEORETICAL STUDIES IT WAS CLEAR THAT IT MAY BE A SECOND ORDER PHASE TRANSITION, CALLED CRITICAL WETTING, OR A FIRST ORDER ONE, THE FIRST ORDER WETTING.





AT A CRITICAL WETTING TRANSITION THERE ARE LARGE FLUCTUATIONS IN THE THICKNESS OF THE ADSORBED LAYER, FROM MICROSCOPIC VALUES TO MACROSCOPIC ONES.

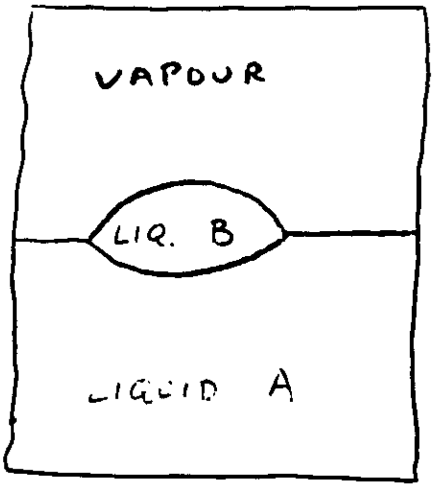
- AT A FIRST ORDER WETTING TRANSITION THE SUBSTRATE IS COVERED BY TWO KIND OF FILM STRUCTURES: A THIN (MICROSCOPIC) FILM AND A THICK (MACROSCOPIC) LAYER. BOTH COEXIST ON THE SUBSTRATE, SEPARATED BY LINE-INTERFACES.

, A CONSIDERABLE INTEREST WAS ATTRACTED TOWARDS THIS SUBJECT DURING THE LAST DECADE. FROM THE THEORETICAL SIDE QUESTIONS LIKE UNIVERSALITY CLASS, GLOBAL PHASE DIAGRAM, FLUCTUATION EFFECTS, RANDOM FIELDS, ETC. HAVE BEEN DISCUSSED

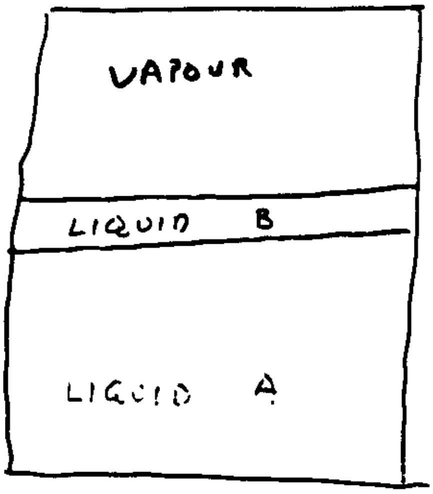
- THEORETICAL PREDICTIONS FOR THE WETTING TEMPERATURE AND THE ORDER OF THE WETTING TRANSITION HAVE BEEN MADE, BASED MAINLY ON THE DENSITY FUNCTIONAL FORMALISM.

- THE MORE REFINED MODELS ARE NOW ABLE TO GIVE GOOD QUANTITATIVE PREDICTIONS FOR SIMPLE FLUIDS ON SMOOTH SUBSTRATES. BUT THERE IS STILL VERY LITTLE KNOWN ABOUT SYSTEMS WITH POLAR MOLECULES, ELECTROLITES, POLIMER SOLUTIONS, ...

THE FIRST CAREFUL EXPERIMENTS SEARCHING FOR WETTING TRANSITIONS WERE REALIZED FOR BINARY LIQUID MIXTURES WHICH SEGREGATE IN TWO LIQUIDS OF DIFFERENT COMPOSITION, WHICH MAY COEXIST WITH EACH OTHER AND WITH A VAPOUR ALONG A TRIPLE COEXISTENCE LINE.



$T < T_w$



$T > T_w$

MIXTURES LIKE:

$CH_3OH - C_6H_{12}$

$C_3H_7OH - C_7F_{14}$

$C_7H_{14} - C_7F_{14}$

$H_2O - C_6H_5OH$

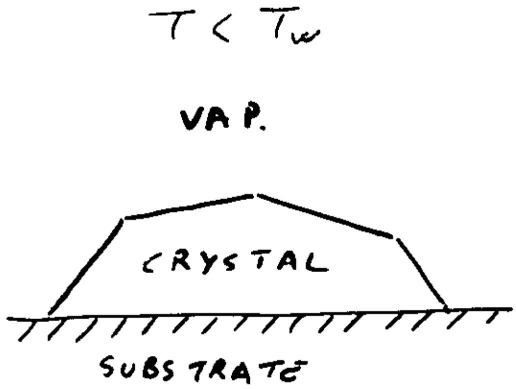
$C_6H_{12} - CH_3CN$

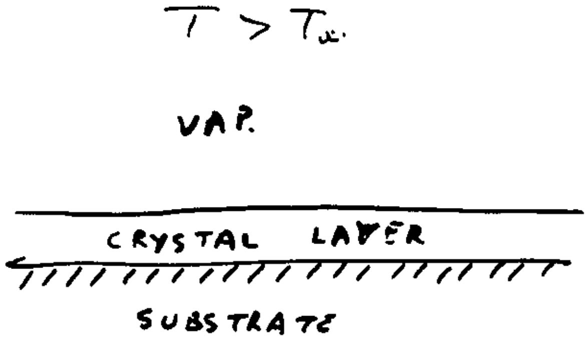
HAVE BEEN STUDIED. HOWEVER, IT WAS REALIZED THAT THE EQUILIBRATION TIMES IN THESE SYSTEMS MAY BE EXTRAORDINARYLY LARGE (UP TO YEARS!), SO THAT MANY EARLIER EXPERIMENTAL RESULTS CANNOT BE CONSIDERED AS EQUILIBRIUM VALUES.

