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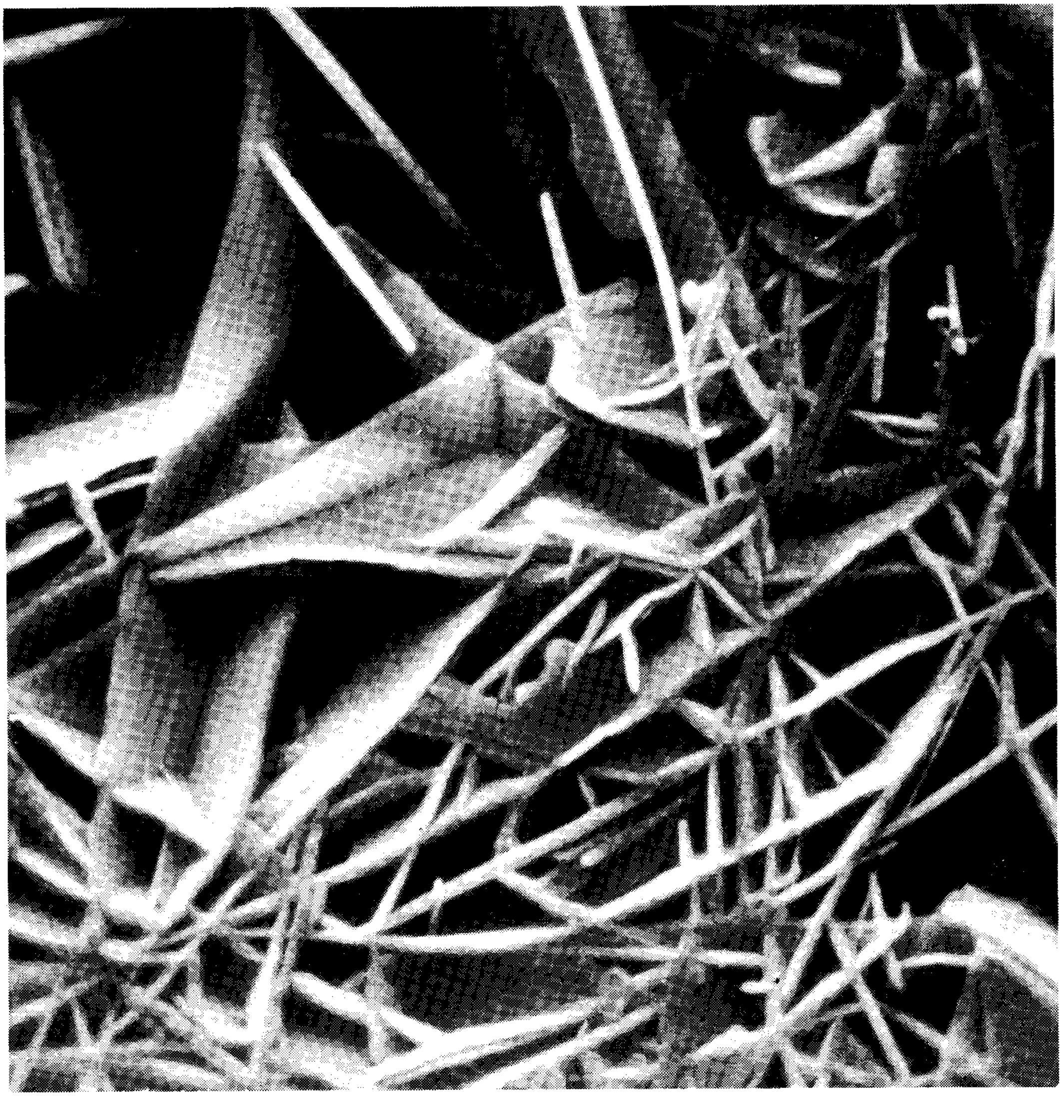
THEORY OF MICROCAPILLARITY

I. Equilibrium and stability



THEORY OF MICROCAPILLARITY

I. EQUILIBRIUM AND STABILITY

JOHAN CLAESSON

PREFACE

This study is intended to be the first part of an investigation of capillary and in particular microcapillary phenomena in porous materials. Further studies will concern, among other things, the thermodynamical character of the instabilities, the motion of water menisci in the pores, a classification of irreversibilities, sorption hysteresis, the relation between pore structure and microcapillary phenomena, the flow of moisture through the pore system, the interaction between solid and pore water in swelling and shrinking, and the extension of the thermodynamical analysis to the case of freezing.

Moisture, salts, and freezing cause great damage to building materials. Combined actions of these agents are often especially detrimental. I think that capillary-osmotic effects are a main cause of these damages. Further studies will be devoted to this topic.

I am deeply indebted to Professor Sven Gösta Nilsson for his unfailing support and guidance during this work. I would also like to express my gratitude to Ingmar Oldberg, Jaak Peetre, and Nils Olof Wallin, who have been very helpful, and to Margareta Bergsten for her excellent typing. I have co-operated with a group of people in Lund concerned in moisture problems in buildings. Discussions with members of this group have been a great stimulus. This study is sponsored by the Swedish Council for Building Research. Their support is gratefully acknowledged.

Lund, April, 1977

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1. CAPILLARY-POROUS SYSTEMS.

Consider a piece of porous material. It consists of solid material and of a pore system, which penetrates the solid. The pore space is filled by moisture or more generally by some substance in different phases. At the pore walls there may be an adsorbed thin layer of the substance. Through capillary condensation some parts of the pore space may be occupied by liquid phases of the substance. The remaining parts of the pore space are filled with gas phases of the substance. Some of these may be totally enclosed by the pore walls and liquid phases. See figure 1:I below. The pore wall will have corners and edges, when the solid contains crystals. Apart from these corners and edges the pore wall will be smooth.

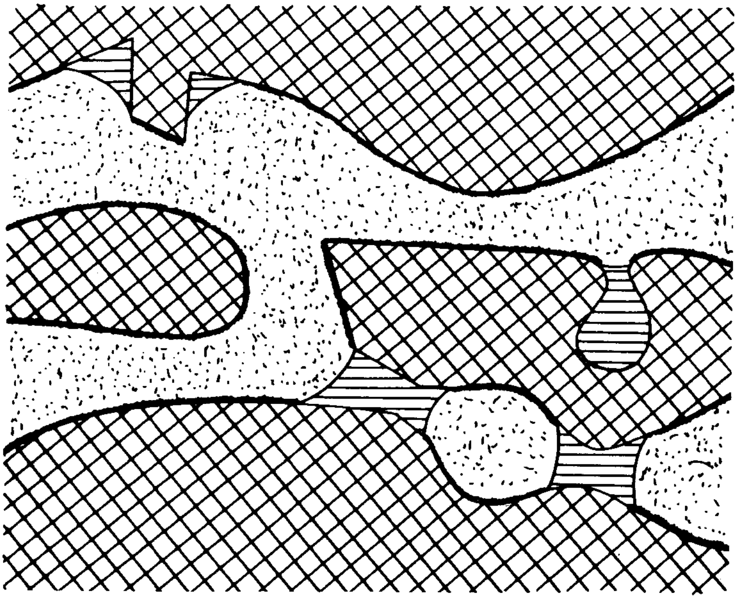


Figure 1:I. Cross-section through a porous material showing solid material (▨), capillary condensed liquid phases (═), gas phases (∷), and adsorbed surface layers (⁓).

We will also consider cases where there are one or several other kinds of molecules in the pore space. Then the gas phases in the pore system consist of a mixture of various kinds of molecules. The condensed liquid phases consist of a solution where the primary substance is the solvent and other substances are solutes.

The piece of porous material may be in contact with various other thermodynamical systems with which it may be able to exchange molecules of the various substances. Thus it may be in contact with a gas phase. It may also be in contact with other porous materials of the same kind or of some other kind. Finally, it may be in contact with a liquid phase of the capillary condensed substance.

For example the considered system may consist of activated carbon surrounded by nitrogen gas at the temperature -195^0 C. Another example is a piece of a porous building material surrounded by water vapor or by humid air at a temperature above 0^0 C. In the latter case there are in the pores except water molecules also the various kinds of molecules of air. Still another example is a piece of brick which is dipped in water or brine.

In order to simplify the terminology it is assumed from now on that the capillary condensing substance is water. With this terminology this study will concern the case, when there are only water molecules in the pores, as well as the more general case, when there also are other kinds of substances present in the pores. Expecially the case when the pores contain water and air will be studied. We will also study cases where the liquid phases contain salts. The temperature is always above the freezing point, so that there is not any ice in the pores.

Natural and manufactured materials are very often more or less porous. Especially building materials, which I have had in mind in this work, are practically all porous. The pore systems are very complicated. It is difficult to give proper characterizations. Consider as an illustration concrete. In the cement paste there are two types of fine pores. When the concrete hydrates, crystal needles grow out from the cement grains 1). The grains, each surrounded by a forest of protruding needles, look like a heap of hedgehogs. In the space between the needles there are pores with linear dimensions of the order of 30 Å. In the space between different grains there are pores with linear dimensions of the order of 1 000 Å or more. The pore volume, defined as the free space in the material accessible from the outside to the water molecules, occupies about 15 % of the total volume of concrete. For brick and cellular concrete corresponding order of magnitude figures are 40 % respectively 75 %.

In spite of the complexity of pore systems and the various gas, liquid, and adsorbed phases that fill them there is an astonishing amount of conclusions that can be drawn from thermodynamical considerations. These conclusions will be valid irrespective of the character and complexity of the pore system.

The more pronounced capillary effects require pores with very small linear dimensions. It is pores with dimensions below 1 000 to 10 000 Å that are of primary interest. Thus it is not visible pores but far smaller ones that cause more marked capillary effects. It is appropriate in this context to talk about microcapillary phenomena and to call this subject microcapillarity. Materials which contain these minute pores, and which are exposed to moisture or some other capillary condensing substance, appear in many natural and industrial processes of physical, chemical, and perhaps even biological character. Therefore microcapillarity has a very large and diverse range of applications.