THE OBSERVATION OF WETTING TRANSITIONS ALONG THE LIQUID - VAPOUR LINE ON A SOLID SUBSTRATE, HAS SHOWN TO BE MORE DIFFICULT THAN EXPECTED.

MOST SIMPLE LIQUID COMPLETELY WET MOST OF THE WELL CHARACTERIZED SUBSTRATES, LIKE GRAPHITE

IT IS IN FACT MUCH EASIER TO OBSERVE THE "WETTING" OF A SOLID SUBSTRATE BY A SOLID PHASE ALONG THE SUBLIMATION LINE:





E.G. THE WETTING TRANSITION FOR CF_4, CH_4 AND Ne ON GRAPHITE HAS BEEN REPORTED.

EXPERIMENTS HAVE ALSO BEEN REALIZED FOR THE WETTING OF SOLID PHASES ALONG THE MELTING LINE, LIKE He^4 (hcp) ON Cu.

COMPLETE WETTING HAS BEEN OBSERVED IN MANY OTHER KINDS OF PHASE TRANSITIONS, LIKE LIQUID - CRYSTALS, WITH PECULIARITIES DUE TO THE DIMENSION OF THE ORDER PARAMETER.

IN A COMPLETE WETTING, EQUILIBRIUM SITUATION THERE IS A MACROSCOPIC WETTING LAYER, WITH A THICKNESS GIVEN BY THE AMOUNT OF MATERIAL PER UNIT AREA

HOWEVER, IN MANY CASES WE OBSERVE THICK BUT MICROSCOPIC LAYERS, WHICH ARE A SIGNATURE OF COMPLETE WETTING BUT WHICH CANNOT GROW (OR HAVE NOT GROWN) TO A MACROSCOPIC THICKNESS, BECAUSE:

i) THE SYSTEM IS CLOSE, BUT NOT QUITE AT THE COEXISTENCE LINE.

ii) THE SYSTEM IS IN A NON-EQUILIBRIUM SITUATION, WITH THE WETTING LAYER GROWING FROM A DROP OR RESERVOIR

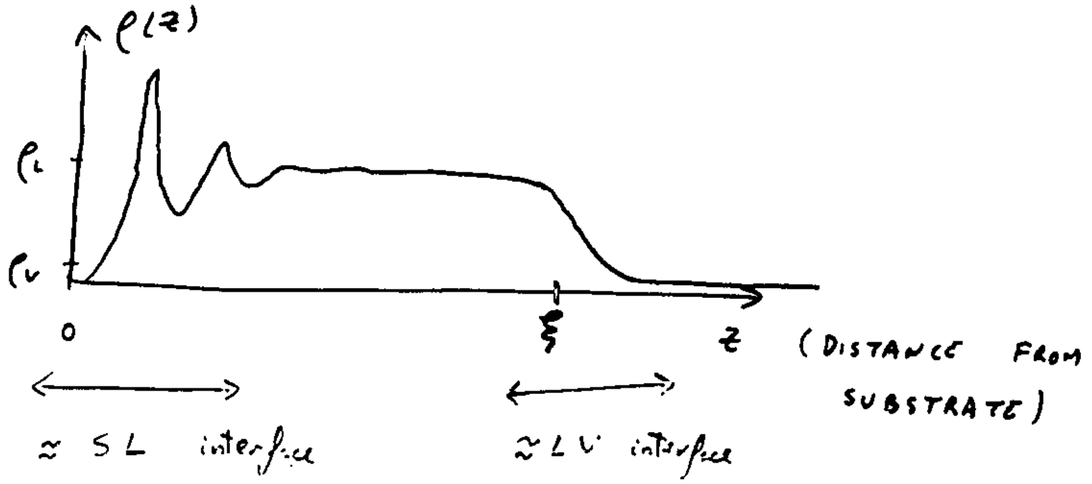
iii) THERE IS NOT ENOUGH MATERIAL TO GROW A MACROSCOPIC LAYER.

IN ALL THESE CASES IT IS OF GREAT THEORETICAL AND PRACTICAL INTEREST TO GET A PRECTION OF THE THICKNESS OF THE WETTING LAYERS.

IN PRINCIPLE, THIS CAN BE DONE WITH FULLY MICROSCOPIC ANALYSIS BASED ON THE DENSITY DISTRIBUTION OF MATERIAL IN THE INTERFACE. IT IS HOWEVER MUCH MORE CONVENIENT TO START WITH A MORE SIMPLE MODEL.

THE WETTING LAYER MODEL

THE REAL DENSITY DISTRIBUTION NEAR A COMPLETE WETTING SITUATION WILL BE SOMETHING LIKE



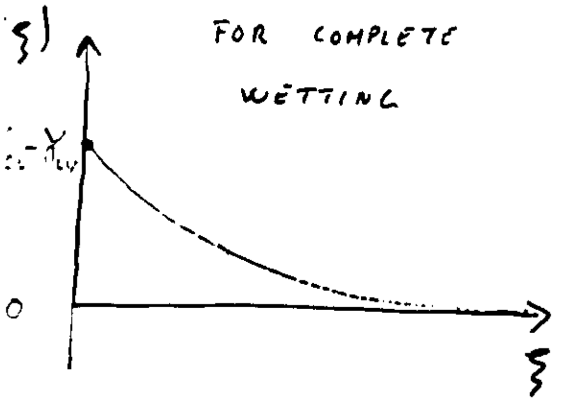
THE FILM THICKNESS ξ MAY BE DEFINED IN SEVERAL EQUIVALENT WAYS, LIKE

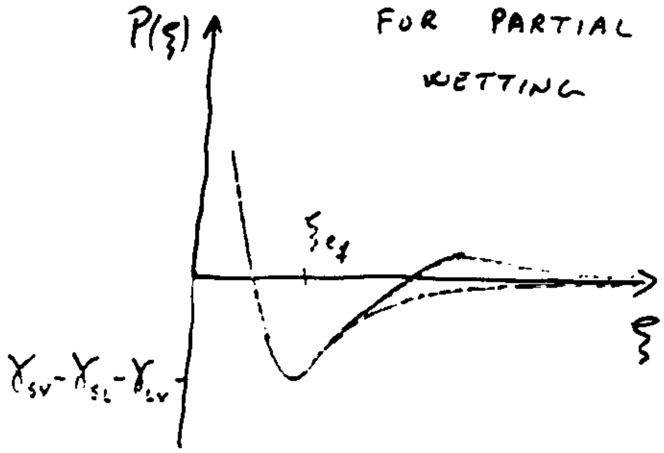
$$\xi \equiv \frac{1}{\rho_L - \rho_V} \int_0^\infty dz \, (\rho(z) - \rho_V)$$

FOR VALUES OF ξ LARGER THAN A FEW MOLECULAR LAYERS (SAY FROM 30 Å UP TO MACROSCOPIC VALUES OF 1 μm), THE STRUCTURE OF THE INTERFACE MAY BE DESCRIBED BY ξ, BECAUSE BOTH THE INNER AND THE OUTER EDGES OF THE FILM HAVE NEARLY FIXED CONFIGURATIONS CORRESPONDING TO THE SL AND THE LV INTERFACES

WHAT IS THE EFFECTIVE FREE ENERGY AS A FUNCTION OF ξ ? $P(\xi)$?

AT BULK COEXISTENCE $P(\xi)$ SHOULD GO TO A CONSTANT VALUE AS $\xi \to \infty$, AND WE MAY TAKE IT AS THE ORIGIN OF FREE ENERGY, SO THAT THE EXPECTED SHAPES FOR $P(\xi)$ ARE :





THE LONG RANGE TAIL OF $P(\xi)$ WILL BE CONTROLLED BY THE KIND OF INTERACTIONS PRESENT IN THE SYSTEM

FOR THE MOST USUAL DISPERSION FORCES WE EXPECT

$$P(\xi) = \begin{cases} \dfrac{A}{12\pi\,\xi^2} & \text{FOR } \xi < \chi \quad \text{(NON-RETARDED)} \\[2ex] \dfrac{B}{3\,\xi^3} & \text{FOR } \xi > \chi \quad \text{(RETARDED VAN DER WAALS FORCES)} \end{cases}$$

WITH $\chi \sim 800$ Å

THE HAMAKER CONSTANTS A, B ARE RELATED TO THE POLARIZABILITY

- IN SYSTEMS WITH SHORT-RANGE INTERACTIONS $P(\xi)$ WILL GO EXPONENTIALLY FOR LARGE ξ

- MORE COMPLEX BEHAVIOURS ARE EXPECTED FOR ELECTROLITES (DOUBLE-LAYERS FORCES), POLIMERS AND OTHER COMPLEX SYSTEMS.

THE EFFECTIVE FREE ENERGY OUT OF BULK COEXISTENCE

WHAT HAPPENS IF THE SYSTEM IS NOT QUITE AT BULK COEXISTENCE, SO THAT THE LIQUID IS ONLY METASTABLE WITH RESPECT TO THE VAPOUR?

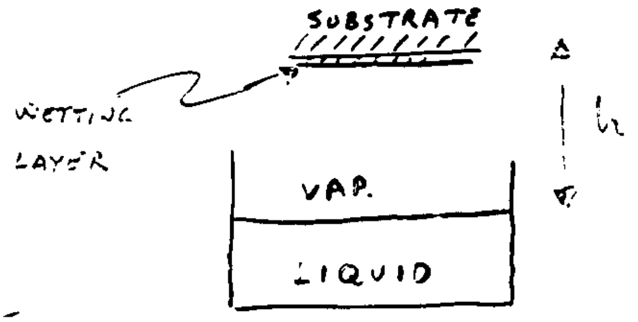
THE GROWTH OF A WETTING LAYER REQUIRES AN INCREASE OF THE GRAND POTENTIAL ENERGY PER UNIT AREA

$$\Delta\Omega = \Delta w \cdot \xi = (p_v - p_L)\,\xi$$

SO THAT A LINEAR TERM HAS TO BE ADDED TO THE $P(\xi)$ CURVES PRESENTED ABOVE.

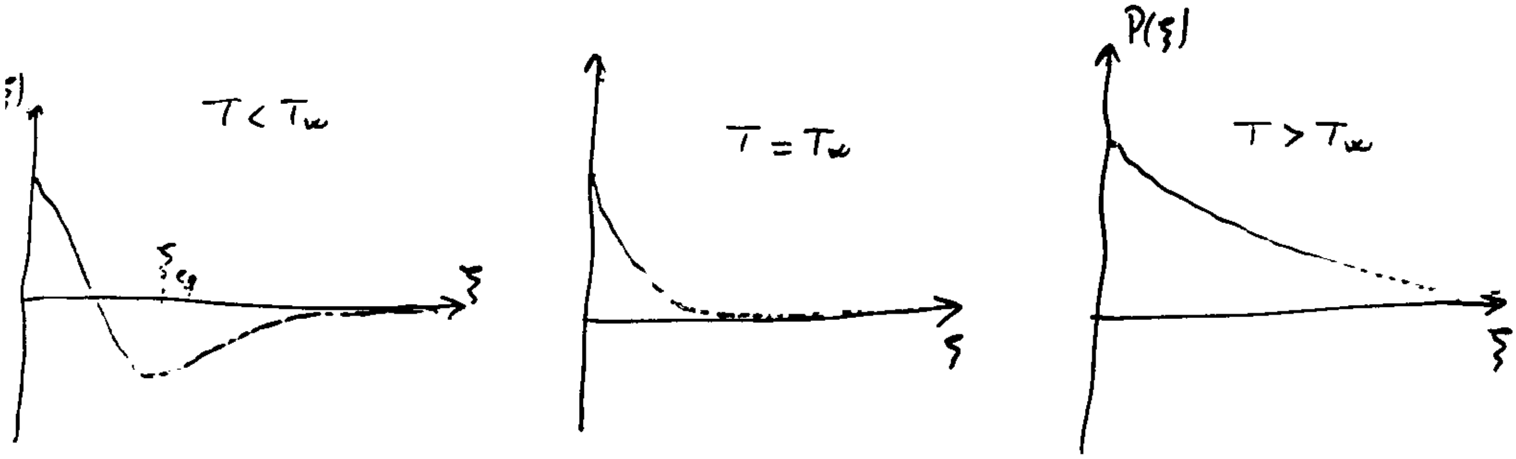
THE SAME EFFECT APPEARS IF THE SUBSTRATE IS A DISTANCE h ABOVE THE LIQUID RESERVOIR IN A GRAVITATIONAL FIELD