Capillarity was a lively and much studied subject in the nineteenth century. But the existence and importance of microcapillary effects were mostly overlooked. Considering the wide range of applications, there is even today surprisingly little done on the fundamentals of microcapillarity. Especially on the theoretical side there is a great need of systematic, fundamental studies of microcapillarity. This work is an attempt to contribute to this aim.

2. THERMODYNAMICAL EQUILIBRIUM.

The conditions for thermodynamical equilibrium between different gas phases and liquid phases are studied in this chapter. More specifically we will study the conditions for diffusional equilibrium, when the boundary between liquid and gas is fixed, and water and air molecules may diffuse between the phases. The conditions for force equilibrium at the movable boundary surfaces between liquid and gas are considered in the next section 2.2. The effects of gravity are studied in section 2.3. Finally the results are summarized in section 2.4.

2.1. Thermodynamical conditions for equilibrium.

Suppose that the piece of porous material together with its surroundings is in thermodynamical equilibrium. Then there is a constant temperature T throughout the whole system. The porous material is assumed rigid, so that the solid parts can stand any forces without deformation. Thus in this analysis there is no need to consider any pressure-volume relations for the solid material.

If two phases, which can exhange molecules of some substance, are in thermodynamical equilibrium, then the chemical potential for this substance must have the same value in the two phases. Thus the chemical potential for water μ_w must have a constant value throughout the various phases in the pores and in the surroundings. It is here assumed that any two phases in the pores and in the surroundings can exchange water molecules through some chain of phases. If the system contains some other volatile and soluble substance a (air), then the chemical potential for this substance μ_a must also have a constant value throughout the phases of the system. The liquid phases may contain a salt or other solved substance b. If the salt can move from one liquid phase to another through diffusion along the adsorbed water layer on the pore walls, then the chemical potential μ_b for the solved salt must have the same value for all liquid phases. Otherwise the chemical potential μ_b will vary from one liquid phase to another. It is important to observe that the pressures in a gas phase and in a neighbouring liquid phase in the pores need not be the same. The pressure equilibrium conditions are discussed in the next section.

Let us first consider the case, when there is not any other substance but water in the pores. Denote by μ_w the value of the chemical potential for the water.

Consider any gas phase α in the pores or in the surroundings. The phase will behave as an undisturbed water-vapor phase, if it is large enough. Denote by $\mu_w^g(T,p_\alpha)$ the chemical potential for free water-vapor as a function of the temperature T and the vapor pressure p_α. Then we must have:

$$\mu_w^g(T,p_\alpha) = \mu_w \tag{2.1:A}$$

Thus all gas phases, which are large enough to behave as a free water-vapor phase, will have the same vapor pressure, which will be denoted p. This is of course also true for a large phase even when all neighbouring water phases are quite small. A natural limit between these large gas phases and smaller ones is the mean free path of a gas molecule. The state of smaller gas phases is not completely determined by T and μ_w. It will also depend on the shape of the pore and of the neighbouring solid walls and liquid phases.

Let us next consider any capillary condensed liquid phase β in the pores. If the phase is large enough, it behaves as a free liquid phase except for thin layers at the boundaries against the solid and against gas phases. Denote by $\mu_w^\ell(T,p_\ell)$ the chemical potential for free liquid water as a function of the temperature T and the pressure p_ℓ. Then for the phase β:

$$\mu_w^{\ell}\ (T,p_{\ell}^{\beta}) = \mu_w \qquad (2.1:B)$$

Thus all liquid phases that are large enough to behave as an undisturbed liquid phase will have the same pressure, which is denoted p_{ℓ} . The criterion for a free liquid phase is that its linear dimensions are larger than the range of the forces between water molecules and between the solid wall and water molecules. It seems safe to state that this limit is well below 100 Å. Below the limit the state of the water phase also depends on the shape of the solid walls and on the forces between the wall and the water molecules.

The above discussion shows that it is important to distinguish between these smaller and larger phases in the pores. The words macrophase and microphase seem appropriate. The limit between microphases and macrophases is of course not very precise. Anyhow a macrophase in the pores is defined as a phase, where the thermodynamical relations are identical with those of the free bulk phase. Then the analysis of the macrophases requires only ordinary thermodynamics. The situation in a microphase is more complicated. In order to completely specify the state of a microphase it is not sufficient to know the values of thermodynamical variables such as temperature and chemical potentials. It is also necessary to know the precise shape of the phase and the nature of neighbouring phases. It would be necessary to use statistical mechanics. The use of a single hydrostatic pressure may be insufficient. Instead it may be necessary to use a pressure tensor, which varies through the phase, in order to describe the pressure situation.

A specific capillary phenomenon is that the value of p_{ℓ} may be negative. This means that the liquid does not experience a pressure but a tensile force. It will be discussed in the next section, how these forces are brought about by the surface tension, and how they are balanced by the solid.

The pressures p and p_ℓ can be calculated from (2.1:A) and (2.1:B), when the value of the chemical potential μ_w is given. The equations also give a well-known relation between p and p_ℓ . Let $p_s(T)$ denote the saturation pressure of pure water at the temperature T. Equilibrium between liquid and vapor at the saturation pressure requires:

$$\mu_w^g\,(T,p_s(T)) = \mu_w^\ell(T,p_s(T)) \qquad (2.1:C)$$

Thus from (2.1:A-C):

$$\mu_w^g\,(T,p) - \mu_w^g\,(T,p_s) = \mu_w^\ell\,(T,p_\ell) - \mu_w^\ell\,(T,p_s) \qquad (2.1:D)$$

The partial derivative of the chemical potential with respect to the pressure p' at fixed temperature equals the mole volume v(T,p') 2). Thus (2.1:D) may be written:

$$\int_{p_s}^{p} v_g\,(T,p')dp' = \int_{p_s}^{p_\ell} v_\ell\,(T,p')dp' \qquad (2.1:E)$$

The gas is assumed to be ideal so that it obeys the gas law:

$$p'\cdot v_g = RT \qquad (2.1:F)$$

Here $R = 8.314\ \mathrm{J\ mol^{-1}K^{-1}}$ is the gas constant and the temperature T is in Kelvin. The mole volume v_ℓ of liquid water is equal to M_w/ρ_ℓ , where $M_w = 0.018$ kg $\mathrm{mol^{-1}}$ is the mole weight of water and $\rho_\ell = \rho_\ell\,(T,p')$ is the density. The density ρ_ℓ does not vary much with temperature and pressure. Putting $\rho_\ell = 1\,000\ \mathrm{kg\ m^{-3}}$ we get with rather good accuracy:

$$v_\ell = v_\ell\,(T,p') \simeq 18\cdot 10^{-6}\ \mathrm{m^3\ mol^{-1}} \qquad (2.1:G)$$

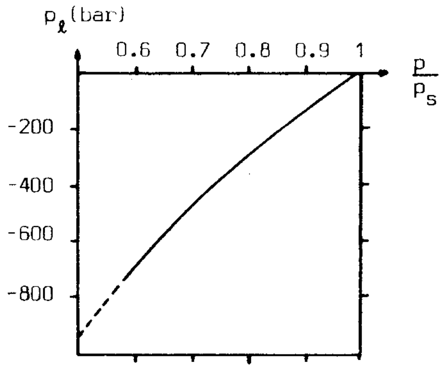
Formulas (2.1:E-G) now give the following relation between p_ℓ and p :

$$p_\ell - p_s = \frac{RT}{v_\ell}\cdot \ln\,(\frac{p}{p_s}) \qquad (2.1:H)$$

For example for T = 290 K we have:

$$p_s = 0.02 \text{ bar} \qquad \frac{RT}{v_\ell} = \frac{8.314 \cdot 290}{18 \cdot 10^{-6}} \text{ Nm}^{-2} = 1340 \text{ bar} \qquad (2.1:I)$$

Thus p_ℓ is negative and numerically much larger than p_s , except when p is extremely close to p_s . Figure 2.1:I below shows the relation between pore water pressure p_ℓ and relative humidity p/p_s for water at the temperature of 17° C.



$\frac{p}{p_s}$	p_ℓ(bar)
0.8	-300
0.9	-140
0.99	- 13
0.999	-1.3
1	+0.02

Figure 2.1:I. Relation between relative humidity p/p_s and pore water pressure p_ℓ at 17° C.

The equilibrium pore water pressure p_ℓ must according to the table above change drastically, when the relative humidity p/p_s falls below 100 %. When for example the relative humidity falls from 100 % to 90 %, the equilibrium pressure p_ℓ must fall from +0.02 bar to -140 bar, that is to a tension of 140 bar. These conspicuous facts require some comments.

Liquid water at normal pressures can not be in equilibrium with water vapor at a relative humidity below saturation. The water would eventually evaporate completely. The equilibrium at say 90 % relative humidity requires that a tension of 140 bar is established in the water. There must exist a mechanism that is able to create and maintain these high tensions. This mechanism, which is peculiar to capillary-porous systems, is described in the next section. It is impossible to maintain these tensions in an ordinary bulk of water.

There is a lot of confusion regarding these water tensions. It is seldom realized that they must exist. This is due to the fact that they lack the support of commonplace experience. But they are a thermodynamical necessity.

The high values for these tensions also require some comments. At the liquid surface there is a continual exchange of molecules between the liquid and the vapor. In equilibrium the transfer rates are the same in both directions. The transfer rate from vapor to liquid ought to be proportional to the number of molecules hitting the surface. When the relative humidity is lowered from 100 % to 90 %, the number of hits and the transfer rate are lowered by roughly 10 %. In order to pass in the other direction from liquid to vapor a molecule must overcome the restoring coercive forces from the surrounding molecules in the liquid. The molecule must get a vigorous kick due to thermal agitation in order to be able to overcome the energy barrier at the surface. A moderate change of the pressure in the liquid will have very little effect on the transfer rate. The pressure must fall 140 bar in order to diminish the transfer rate with the above 10 %.