$$\Delta\Omega = \rho_L \cdot g \cdot h \cdot \xi$$

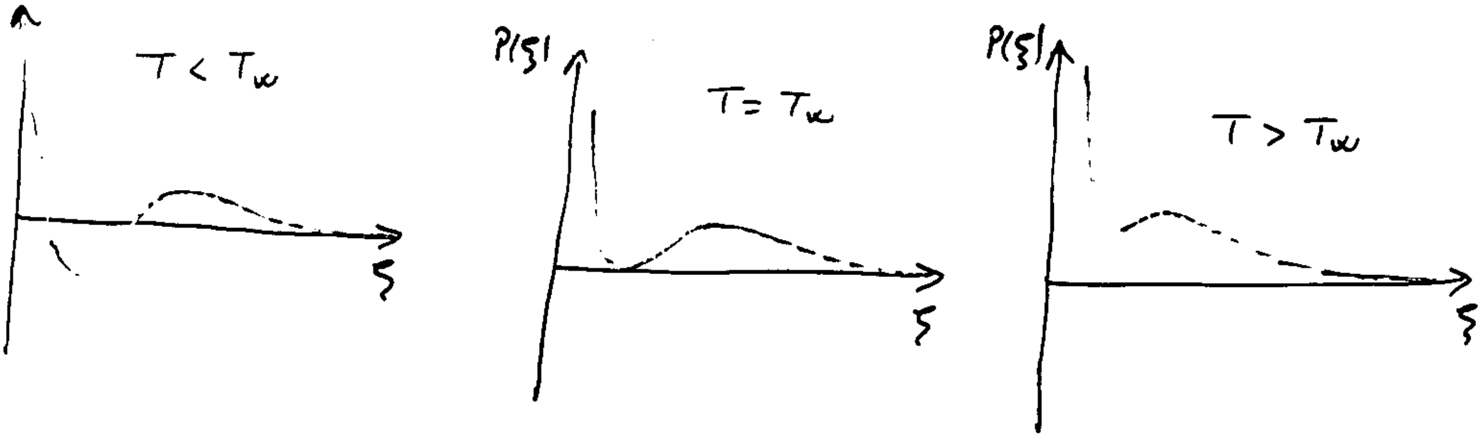


HOW DOES $P(\xi)$ BEHAVE AT THE WETTING TRANSITION?

IF THE TRANSITION IS CONTINUOUS (CRITICAL WETTING) THE MINIMUM OF $P(\xi)$ HAS TO DISPLACE FROM FINITE VALUES (AT $T < T_w$), TO INFINITE (I.E. MACROSCOPIC) VALUES (AT $T > T_w$):

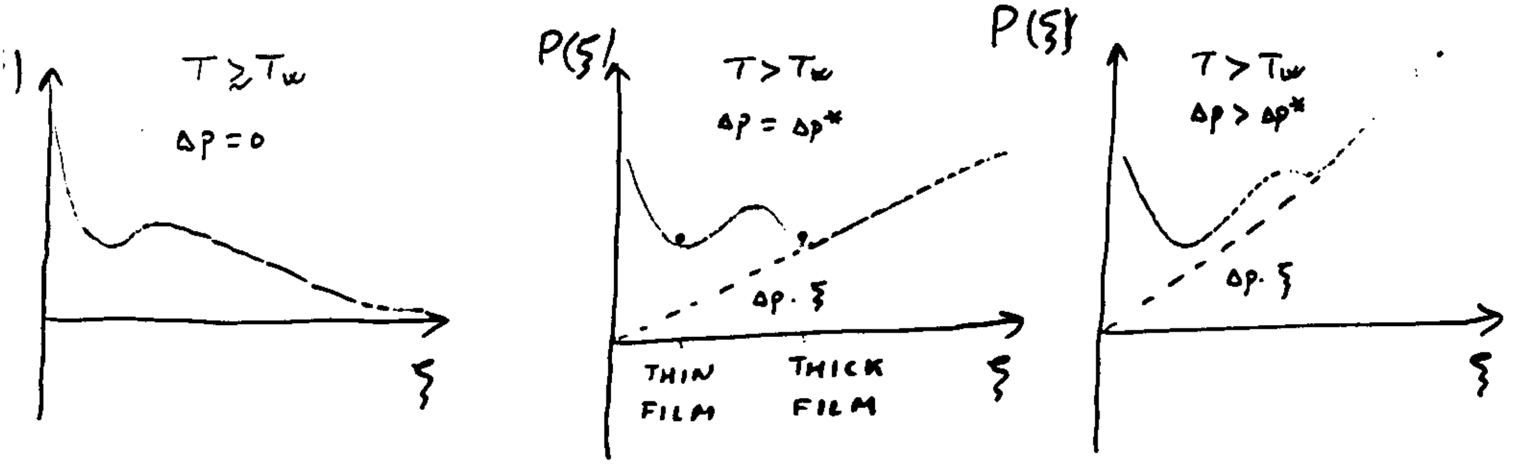


F THE TRANSITION IF OF FIRST ORDER, THERE SHOULD BE TWO COMPETING MINIMA, ONE WITH FINITE (MICROSCOPIC) ξ AND THE OTHER FOR INFINITE (MACROSCOPIC) ξ:



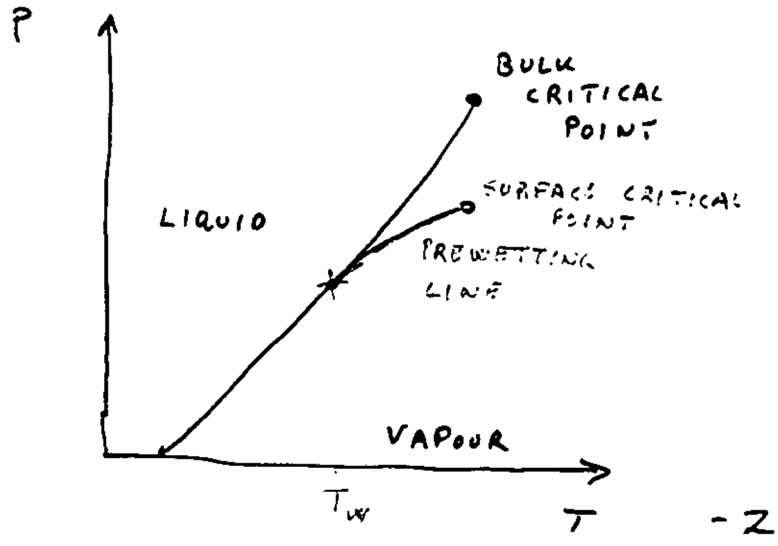
IF WE NOW ADD THE LINEAR

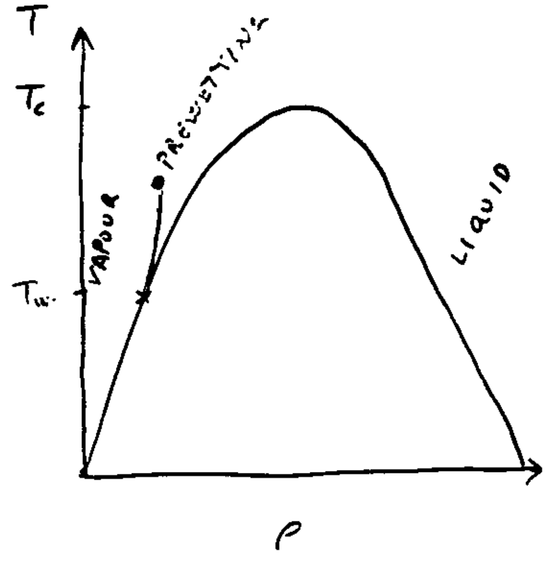
UNDERSATURATION OF THE VAPOUR (OR TO THE PRESENCE OF A GRAVITATIONAL FIELD), WE GET FOR THE FIRST ORDER WETTING CASE THE FOLLOWING CONCLUSION:



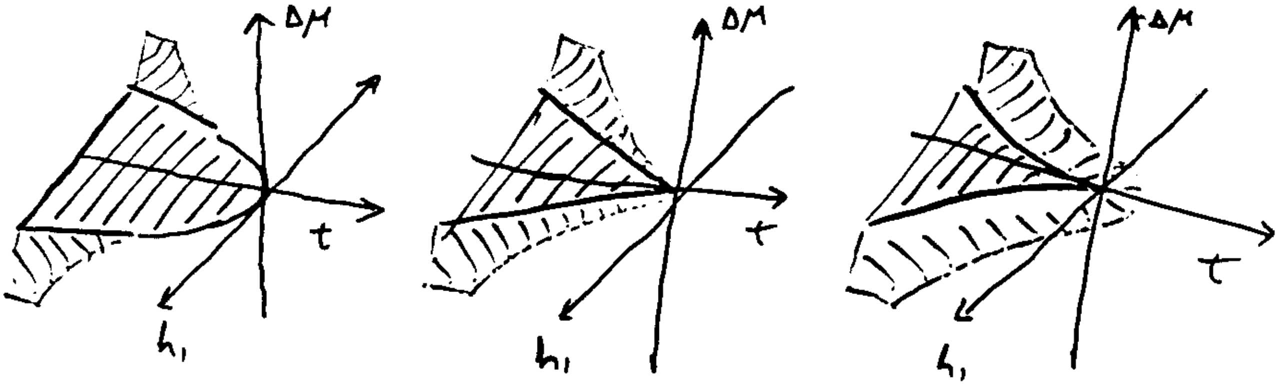
FOR T CLOSE BUT ABOVE T_w THERE IS A SURFACE PHASE TRANSITION, OUTSIDE (BUT CLOSE) TO THE BULK COEXISTENCE LINE.

THIS IS CALLED THE PREWETTING LINE. IT SHOULD BECOME TANGENT TO THE BULK COEXISTENCE LINE AS $T \to T_w$, AND IT SHOULD END IN A SURFACE CRITICAL POINT.





THE GLOBAL PHASE DIAGRAMS FOR WETTING AND PREWETTING TRANSITIONS HAVE BEEN DESCRIBED FOR ISING-LIKE SYSTEMS IN TERMS OF THE SURFACE FIELD AND SURFACE ENHANCEMENT OF THE INTERACTIONS BY NAKANISHI AND FISHER (1985):



▨ BULK COEXISTENCE

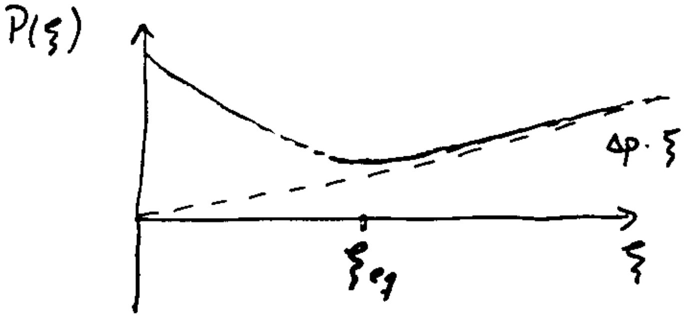
▨ SURFACE PREWETTING COEXISTENCE

— FIRST ORDER W. T.