Let us now consider the case when there are water and air in the pores. The air will be considered as a pure substance. The analysis of the more true situation, when the air is regarded as a mixture of nitrogen, oxygen, and so on, would offer no additional difficulties and the conclusions below would have been the same.

In thermodynamical equilibrium the chemical potentials for water and air are constant throughout the various phases of the pores and of the surroundings.

Consider any gas phase in the pores or in the surroundings. The state is determined by the temperature T, the water-vapor pressure p, and the total gas pressure p_g . Note that p_g and p will be the same values for all these gas phases, since the two chemical potentials for water and air have the same values throughout.

Consider next any capillary condensed liquid macrophase in the pores. It consists of liquid water with a temperature T and a pressure p_ℓ . It has a mole fraction x_a of solved air. Since the temperature and the two chemical potentials have the same values for all these phases, then the water pressure p_ℓ and the mole fraction of air x_a will have the same values for all phases.

We have arrived at the important but perhaps rather obvious conclusion, that all gas phases are in exactly the same state, when the system is in equilibrium. A gas bubble deep inside the pore system, shielded from an outside surrounding gas phase by chains of liquid phases in the pores, must still have the same pressure p_g and vapor pressure p as the outside surrounding phase. It may take very long time to establish air equilibrium, since, due to the minute amounts of dissolved air in the water, the air diffusion rate will be very small. Similarly all liquid phases must be in exactly the same state in equilibrium. When the system is in contact with an outside liquid phase with a pressure p_ℓ , then this pressure must in equilibrium prevail throughout all liquid phases. The modifications necessary, when effects of salts are included in the analysis, are discussed below.

The exact relation between p and p_ℓ , when air is present, is more complicated. The chemical potential μ_w^ℓ for the water in liquid phase will now depend also on the mole fraction of solved air x_a : $\mu_w^\ell \quad \mu_w^\ell(T,p_\ell,x_a)$. The solution is ideal, if it is sufficiently dilute, that is if x_a is sufficiently small. Then from [2a)] the chemical potential μ_w^ℓ is given by:

$$\mu_w^\ell\ (T,p_\ell,x_a) = \mu_w^\ell\ (T,p_\ell,0) + RT\cdot\ln\ (1-x_a) \qquad (2.1:J)$$

For air of atmospheric pressure and room temperature x_a is of the order $0.5\cdot 10^{-6}$. The solution is extremely dilute and (2.1:J) is a very good approximation. The gas phases are with good accuracy ideal so that (2.1:F) and the left sides of (2.1:D and E) are unchanged. This will be true even in the special case of high gas pressures well above atmospheric pressure. In formulas (2.1:D and E) we shall only add $RT\cdot\ln\ (1-x_a)$ on the right side. Then we get instead of (2.1:H):

$$p_\ell - p_s = \frac{RT}{v_\ell}\cdot\ln\ (\frac{p}{p_s}) - \frac{RT}{v_\ell}\cdot\ln\ (1-x_a) \qquad (2.1:K)$$

Now x_a is of the order $0.5\cdot 10^{-6}$. Thus we still have with very good accuracy:

$$p_\ell - p_s = \frac{RT}{v_\ell}\cdot\ln\ (\frac{p}{p_s}) \qquad (2.1:L)$$

At ordinary temperatures p_s is negligible compared to p_ℓ, except when $\frac{p}{p_s}$ is extremely close to unity.

The assumptions behind (2.1:L) were the following. The gas was assumed ideal. The compressibility of the liquid was neglected. Finally the solution of air in the water was ideal and the mole fraction x_a was neglected compared to 1. Formula (2.1:L) will also be valid when there are other substances with very small solubility in the water.

Many building materials contain or are exposed to salts. These salts may dissolve in the water in the pores. It is therefore important to consider also this case, when the liquid phases contain a salt. Let m^α denote the molality (that is the number of moles of solute per kilogram solvent) for the salt in a liquid phase α. We assume that the salt cannot diffuse from one phase to another. Then the molality m^α will in general be different from phase to phase.

The liquid phases will now be in different thermodynamical states even in perfect equilibrium. Formula (2.1:L) is no longer valid. But still the chemical potentials for water and air must be the same throughout the whole system. Thus all gas phases will still have the same total pressure p_g and vapor pressure p .

The chemical potential μ_w^ℓ for the water in a liquid phase α will now depend also on the molality m^α of dissolved salt. The influence of the minute amounts of dissolved air is of course again negligible . Chemical equilibrium for water gives a relation between p, p_ℓ^α , and m^α . Instead of (2.1:D) we may now write:

$$\mu_w^g (T,p) - \mu_w^g (T,p_s) = \mu_w^\ell (T,p_\ell^\alpha,m^\alpha) - \mu_w^\ell (T,p_s,m^\alpha) +$$

$$+ \mu_w^\ell (T,p_s,m^\alpha) - \mu_w^\ell (T,p_s,0) \qquad (2.1:M)$$

The partial derivate of a chemical potential with respect to the pressure at fixed temperature and molality equals the corresponding so called partial molar volume [2b)]. The partial molar volume for water V_w^ℓ gives the increase in volume, when, at fixed temperature and pressure, one mole of pure water is added to a very large water phase that has the molality in question. V_w^ℓ is then a function of T, p_ℓ , and m. But it will differ very little from the mole volume v_ℓ of pure water given by (2.1:G).

In order to evaluate (2.1:M) we must also know how the chemical potential varies with the molality m . The chemical potential of the solvent in salt solutions is often expressed in terms of the so-called molal osmotic coefficient ϕ [3a)]. The quantity ϕ is defined by the equation

$$\mu_w^\ell (T,p_\ell,m) = \mu_w^\ell (T,p_\ell,0) - RT\cdot\nu M_w \phi m \qquad (2.1:N)$$

Here $\mu_w^\ell (T,p_\ell,0)$ is the chemical potential for pure water and ν denotes the number of ions of a salt molecule. ϕ is a function of T, p_ℓ , and m and (2.1:N) is merely another way to express the chemical potential. But the point is that normally ϕ is not very far from unity. Reference $^{3b)}$ gives measured values of ϕ as a function of molality for many salts.

Take as an example sodium chloride Na Cl. There are two ions per salt molecule: $\nu = 2$. Figure 2.1:II below shows ϕ as a function of the molality $m_{Na\ Cl}$ at 25^{o} C $^{3b)}$. The values refer to normal pressures or more precisely to the corresponding vapor pressure. But the pressure dependence for ϕ is very small. The variation of ϕ with the temperature is rather insignificant $^{3b)}$.

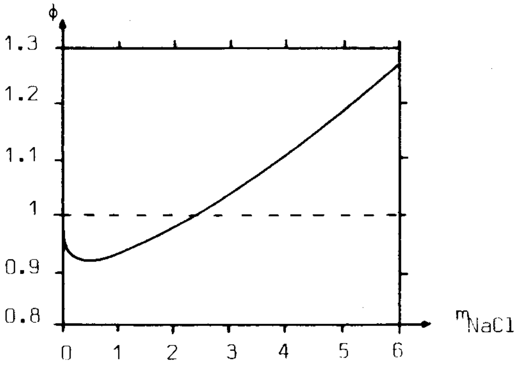


Figure 2.1:II. Molal osmotic coefficient ϕ as a function of the molality m for sodium chloride at 25^{o} C.

Now (2.1:M) may be transformed to:

$$\int_{p_s}^{p} v_g(T,p')dp' = \int_{p_s}^{p_\ell^\alpha} V_w^\ell\,(T,p',m^\alpha)dp' - RT\,\nu\,M_w\,\phi^\alpha\,m^\alpha \qquad (2.1:O)$$

With formula (2.1:F) and using $V_m^\ell \simeq v_\ell$ we get with good accuracy the important formula:

$$p_\ell^\alpha - p_s = \frac{RT}{v_\ell}\ln\left(\frac{p}{p_s}\right) + \frac{RT\,M_w}{v_\ell}\,\nu\,\phi^\alpha\,m^\alpha \qquad (2.1:P)$$

Usually p_s is negligible compared to p_ℓ^α. The second term on the right may be termed an osmotic pressure π:

$$\pi = \frac{RT\,M_w}{v_\ell}\,\nu\,\phi\,m \qquad (2.1:Q)$$

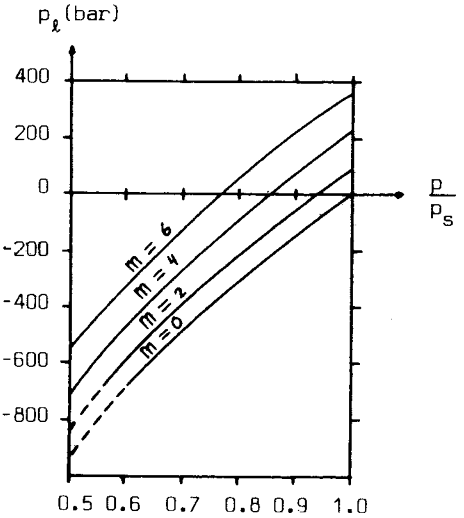
Formula (2.1:P) differs from (2.1:L) only by the additional osmotic pressure term due to the presence of a salt. Figure 2.1:I is still applicable if p_ℓ is replaced by $p_\ell^\alpha - \pi^\alpha$.

Numerically we have for T = 290 K neglecting p_s :

$$p_\ell^\alpha = 1340 \ln \left(\frac{p}{p_s}\right) + 24.1\ \nu\ \phi\ m^\alpha \qquad \text{(bar)} \qquad (2.1{:}R)$$

The formula gives the pressure in bar. The factor ν is a small natural number and ϕ is close to 1.