— CRITICAL W. T.

WETTING LAYERS IN THE COMPLETE WETTING

AT T WELL ABOVE T_W, HOW DOES A WETTING LAYER GROW AS WE APPROACH COEXISTENCE?



THE EQUILIBRIUM VALUE OF ξ IS A BALANCE BETWEEN THE UNDERSATURATION CONTRIBUTION

$$\sim \Delta p \cdot \xi$$

AND THE LONG RANGE TAIL OF $P(\xi)$ AT BULK COEXISTENCE.

FOR VAN DER WAALS FORCES WE HAVE

$$P(\xi) \simeq \frac{a}{\xi^q} + \Delta p \cdot \xi \quad ; \quad \text{with } q = 2 \text{ NON-RETARDED}, \; 3 \text{ RETARDED}$$

(large ξ)

THE MINIMUM IS GIVEN BY

$$\xi = \left(\frac{q \cdot a}{\Delta p} \right)^{\frac{1}{q+1}} \sim \begin{cases} \sim \Delta p^{-1/3} & \text{NON-RETARDED} \\ \sim \Delta p^{-1/4} & \text{RETARDED} \end{cases}$$

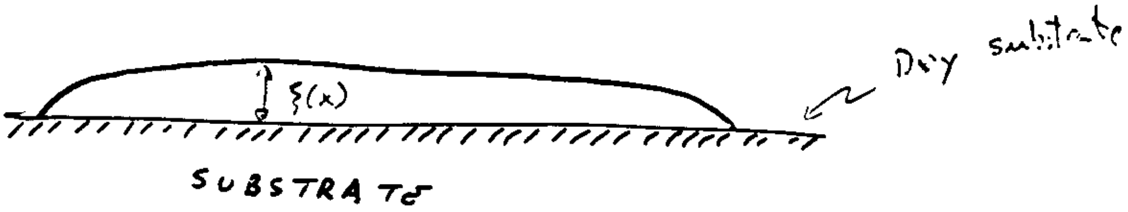
WHICH GIVES A DIRECT MEASUREMENT OF THE DISPERSION FORCES

IF $P_0(\xi)$ SHOWS AN EXPONENTIAL DECAY INSTEAD OF A POWER LAW, THE WETTING LAYER WILL GROW LOGARITHMICALLY WITH Δp

WITH A MACROSCOPIC RESERVOIR OF LIQUID.

WHAT HAPPENS IF WE PUT A FINITE DROP ON A DRY SUBSTRATE?

THE DROP WILL SPREAD OVER THE SUBSTRATE UP TO A FINAL "PANCAKE" SHAPE $\xi(x)$



THE EQUILIBRIUM SHAPE WILL BE THE SOLUTION OF THE EQUATION

$$-\gamma \frac{d^2\xi}{dx^2} + \frac{dP}{d\xi} = 0$$

WHERE $P(\xi)$ MAY INCLUDE GRAVITATIONAL CONTRIBUTIONS.

A FIRST INTEGRAL MAY BE OBTAINED IN TERMS OF THE SPREADING COEFFICIENT S, AS

$$\frac{1}{2}\gamma\left(\frac{d\xi}{dx}\right)^2 = P(\xi) - S$$

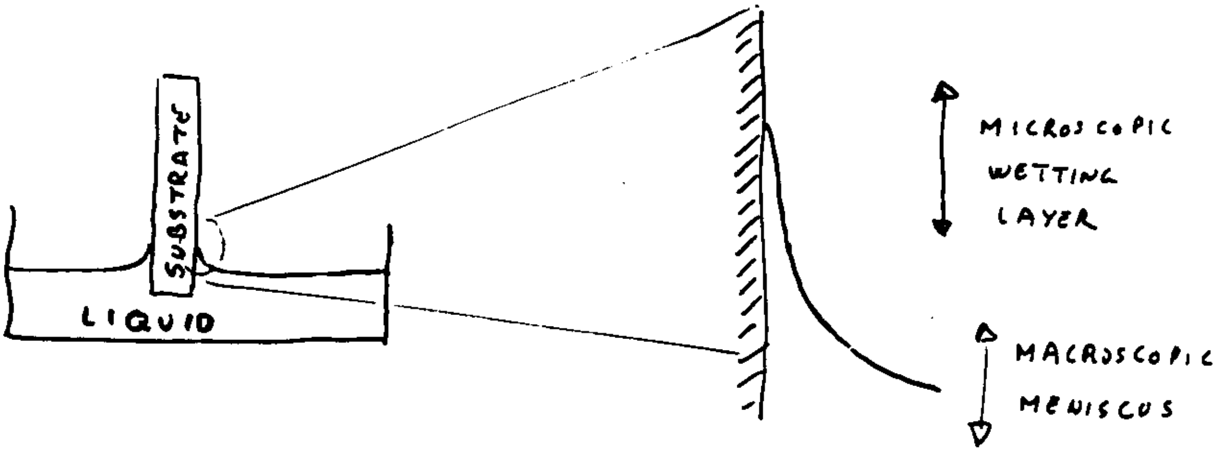
SO THAT THE MAXIMUM VALUE OF ξ IS GIVEN BY

$$\boxed{P(\xi_{MAX}) = S} \Longleftrightarrow$$

FINITE DROPS SPREAD BETTER THE LARGER

EXPERIMENTAL AND THEORETICALLY.

ONE WHICH MAY BE OF IMPORTANT PRACTICAL USE IS THE "VERTICAL WALL"



IN THIS CASE THE THICKNESS OF THE WETTING FILM DEPENDS ON THE HEIGTH, $\zeta(z)$,

FOR VAN DER WAALS FORCES, DE GENNES AND JOANNY GET

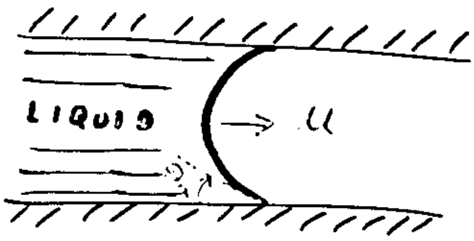
$$\zeta(z) \sim z^{-1/3} \cdot \lambda^{-2/3}$$

UP TO THE THICKNESS OF THE "PANCAKE" CONFIGURATION

THERE ARE MANY INTERESTING PROBLEMS IN THE DYNAMICS OF WETTING AND SPREADING. HOWEVER THE NEED OF VERY CAREFUL CONTROL AND CHARACTERIZATION OF THE SAMPLES, REDUCES THE TRUSTABLE EXPERIMENTAL RESULTS.

HOFFMAN EXPERIMENTS (1975)

BY FORCING A LIQUID IN A CAPILLARY WITH VELOCITY U

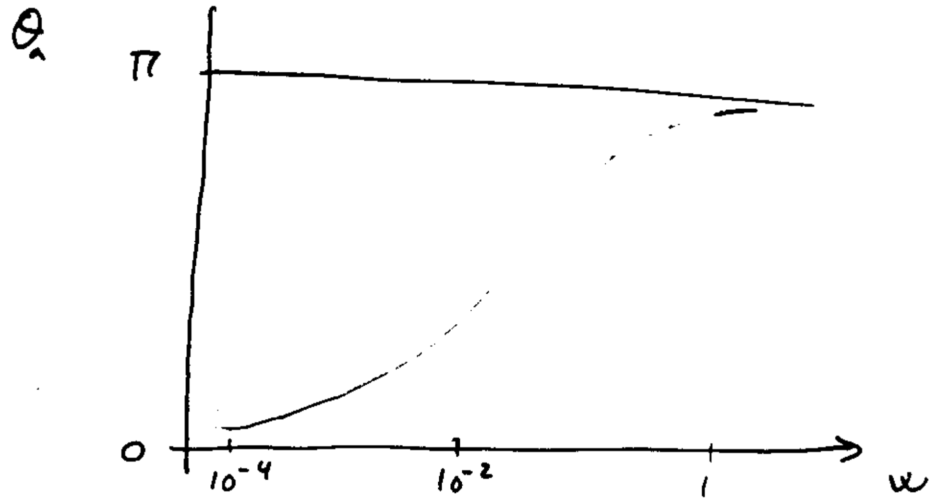


HOFFMAN MEASURED THE AVANCING CONTACT ANGLE θ_a, FOR DIFFERENT LIQUIDS AS A FUNCTION OF U.

IF U IS WRITTEN AS A DIMENSIONLESS PARAMETER

$$w \equiv \frac{U \cdot \eta}{\gamma} \quad , \quad \eta \equiv \text{viscosity}$$

A QUITE UNIVERSAL RELATION IS FOUND : $w = F(\theta_a)$ WITH A FUNCTION F LIKE



[FOR COMPLETE WETTING]

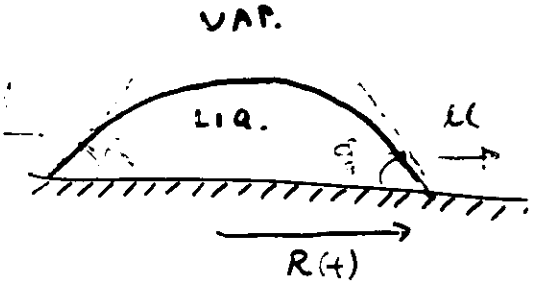
IN THE LOW SPEED LIMIT, $w \ll 1$, TANNER (1979) GOT A WELL DEFINED LAW

$$\boxed{\theta_a \sim w^{1/3}}$$

WHICH HAS BEEN EXPLAINED BY HERVET AND DE GENNES FROM A THEORETICAL ANALYSIS.

THE RATE OF SPREADING OF A DROPLET

IF A DROP IS SPREADING OVER A SUBSTRATE, AND WE ASSUME THAT IT HAS A SPHERICAL CAP SHAPE. WE MAY USE TANNER'S LAW TO RELATE THE VELOCITY OF THE EDGE WITH THE CONCTACT ANGLE.



THE WETTED AREA πR^2 GROWS WITH TIME, WITH THE CONSTRAIN OF CONSTANT VOLUME, Ω, (FOR NEGLIGEABLE EVAPORATION)