Figure 2.1:III below shows relation (2.1:P) for sodium chloride at room temperature and gives the osmotic pressure π for different molalities m .



m	π (bar)
1	45
2	95
3	150
4	220
5	290
6	370

Figure 2.1:III. Relation between pore water pressure p_ℓ and relative humidity $\frac{p}{p_s}$ for different molalities m of sodium chloride at room temperature.

The table shows the osmotic pressure π at different molalites m .

These numerical examples show that the effects on the pore water pressure from salts may become very large. Let us consider two liquid phases for which the molalities differ by 1. Then the equilibrium difference in pore water pressure or tension will be in the order of 50 bar. I suspect that these osmotically caused differences in pore-water tension are a main cause of damage of building materials. This is discussed in a subsequent chapter.

2.2. Force equilibrium conditions.

The pressure in the gas phases is p_g and the pressure in a liquid phase is p_ℓ . These two pressures will mostly be different. Let us consider any of the boundary surfaces between a liquid phase and a gas phase in the pores. See figure 2.2:I. Denote the surface by S.

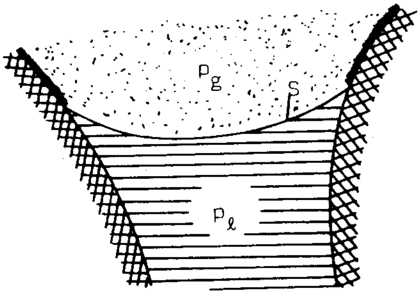


Figure 2.2:I. Cross-section of a pore showing a water meniscus S between a liquid phase with pressure p_ℓ and a gas phase with pressure p_g .

Such a surface between a gas phase and a liquid phase will be called a water meniscus. A liquid phase in the pores is bounded by pore walls and by a water meniscus or by a number of water menisci. The unit normal at a point of a water meniscus pointing in the direction from liquid to gas will be denoted $\bar{n}$. The boundary curve to a meniscus S will be denoted Γ , where Γ is a closed curve along the walls. Let $\bar{m}$ denote the unit vector at the boundary Γ , which is tangential to S, perpendicular to Γ and directed outwards from the surface S. We will call $\bar{m}$ the outward tangent vector to S at Γ . These notations will be used throughout this work. They are illustrated in figure 2.2:II below.

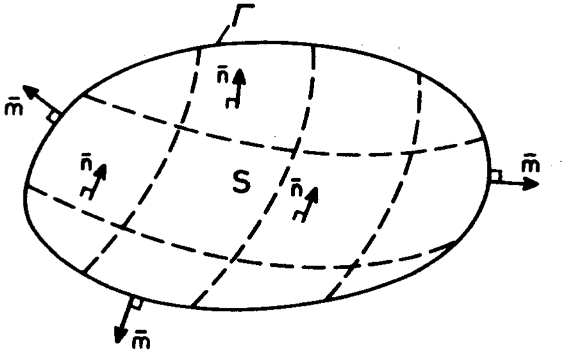


Figure 2.2:II. Water meniscus S with unit normal $\bar{n}$ and boundary Γ . $\bar{m}$ denotes the outward tangent vector to S at Γ .

Consider now any part S_1 of the meniscus S. The boundary curve to S_1 is denoted Γ_1 , and $\bar{m}$ is the outward tangent vector to S_1 at Γ_1 . The forces acting on S_1 must balance. There is a pressure p_g acting on S_1 from the gas and a pressure p_ℓ acting on S_1 from the liquid. Let $\gamma_{\ell g}$ denote the surface tension of the liquid-gas interface. This surface tension of the water meniscus acts on S_1 along the boundary Γ_1 . It will act in the direction of $\bar{m}$. These forces acting on S_1 are illustrated in figure 2.2:III below.

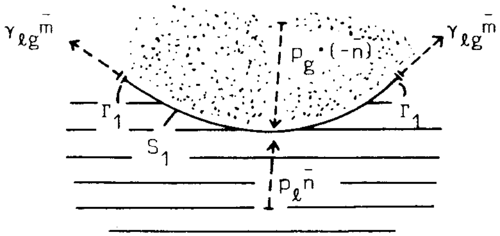


Figure 2.2:III. Forces acting on a part S_1 of a water meniscus.

Using a surface integral over S_1 and a line integral along Γ_1 the total force acting on S_1 may be written:

$$\iint_{S_1} (p_g - p_\ell)(-\bar{n})dS + \oint_{\Gamma_1} \gamma_{\ell g}\, \bar{m}\, ds \tag{2.2:A}$$

The net force from the pressures on an infinitesimal part of S_1 with the area dS is $(p_g - p_\ell)dS$. This force is acting in the direction of $-\bar{n}$. Thus the surface integral gives the force on S_1 from the pressures p_g and p_ℓ. The force from the surface tension acting on an infinitesimal arc of Γ_1 with the length ds is $\gamma_{\ell g} ds$. This force is acting in the direction of $\bar{m}$. Thus the line integral along Γ_1 gives the total force on S_1 from the surface tension.

The line integral along the closed curve Γ_1 in (2.2:A) may be transformed into a surface integral over the surface S_1, which has Γ_1 as boundary. From appendix A on differential geometry we have the general formula, valid for any surface S_1 with boundary curve Γ_1 :

$$\oint_{\Gamma_1} \bar{m}\, ds = \iint_{S_1} 2\kappa\, \bar{n}\, dS \tag{2.2:B}$$

Here κ is the so-called mean curvature of the surface at each point on it.

The mean curvature is a basic concept in the theory of surfaces 11). We will briefly explain the meaning of it. Let P be a point on any surface and let $\bar{t}$ denote a direction in the tangent plane of the surface at P .

Consider those circles, which have their centres on the straight line passing through P in the normal direction to the surface, and which are tangent to the surface at P with tangent direction $\bar{t}$. There is a certain circle among these that fits best to the surface near the tangent point P . The inverted value of the radius of this best fitting circle is the curvature of the surface at P for the direction $\bar{t}$. The radius is counted positive, if the centre lies on the positive side of the surface, and it is counted negative, when the centre lies on the other side. The positive side of S is defined as the side into which $\bar{n}$ is pointing. Thus the positive side is the gas side of the water meniscus. The mean curvature κ is equal to the mean value of the curvatures for two perpendicular directions in the tangent plane. The value of κ is not changed when these two perpendicular directions are rotated around the normal to the surface at P. A sphere with radius R and with the normal pointing inwards has the mean curvature $0.5(1/R + 1/R) = 1/R$. The curvature is zero in any direction for a plane, since the centre of the best fitting circle now lies at infinity. Take as a last example a cylinder with radius R and with the normal pointing outwards. Let the two directions be perpendicular and parallel to the axis of the cylinder. Then we get the mean curvature $0.5(1/-R + 1/\infty) = - 1/2 R$. The mean curvature κ is positive if the surface is concave viewed from the gas side. Conversely κ is negative, if the surface is convex.

Since $\gamma_{\ell g}$ is a constant, we have from (2.2:A and B) the total force on S_1 :

$$\iint_{S_1} (2\gamma_{\ell g}\kappa - p_g + p_\ell)\bar{n}\, dS \qquad (2.2:C)$$

This force must be equal to zero for any part S_1 of S . Then the integrand must vanish at all points of S :

$$p_g - p_\ell \quad 2\gamma_{\ell g}\kappa \qquad (2.2:D)$$

This fundamental equation originates from Laplace.

Consider, in order to further clarify the effect of the surface tension $\gamma_{\ell g}$, a very small part S_1 of the meniscus. The mean curvature κ and the normal $\bar{n}$ will vary very little over S_1. For the total force from the surface tension on S_1 we have again:

$$\oint_{\Gamma_1} \gamma_{\ell g}\, \bar{m}\, ds = \iint_{S_1} \gamma_{\ell g}\, 2\kappa\, \bar{n}\, dS \approx 2\gamma_{\ell g}\, \kappa|_{S_1} \cdot \bar{n}|_{S_1} \cdot \iint_{S_1} dS \qquad (2.2:E)$$

The last double integral gives the area of S_1. The resulting force from the surface tension on a very small part of the meniscus points in the normal direction $\bar{n}$ of the surface. $2\gamma_{\ell g}\kappa$, where κ is the curvature in the point of the surface, gives the magnitude of this resulting force per unit area.

We have an immediate interpretation of (2.2:D). See figure 2.2:IV. $p_g - p_\ell$ is the net force per unit area from the pressures. It points in the direction $-\bar{n}$. This force is balanced by the force $2\gamma_{\ell g}\kappa\bar{n}$ per unit area due to the surface tension of the curved surface.

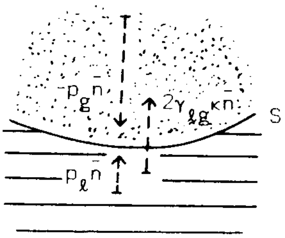


Figure 2.2:IV. Force balance for a curved water meniscus according to (2.2:D).

The Laplace equation (2.2:D) ensures force equilibrium at all points of the water menisci. It was shown in the previous section that the gas pressure p_g was the same throughout the entire system in equilibrium. In the case without salts also the pore water pressure was constant throughout.

Then the mean curvature κ will have the same value at all points on all menisci. The pore water pressure p_ℓ^α will be different for different liquid phases α, when the water contain salts. But the mean curvature κ will be the same at all points on the water menisci which belong to the same phase α. Anyhow the mean curvature is constant throughout each single meniscus in equilibrium.

The inverted value of κ may be called the mean radius of curvature for the meniscus. It is an important quantity, since it provides information on the linear dimensions of the pores. We will use the symbol R_S for this mean radius of curvature of a water meniscus S :

$$R_S = \frac{1}{\kappa} = \frac{2\gamma_{\ell g}}{p_g - p_\ell} \qquad (2.2{:}F)$$

The linear dimensions of a pore in the region around a meniscus S will normally or at least in many cases be of the order of the mean radius of curvature, R_S.

The formulas (2.2:D) and (2.1:L) give R_S as a function of the relative humidity in the salt-free case:

$$R_S = \frac{2\gamma_{\ell g}}{-\frac{RT}{v_\ell}\ln\left(\frac{p}{p_s}\right) + p_g - p_s} \qquad (2.2{:}G)$$

Here p_g and p_s are negligible, when $\frac{p}{p_s}$ is not too close to 1. Formulas (2.2:D) and (2.1:P) give an analogous formula for R_S^α, when there is a salt with molality m^α in the water phase α. It should in this case be observed that the surface tension $\gamma_{\ell g}$ has a minor dependence on the molality of the salt.

As a numerical example we get in the salt-free case for T=290 K and p_g = 1 bar (with RT/v_ℓ = 1340 bar and $\gamma_{\ell g}$ = 0.074 N m^{-1}):

$$R_S = \frac{10.9}{-\ln\left(\frac{p}{p_s}\right) + 0.00073} \quad (\text{Å}) \qquad (2.2{:}H)$$

The second term in the denominator gives the small effect of the gas pressure p_g due to the air. The radius R_S is in Å (10^{-10} m). Table 2.2:I below gives this relation and also the corresponding pore water pressures.

$\frac{p}{p_s}$	0.5	0.6	0.7	0.8	0.9	0.95	0.98	0.99	0.995	0.999	1	1.00073
R_S(Å)	16	21	31	49	100	210	520	1000	1900	6300	15000	∞
p_ℓ (bar)	-930	-680	-480	-300	-140	-69	-27	-13	-6.7	-1.3	+0.02	1

Table 2.2:I. Corresponding values of relative humidity $\frac{p}{p_s}$, mean radius of curvature R_S , and pore water pressure p_ℓ in the salt-free case at the temperature 290 K and atmospheric pressure.

As a second numerical example we take the case when the water contains sodium chloride with a molality m=2. We take again T=290 K and p_g = 1 bar. The surface tension $\gamma_{\ell g}$ will increase slightly with m . From 5) we get for m=2 that $\gamma_{\ell g} = 0.076$ N m^{-1}. Numerically we have with formulas (2.2:F) and (2.1:P) using the table of figure 2.1:III:

$$R_S = \frac{11.3}{-\ln(\frac{p}{p_s}) - 0.070} \quad (\text{Å}) \qquad (2.2:I)$$

The second term in the denominator gives the effect of the salt. The radius R_S is in Å. Table 2.2:II below shows this relation and the corresponding pore water pressures.

$\frac{p}{p_s}$	0.5	0.6	0.7	0.8	0.85	0.9	0.92	0.9324	0.95	1
R_S (Å)	18	26	39	74	120	320	840	$\pm\infty$	-600	-160
p_ℓ (bar)	-830	-590	-380	-200	-120	-46	-17	+1	+26	+95

Table 2.2:II. Corresponding values of relative humidity p/p_S, mean radius of curvature R_S, and pore water pressure at the temperature of 290 K and at atmospheric pressure, when the water contains sodium chloride with a molality m=2.

The water meniscus is convex viewed from the gas side, when R_S is negative. Then the pore water pressure p_ℓ is greater than the gas pressure p_g (=1 bar).

The tables 2.2:I and II show that high water tensions $-p_\ell$ require very small values on R_S. For example in order to get the water tension $-p_\ell$ = 140 bar corresponding to a relative humidity of 90 % in the salt-free case, R_S must equal 100 Å. The pronounced capillary effects with water tensions above say 10 bar require radii R_S below 1000 Å.

The above formulas and tables refer to macrophases, that is to liquid phases, where the formulas of ordinary thermodynamics are valid. This has been discussed in section 2.1. But the deductions of this section do not require that an adjacent gas phase is a gas macrophase. The formulas will lose their validity and even meaning, when the mean radius of curvature R_S becomes extremely small. The surface tension and the forces between the liquid water molecules at and near the meniscus will be influenced by the curvatures of the meniscus. But, because of the short range of the forces between water molecules in the liquid, the meniscus must be heavily curved, if these effects are to be noticeable. The deviations from macrophase thermodynamics will increase gradually, when the phase becomes smaller and smaller. But drastic changes are not to be expected, and the liquid phase ought to retain most of its macrophase behaviour even for very small values on R_S . I would venture to state that down to a radius R_S = 20 Å, the formulas ought to be at least approximately valid. Accepting this limit the formulas will be valid down to a relative humidity of 60 % corresponding to a pore water tension of 700 bar. Below this limit the bulk liquid water phase will gradually vanish. There will be left only adsorbed water layers and zones on the pore walls and in minute crevices and constrictions in the pore system.

In the preceding section 2.1 we found that the liquid water in the pores must be under high tension in order to be in thermal equilibrium for relative humidities below 100 %. In the ordinary macroscopic world there is not any mechanism available to create and maintain these high tensions in the water.

We have shown above that the surface tension of a curved water meniscus creates a force $2\gamma_{\ell g}\kappa$ per unit area of the meniscus. See figure 2.2:V.

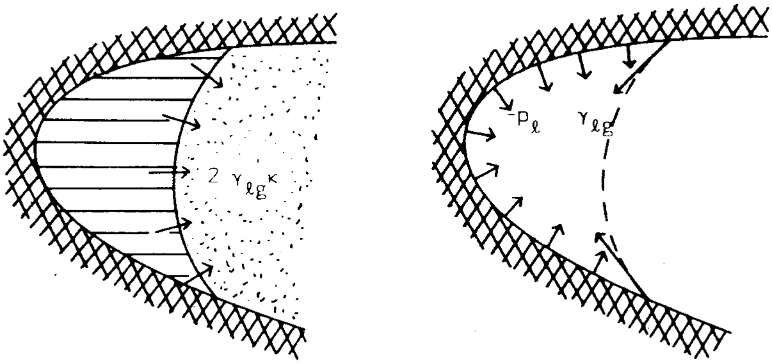


Figure 2.2:V. Cross-section of a liquid phase in a pore. The left figure illustrates the force $2\kappa\gamma_{\ell g}$ (per unit area) from the surface tension $\gamma_{\ell g}$ of the meniscus with mean curvature κ . This force is the origin of the high tensions in the pore water. The right figure shows the forces, due to

the tension in the liquid phase $-p_\ell$ and the surface tension $\gamma_{\ell g}$, that act on the pore walls.

This is the needed cause of high tensions in the pore water. The force $2\gamma_{\ell g}\kappa$ per unit area acts in the normal direction of the meniscus and induces, according to (2.2:D), a pore water tension $-p_\ell = 2\gamma_{\ell g}\kappa - p_g$. Coersive forces between the water molecules will keep the liquid together and prevent rupture. The curved meniscus S needs the support of the pore walls at the boundary curve Γ for its maintenance. The pore must be very small in order to be able to support the small and very curved water meniscus. Attractive forces between the liquid water and the pore wall will keep the water phase attached to the pore wall. The pore walls must counteract the pore water tension and the surface tension of the water meniscus. These forces from the liquid phase on the pore walls are shown in the right figure of 2.2:V. We have demonstrated that these forces may become very large. They are a main cause of damage in porous building materials.

Let us finally study the force balance at the boundary Γ of the water meniscus S, where gas, liquid, and solid meet. Between any two bulk phases there is an extremely thin transition zone. These zones may be treated as additional surface phases. This will be discussed in section 3.2. There is a surface phase at the meniscus S between liquid and gas. The quantity $\gamma_{\ell g}$ associated with the surface phase may be interpreted as a surface tension acting along the surface perpendicular to any cut in the surface. At the boundary between the pore wall and the gas there is also a surface phase containing the adsorbed layers of water molecules at the pore wall. The thermodynamical analogue to $\gamma_{\ell g}$ for this surface phase is denoted γ_{sg}. See section 3.2. The subscript sg stands for solid - gas. The corresponding quantity for the surface phase between solid and liquid is denoted $\gamma_{s\ell}$. These three surface phases meet at Γ. See figure 2.2:VI.

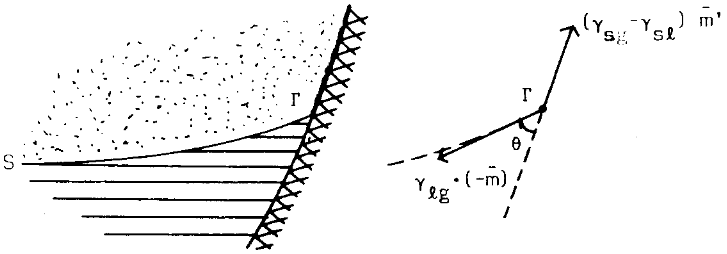


Figure 2.2:VI. Cross-section perpendicular to the boundary curve Γ where the three surface phases liquid-gas, solid-gas, and solid-liquid meet. The forces that act on the boundary curve per unit length are shown to the right. θ is the contact angle.

It is demonstrated in section 3.4.1. that the difference $\gamma_{sg} - \gamma_{s\ell}$ may be interpreted as a force per unit length acting on the boundary curve Γ in the direction of $\bar{m}'$. Throughout this work $\bar{m}'$ denotes the unit vector at Γ, which is tangential to the pore wall, perpendicular to Γ and points into the gas side. See figure 2.2:VI. Force equilibrium along the pore wall gives the well-known equation due to Young for the contact angle θ:

$$\gamma_{\ell g} \cos(\theta) = \gamma_{sg} - \gamma_{s\ell} \qquad (2.2:3)$$

The contact angle θ is the angle on the liquid side between the water meniscus and the pore wall in a plane perpendicular to Γ . The remaining force $\gamma_{\ell g} \sin(\theta)$ acting perpendicular to the wall is balanced by forces from the solid wall. The contact angle θ is a function of the thermodynamical state of the system. The contact angle will be different for different types of pore wall.