IT IS FOUND THAT

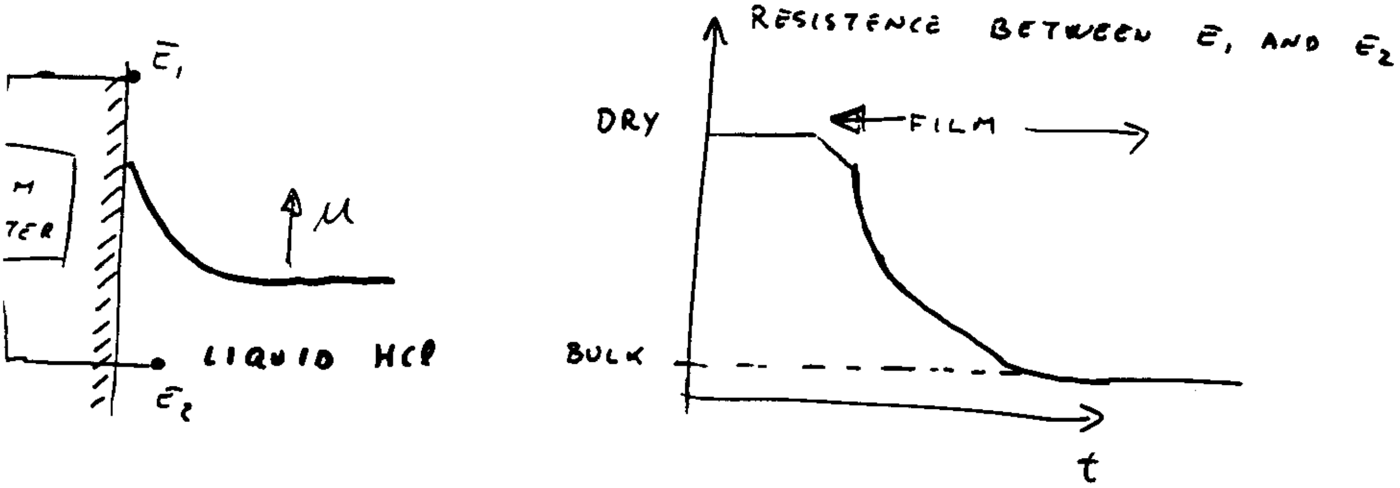
$$\pi R^2(t) \simeq t^n \Omega^p$$

with

$n \simeq 0.20$

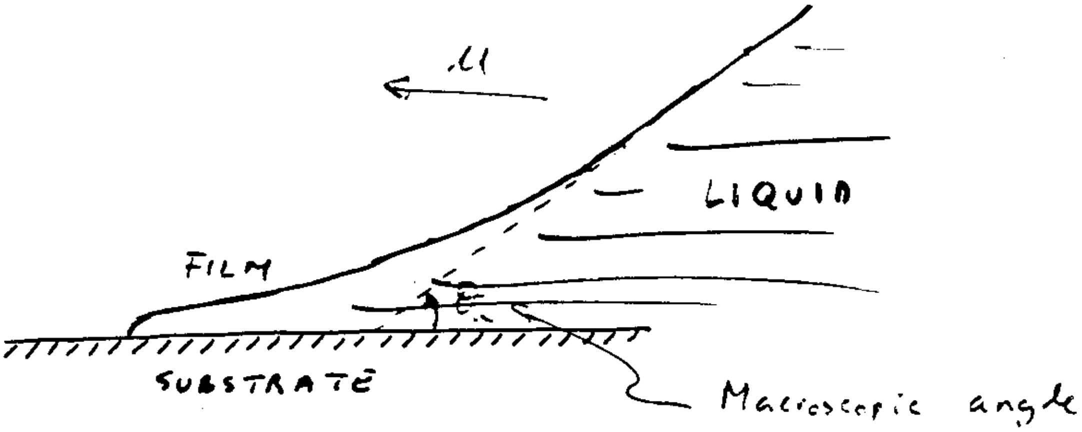
$p \simeq 0.60$

AS EARLY AS IN 1919, HARDY OBSERVED THE PRESENCE OF A MICROSCOPIC FILM ($\xi < 1\mu m$) SPREADING BEYOND THE MACROSCOPIC EDGE OF A DROP, IN A SCALE OF MILIMETERS.



(GHIRADELLA ET. AL. 1975)

AT FIRST THIS WAS THOUGH TO BE AN EFFECT OF RE-CONDENSATION AFTER EVAPORATION FROM THE LIQUID. HOWEVER, IT WAS LATER REALIZED THAT IT IS A RESULT OF THE REQUIREMENTS OF ENERGY DISSIPATION IN THE PROCESS OF SPREADING (DE GENNES..)



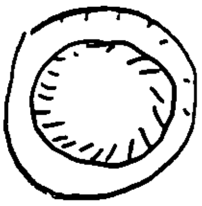
MANY OTHER SYSTEMS MAY BE CONSIDERED IN RESPECT TO THE WETTING PHENOMENA, AND SOME PARTICULAR GEOMETRIES MAY BE OF PRACTICAL INTEREST, LIKE

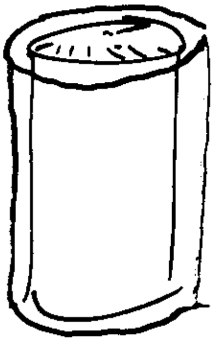
POROUS MATERIALS

FOR POROUS WITH RADIUS LOWER THAN $1\mu m$ THERE MAY BE A STRONG COUPLING BETWEEN THE WETTING AND THE CAPILLARY CONDENSATION.

IN GENERAL, THE COMPLETE WETTING FAVOURS THE LIQUID INSIDE THE POROUS.

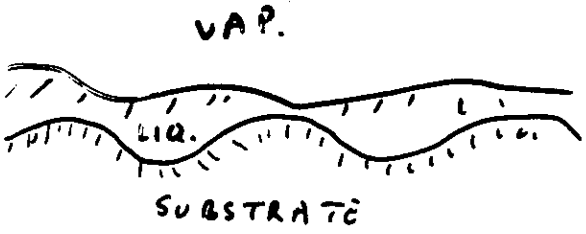
WETTING OF SPHERICAL OR CYLINDRICAL SURFACES





THIS PROBLEM HAS BEEN STUDIED WITH SIMPLE MODELS AND IT PRESENTS PECULIARITIES DUE TO THE CURVATURE OF THE SUBSTRATE.

WETTING ON ROUGH SUBSTRATES



THE PRESENCE OF REGULAR OR RANDOM GROOVES ON THE SUBSTRATE LEADS TO CONTACT ANGLE HYSTERISIS AND OTHER INTERESTING PHENOMENA.

AND MANY OTHERS...