The pore walls are smooth surfaces except for corners and edges due to crystal structures in the solid. The force balance at points, where the boundary Γ meets or crosses corners and edges of the pore wall, requires a closer examination. The normal to the pore wall has a discontinuity in such a point. Near these points of discontinuity the pore wall consists of two plane surfaces, denoted 1 and 2, which meet along a straight line. Let the straight line be the x-axis according to figure 2.2:VII.

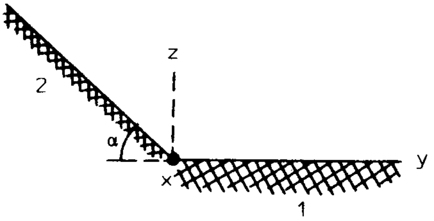


Figure 2.2:VII. Cross-section through the pore wall at a corner $(0<\alpha<\pi)$ or an edge $(0>\alpha>-\pi)$.

Surface 1 is given by the half-plane $z=0$, $y\geq 0$. Surface 2 is tilted an angle α from the plane $z=0$. The angle α may have any value between $-\pi$ and $+\pi$. A positive α gives a corner and a negative α gives an edge. The unit normals to the two surfaces pointing into the pore space are denoted $\bar{n}_1$ and $\bar{n}_2$:

$$\bar{n}_1 = (0,0,1) \qquad \bar{n}_2 = (0, \sin\alpha, \cos\alpha) \qquad (2.2{:}K)$$

Different surfaces of a crystal often have different thermodynamical properties. We therefore allow the two surfaces to have different contact angles θ_1 and θ_2.

Suppose now that the boundary Γ of a water meniscus crosses a corner or edge on the pore wall. Along the portion of Γ that lies on surface 1 the contact angle is θ_1, or $\cos\theta_1 = \bar{n}_1 \cdot \bar{n}$. Along the other portion on surface 2 the contact angle is θ_2 or $\cos\theta_2 = \bar{n}_2 \cdot \bar{n}$. We postulate for physical reasons that the normal $\bar{n}$ to S varies smoothly even up to the critical point on the x-axis, where Γ crosses the corner. Then both contact angle conditions must be satisfied at this point of discontinuity. Let $\bar{n}_c$

denote the normal to S at the critical point. The two contact angle conditions $\bar{n}_c \cdot \bar{n}_1 = \cos\theta_1$, and $\bar{n}_c \cdot \bar{n}_2 = \cos\theta_2$ give with $\bar{n}_c$ expressed in polar coordinates:

$$\bar{n}_c = (\sin\theta_1 \cdot \cos\phi_c\ ,\ \sin\theta_1 \cdot \sin\phi_c\ ,\ \cos\theta_1) \qquad (2.2{:}L)$$

$$\sin(\phi_c) = \frac{\cos\theta_2 - \cos\alpha \cdot \cos\theta_1}{\sin\alpha \cdot \sin\theta_1} \qquad (2.2{:}M)$$

We get solutions, when the right hand of (2.2:M) lies between -1 and +1. The condition for this is precisely:

$$|\theta_1 - \theta_2| \leq |\alpha| \leq \pi - |\pi-\theta_1-\theta_2| \qquad (2.2{:}N)$$

Then we get two solutions which only differ in the sign of the x-component of $\bar{n}_c$.

In conclusion we have found that the boundary curve Γ of a water meniscus may pass a corner or edge on the pore wall precisely when (2.2:N) is fulfilled. There are only two (symmetric) possible orientations of the meniscus at the point of discontinuity given by (2.2:L and M).

Let us next consider the case, when the boundary curve Γ _lies along the edge or corner._ The liquid phase may cover either surface 1 or surface 2. Suppose first that the liquid covers surface 1. Let θ_c denote the angle between the water meniscus S and surface 1 in a plane perpendicular to Γ. θ_c may be any value between zero and $\pi - \alpha$, where $-\pi<\alpha<\pi$. See figure 2.2:VIII.

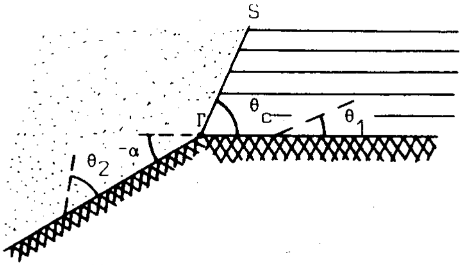


Figure 2.2:VIII. Cross-section perpendicular to the boundary curve Γ of a water meniscus S, when Γ follows an edge of the pore wall. θ_1 and θ_2 are the contact angles at the wall on each side of the edge.

The surface tension $\gamma_{\ell g}$ gives a force $\gamma_{\ell g} \cdot \cos(\theta_c)$ which tries to pull the boundary Γ back into surface 1. On surface 1 the force $\gamma_{sg}^1 - \gamma_{s\ell}^1 = \gamma_{\ell g}\cos(\theta_1)$ acts in the opposite direction. The meniscus and the boundary curve Γ will be pulled back into surface 1, when $\gamma_{\ell g}\cos(\theta_c) > \gamma_{\ell g}\cos(\theta_1)$, that is when $\theta_1 > \theta_c$. Thus we must have that $\theta_c \geq \theta_1$, when the boundary Γ follows a corner or edge on the pore wall.

An analogous argument applies to surface 2. The angle of contact between surface 2 and the meniscus (on the liquid side) is equal to $\theta_c + \alpha$. The force $\gamma_{sg}^2 - \gamma_{s\ell}^2 = \gamma_{\ell g}\cos(\theta_2)$ tries to pull the boundary Γ out on surface 2. The force $\gamma_{\ell g}\cos(\theta_c+\alpha)$ from the surface tension opposes this. This latter force must be the stronger one: $\gamma_{\ell g}\cos(\theta_c+\alpha) \geq \gamma_{\ell g}\cos\theta_2$. Thus we must have that $\theta_c + \alpha \leq \theta_2$.

In conclusion we have that the boundary curve Γ of a water meniscus may lie along a corner or edge on the pore wall, while the liquid covers surface 1, precisely when:

$$\theta_1 \leq \theta_c \leq \theta_2 - \alpha \qquad (2.2:0)$$

Here θ_c is the angle of contact between the meniscus and surface 1. See figure 2.2:VIII. We note that (2.2:O) requires that

$$\alpha \leq \theta_2 - \theta_1 \tag{2.2:P}$$

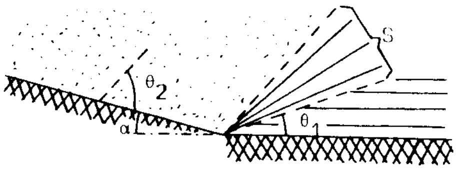
Consider next the other possibility, when the liquid phase covers surface 2 instead. Let θ_c' denote the angle of contact between S and surface 2 (on the liquid side). Then instead of (2.2:O) we have the condition:

$$\theta_2 \leq \theta_c' \leq \theta_1 - \alpha \tag{2.2:Q}$$

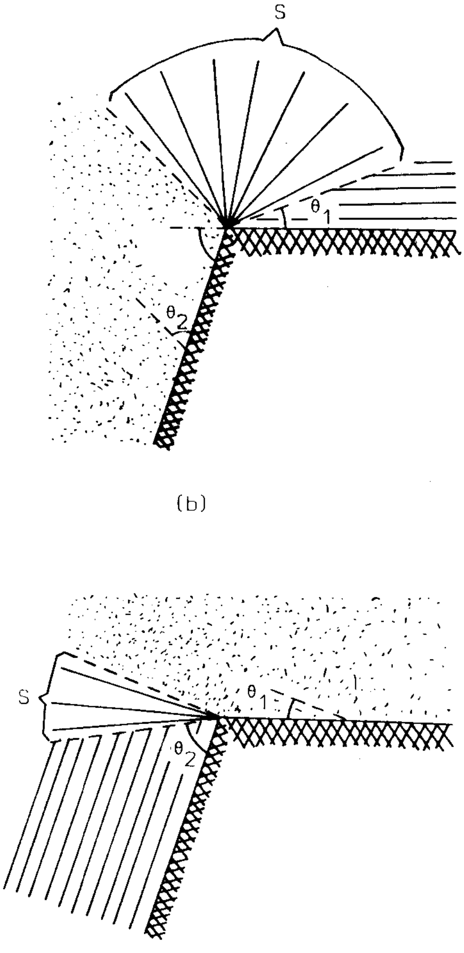
We note that (2.2:Q) requires that:

$$\alpha \leq \theta_1 - \theta_2 \tag{2.2:R}$$

Let us summarize the obtained results when the boundary curve follows an edge or a corner. Suppose first that $\alpha > |\theta_1 - \theta_2|$. Then from (2.2:P and R) we have that the boundary of the meniscus cannot follow the corner. Suppose next that $|\theta_1 - \theta_2| \geq \alpha > - |\theta_1 - \theta_2|$. Then a meniscus may lie along the corner or edge with the liquid side covering the surface with smallest contact angle. The angle of contact θ_c or θ_c' must satisfy (2.2:O) or (2.2:Q). This situation is illustrated in figure 2.2:IX(a). Finally, when $\alpha \leq - |\theta_1 - \theta_2|$, the liquid side may cover either surface 1 or surface 2. The angle of contact must satisfy (2.2:O) and (2.2:Q), respectively. These two cases are illustrated in figure 2.2:IX(b) and (c).



(a)



(b)

(c)

Figure 2.2:IX. Cross-section perpendicular to the boundary curve Γ of a water meniscus S, when Γ follows a corner or an edge on the pore wall. The figures show the possible positions for S.

(a): $-|\theta_1 - \theta_2| < \alpha < |\theta_1 - \theta_2|$

(b), (c): $\alpha < -|\theta_1 - \theta_2|$

Let us finally summarize the obtained results, when the boundary curve of a water meniscus passes or follows an edge or a corner on the pore wall. α may assume any value between $-\pi$ and $+\pi$. From (2.2:N), (2.2:P and R) we get the following different cases.

(1) $-\pi < \alpha < -\pi + |\pi - \theta_1 - \theta_2|$. The boundary Γ may follow the edge while the liquid covers either surface 1 or surface 2.

(2) $-\pi + |\pi - \theta_1 - \theta_2| < \alpha < -|\theta_1 - \theta_2|$. The boundary Γ may follow the edge, while the liquid covers either surface 1 or surface 2. There exist also two (symmetric) orientations of S where the boundary Γ of the meniscus passes the edge.

(3) $-|\theta_1 - \theta_2| < \alpha < |\theta_1 - \theta_2|$. The boundary Γ may follow the edge while the liquid side covers the surface with the smallest contact angle.

(4) $|\theta_1 - \theta_2| < \alpha < \pi - |\pi - \theta_1 - \theta_2|$. There exist two orientations of S, where the boundary Γ of the meniscus passes the corner.

(5) $\pi - |\pi - \theta_1 - \theta_2| < \alpha < \pi$. The boundary Γ of a meniscus can neither pass nor follow the corner.

One might ask what happens in the last case (5), when there are not any possibilities. This lies outside the scope of the present chaper, so we will only briefly indicate what happens. We will restrict the discussion to the more important case when $\pi - \theta_1 - \theta_2 > 0$. We have to contemplate what will happen when $\theta_1 + \theta_2 < \alpha < \pi$. Let us first consider the limit, when $\theta_1 + \theta_2 = \alpha$. Then there is a plane meniscus, parallel to the corner-line with the liquid phase in the corner, which fits to the pore walls with the prescribed contact angles θ_1 and θ_2 . See figure 2.2:X.

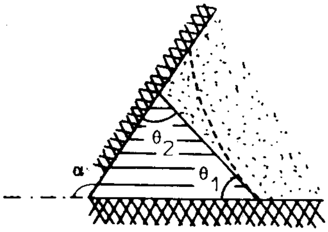


Figure 2.2:X. The figure shows a liquid phase with a plane meniscus fitting to the pore walls for $\alpha = \theta_1 + \theta_2$.

Suppose now that the angle θ_2 is diminished so that $\theta_1 + \theta_2 < \alpha$. By changing the plane meniscus into an appropriate cylindrical surface we get a meniscus with the new prescribed contact angle θ_2 . (The broken line in figure 2.2:X indicates a possible position for the cylindrical surface.) The radius of the appropriate cylinder will become smaller and smaller, when the liquid phase is diminished. The mean curvature can be made as large as we choose. But in chapter 2.1. we have shown that high mean curvatures correspond to small relative humidities p/p_s . When there is a certain positive relative humidity, water will condensate in the crevice at the corner. We will get a growing liquid phase, where the menisci have the cylindrical form. This capillary condensation will continue, until the radius of the cylindrical meniscus has decreased to the value given by formula (2.2:G) corresponding to the given relative humidity. In conclusion we have that the corner of any crevice with $\theta_1 + \theta_2 < \alpha$ will be filled by capillary condensed water. An equilibrium situation, where a boundary curve passes or follows the corner-line will never arise.

2.3. The effects of a gravitational field.

The effects of gravity are much discussed in the classical theory of capillarity. But a gravitational field is usually of minor importance in a capillary-porous system, since the water menisci have very small extension. A standard method when studying the behaviour of moisture in a piece of a porous material is to expose it to a strong gravitational field in a centrifugal machine. In this situation gravity will be of importance. We will in this section briefly indicate the effects of a gravitational field.

The local equilibrium conditions at a point will not be changed by a gravitational field. But the thermodynamical state will change from point to point. Thus the local equilibrium conditions in the previous sections are still valid. But for example the pore water pressure p_ℓ in a liquid phase will vary in the usual hydrostatic way in the gravitational field.

Let Φ denote the gravitational potential per unit mass (J/kg). Then $\Phi_1 - \Phi_2$ is the work required in order to move a unit mass from point 2 to point 1. For the ordinary gravitation on the earth we have $\Phi = gz$, where g is the acceleration due to gravity and z is the altitude. In a centrifugal machine the gravitational potential is:

$$\Phi = -\frac{\omega^2 r^2}{2} \qquad (2.3:A)$$

Here ω is the angular velocity and r is the distance from the axis of rotation.

The only change now compared with the preceding sections is that the chemical potentials μ_i for the different components i (water, air, and salts) are to be replaced by the sum of the chemical potential and gravitational potential. The gravitational potential per mole of component i is $M_i\Phi$, where M_i is the weight of one mole of component i. Thus we shall replace μ_i by $\mu_i + M_i\Phi$. See [6a]. For the water component we then have that $\mu_w + M_w\Phi$ is constant throughout the entire system in equilibrium. In the same way we have for air that $\mu_a + M_a\Phi$ is constant throughout the system. Finally for a salt b in a liquid phase α we have that $\mu_b^\alpha + M_b\Phi$ is constant throughout the phase α. This means that p, p_g, x_a, and m_b^α will vary through the gravitaional field. But these variations will be very small.

In comparison to these variations the changes in pore-water pressure will be much greater. Let us only consider the case without air and salts. Then we have for two points 1 and 2 lying in liquid phases:

$$\mu_w^\ell (T,p_{\ell 1}) + M_w\Phi_1 = \mu_w^\ell (T,p_{\ell 2}) + M_w\Phi_2 \tag{2.3:B}$$

The difference in chemical potentials may be written $v_\ell \cdot (p_{\ell 1} - p_{\ell 2})$, where $v_\ell = M_w/\rho_\ell$ is the volume of one mole of liquid water and ρ_ℓ is the density. Compare with formulas (2.1:D and E). Thus we get:

$$p_{\ell 1} - p_{\ell 2} = \rho_\ell (\Phi_2 - \Phi_1) \tag{2.3:C}$$

This is the usual hydrostatic pressure change.

It is important to note that this hydrostatic pressure difference must exist even between two separate liquid phases in thermodynamical equilibrium. The pore-water pressure in two liquid phases at different heights in a gravitational field must increase from one phase to the other in the usual hydrostatic way even though there is not any liquid connection between them. In an intermediate gas phase the vapor pressure p also changes according to a hydrostatic pressure change in a gas. This change is very small due to the low density of the vapor compared to the liquid. But we have seen in section 2.1. that a small change in vapor pressure corresponds to a large change in pore-water pressure. Then the comparatively large changes in pore-water pressure will be induced by the small changes in vapor pressure.

2.4. Summary of equilibrium conditions.

Summarizing the results of the preceding sections we have in the case, when the pores may contain water and air in thermodynamical equilibrium; All gas macrophases in the pores and in the surroundings will be in the same state specified by a temperature T, a gas pressure p_g, and a water-vapor pressure p. All liquid macrophases will be in the same state characterized by the temperature T, the pressure p_ℓ and a certain mole fraction of solved air. The pressure p_ℓ may assume negative values; then the liquid experiences a tension. We have with good accuracy:

$$p_\ell - p_s = \frac{RT}{v_\ell} \ln \left(\frac{p}{p_s}\right) \tag{2.4:A}$$

where $p_s = p_s$ (T) is the saturation vapor pressure, R the gas constant, and v_ℓ the volume of one mole of liquid water. The temperature T is in Kelvin. At the temperature T=290 K we get RT/v_ℓ = 1340 bar.

When the liquid phases also contain a salt, all gas phases will still be in the same state. But the molality m of the salt and thereby the state will in general be different for different liquid phases. We now have at thermodynamical equilibrium for a liquid phase α with pore-water pressure p_ℓ^α and molality m^α of the salt:

$$p_\ell^\alpha - p_s = \frac{RT}{v_\ell} \cdot \ln \left(\frac{p}{p_s}\right) + \frac{RT\ M_w}{v_\ell} \nu\ \phi^\alpha\ m^\alpha \tag{2.4:B}$$

Here M_w is the weight of one mole of water, ν the number of ions per salt molecule, and ϕ^α the molal osmotic coefficient. Normally ϕ^α is not very far from unity.

Force equilibrium at the water menisci requires that

$$p_g - p_\ell = 2\ \gamma_{\ell g} \cdot \kappa \tag{2.4:C}$$

Here $\gamma_{\ell g}$ is the surface tension for the liquid-gas interface. κ is the mean curvature at a point of a water meniscus. This equation is due to Laplace. Thus the mean curvature κ is constant over a water meniscus. The mean curvature κ will be constant throughout the whole system in the salt-free case.

The contact angle θ at the boundary Γ between a water meniscus S and the pore wall will have a constant value along Γ , as long as the type of pore wall is the same.

Formulas (2.4:A and C) give for the salt-free case a relation due to Kelvin:

$$R_s = \frac{2\,\gamma_{\ell g}}{-\frac{RT}{v_\ell}\cdot \ln\left(\frac{p}{p_s}\right) + p_g - p_s} \qquad (2.4:D)$$

Here $R_s = 1/\kappa$ is the mean radius of curvature for the water meniscus S.

3. THERMODYNAMICAL STABILITY.

3.1. Introduction.

The equilibrium of our capillary system must be thermodynamically stable. There are two equivalent formulations of the criterion for stability [7]. Stability requires that the entropy of the system is maximal relative to any conceivable small internal change or variation in the system such that the total energy is constant. Alternatively stability requires that the energy of the system is minimal relative to any conceivable small internal variation in the system such that the total entropy is held constant. We shall use energy minimum as stability criterion.

By an internal variation we mean any possible change within the isolated system. Small amounts of heat or entropy, water, and air may be transferred between various parts and phases of the system. The water menisci in the pores may be deformed and displaced to new positions. This latter possibility gives an important type of internal variation peculiar to capillary systems. Stability requires that, for any small internal variation of these types, the virtual state of the system after the variation has a higher total energy.

The main object of this chapter is to study the stability, when water menisci are displaced. It is assumed that there is no freezing. Effects of salts or gravity will not be considered. Finally, the solid is treated as completely rigid.

The thermodynamics of the different phases and the mathematics of second-order variations in the energy of a phase are discussed in sections 3.2. and 3.3. This is a prerequisite for section 3.4., where the stability of a water meniscus together with a surrounding region is studied. A mathematical theory of stability for a water meniscus is developed in section 3.5. The theory is applied in some cases, where the water menisci have cylindrical and spherical shapes. The results on stability are summarized in section 3.6. The extension to the case, when the region contains more than one meniscus, and a discussion of the thermodynamical character of the instabilities are left to a planned continuation of this book.

3.2 Thermodynamics of the different phases.

Apart from the solid material there are five types of regions or phases in the pore system. These are gas phases, liquid phases, and three types of surface phases.

The fundamental thermodynamical equation for the energy U_g of a gas phase is:

$$dU_g = TdS_g - p_g\, dV_g + \mu_w\, dN_w^g + \mu_a\, dN_a^g \quad . \tag{3.2:A}$$

Here S_g is the entropy, V_g the volume, N_w^g the number of moles of water and N_a^g the number of moles of air. For the energy U_ℓ of a liquid phase we have:

$$dU_\ell = TdS_\ell - p_\ell\, dV_\ell + \mu_w\, dN_w^\ell + \mu_a\, dN_a^\ell \quad . \tag{3.2:B}$$

The energy U_s of a given material part of the solid structure is a function of the entropy S_s and of the strain tensor throughout the solid. We treat the solid as rigid. Then the energy U_s is a function only of the entropy. We thus have:

$$dU_s = T\, dS_s \quad . \tag{3.2:C}$$

At the boundary between two bulk phases there is a transition region. We have transition regions at the solid pore walls between solid and gas and between solid and liquid. At the water menisci we have a transition region between liquid and gas. The geometrical variables needed to specify the state of our thermodynamical system are now not only the volumes V_g and V_ℓ of bulk phases but also the areas $A_{s\ell}$, A_{sg} and $A_{\ell g}$ of solid-liquid, solid-gas and liquid-gas surfaces.

In the treatment of boundary regions we shall follow the method of Gibbs. The procedure is described in more detail in [6b)]. A geometrical boundary plane is imagined somewhere in the extremely thin transition region between the two bulk phases. The original system is replaced by a new thermodynamical system. In this new system the two homogeneous bulk phases are extended into the transition zone up to the imagined geometrical boundary. The new system consists of the two extended bulk phases plus a surface phase at the geometrical boundary. The surface phase is chosen so that the original system and our new system behave thermodynamically in exactly the same way. The system of two bulk phases and a transition region in between is replaced by two bulk phases meeting at a boundary surface plus a surface phase.

A bulk phase is determined by the entropy, the volume and the amounts of the different components. A surface phase is determined by the entropy, the area and the amounts of the different components. The fundamental thermodynamical equation for the surface phase between liquid and gas is in the formulation of Gibbs:

$$dU_{\ell g} = TdS_{\ell g} + \gamma_{\ell g} \cdot dA_{\ell g} + \mu_w \, dN_w^{\ell g} + \mu_a \, dN_a^{\ell g} \qquad (3.2:D)$$

$U_{\ell g}$ is the energy of the surface phase. $A_{\ell g}$ is the area of the surface and $\gamma_{\ell g}$ is the surface tension. This formula is not strictly valid for a curved water surface. The energy also depends on the curvatures of the surface. This dependence will be neglectable, if the radii of curvature of the surface are much greater than the range of the forces between the molecules in the surface transition region. The range of these forces are of the order of the diameter of a molecule. Thus the above formula may be approximately applicable even for surfaces, where the radii of curvature are as small as say 20 Å .

For the surface phases between solid and gas and between solid and liquid we have in the same way:

$$dU_{sg} = TdS_{sg} + \gamma_{sg}\, dA_{sg} + \mu_w\, dN_w^{sg} + \mu_a\, dN_a^{sg} \tag{3.2:E}$$

$$dU_{s\ell} = TdS_{s\ell} + \gamma_{s\ell}\, dA_{s\ell} + \mu_w\, dN_w^{s\ell} + \mu_a\, dN_a^{s\ell} \tag{3.2:F}$$

The coefficients γ_{sg} and $\gamma_{s\ell}$ have often caused a lot of confusion. They are sometimes called surface tensions. The measurement of γ_{sg} requires that the area A_{sg} could be varied independently. This is not possible for our rigid solid. (The problem remains also for an elastic solid.) But for the combined system of a solid-gas phase and an adjacent solid-liquid phase we can in principle vary A_{sg} by moving the bulk liquid phase along the solid. In this variation we have that $dA_{s\ell} = -dA_{sg}$. It is then possible to measure

$$\gamma_{sg} \cdot dA_{sg} + \gamma_{s\ell}\, dA_{s\ell} = (\gamma_{sg} - \gamma_{s\ell}) \cdot dA_{sg} \tag{3.2:G}$$

Thus only $\gamma_{sg} - \gamma_{s\ell}$ is a well defined thermodynamical quantity. Only this difference will turn up in the formulas.

3.3. The second-order variation of the energy of a phase.

Consider any phase α in our pore system. The energy U_α is a function of the entropy S_α, the extension Y_α of the phase, and the number of moles N_w^α and N_a^α of water respectively air:

$$U_\alpha = U_\alpha\,(S_\alpha, Y_\alpha, N_w^\alpha, N_a^\alpha) \tag{3.3:A}$$

Y_α is the volume, when α is a gas phase or a liquid phase ($\alpha = \ell, g$), and it is the area when α is a surface phase ($\alpha = s\ell$, sg, ℓg). U_α is a function only of the entropy, when the phase α is a part of the solid: $U_s = U_s\,(S_s)$.

From (3.2:A-F) we have for U_α :

$$dU_\alpha = TdS_\alpha + y_\alpha \, dY_\alpha + \mu_w \, dN_w^\alpha + \mu_a \, dN_a^\alpha \qquad (3.3:B)$$

For a solid phase (α=s) there is only the first term on the right side. Here, for the different types of phases, y_α and Y_α are:

$$\begin{array}{lllll} y_g = -p_g & y_\ell = -p_\ell & y_{s\ell} = \gamma_{s\ell} & y_{sg} = \gamma_{sg} & y_{\ell g} = \gamma_{\ell g} \\ Y_g = V_g & Y_\ell = V_\ell & Y_{s\ell} = A_{s\ell} & Y_{sg} = A_{sg} & Y_{\ell g} = A_{\ell g} \end{array} \qquad (3.3:C)$$

For convenience we will occasionally use the notations:

$$X_1 = S_\alpha \qquad X_2 = Y_\alpha \qquad X_3 = N_w^\alpha \qquad X_4 = N_a^\alpha \qquad (3.3:D)$$

Let us now consider any variation in our thermodynamical system. A phase α changes from the original equilibrium to a new (internal) equilibrium state. The four variables X_i of the phase α are then changed to new values:

$$X_i \rightarrow X_i + \Delta X_i \qquad i = 1,2,3,4 \qquad (3.3:E)$$

The change in energy is, using a Taylor expansion:

$$\Delta U_\alpha = \sum_{i=1}^{4} U_i \, \Delta X_i + \frac{1}{2} \sum_{i=1}^{4} \sum_{j=1}^{4} U_{ij} \, \Delta X_i \, \Delta X_j + \dots \qquad (3.3:F)$$

U_i and U_{ij} are the partial derivatives of U_α :

$$U_i = \frac{\partial U_\alpha}{\partial X_i} \qquad U_{ij} = \frac{\partial^2 U_\alpha}{\partial X_i \, \partial X_j} \qquad (3.3:G)$$

It is important to distinguish clearly between the independent variations and the induced variations or changes of other thermodynamical quantities. To denote independent variations we will use Latin d. Consider as an example a variation where a water meniscus is slightly displaced. The displacement at a point on the meniscus is given by a small vector $d\bar{r}$. The independent variation $d\bar{r}$ is a vector function defined for each point of the meniscus. The displacement $d\bar{r}$ gives a change ΔX_2 in X_2, that is in the volume or the area of the phase. ΔX_2 is a functional of the independent variation $d\bar{r}$. We may expand ΔX_2 in terms of increasing order in $d\bar{r}$. The first and second order terms we denote δX_2 and $\delta^2 X_2$.

In general we have:

$$\Delta X_i = \delta X_i + \delta^2 X_i + \dots \qquad i = 1,2,3,4 \tag{3.3:H}$$

Here ΔX_i is the total change in X_i in the variation. δX_i and $\delta^2 X_i$ are the first and second order terms of the expansion of ΔX_i in the small independent variations. In the special case when dX_i is one of the independent variations, we have:

$$\Delta X_i = dX_i \quad \text{or} \quad \delta X_i = dX_i \, , \; \delta^2 X_i = 0 \, , \dots \tag{3.3:I}$$

We now have:

$$\Delta U_\alpha = \delta U_\alpha + \delta^2 U_\alpha + \dots = \tag{3.3.J}$$
$$= \sum_{i=1}^{4} U_i (\delta X_i + \delta^2 X_i + \dots) + \frac{1}{2} \sum_{i=1}^{4} \sum_{j=1}^{4} U_{ij} \cdot (\delta X_i + \dots) \cdot (\delta X_j + \dots) + \dots$$

The first-order variation in the energy U_α is nothing new:

$$\delta U_\alpha = \sum_{i=1}^{4} U_i \, \delta X_i \tag{3.3:K}$$

The second-order variation in the energy U_α is then:

$$\delta^2 U_\alpha = \sum_{i=1}^{4} U_i \cdot \delta^2 X_i + \frac{1}{2} \sum_{i=1}^{4} \sum_{j=1}^{4} U_{ij} \cdot \delta X_i \cdot \delta X_j \tag{3.3:L}$$

From the fundamental equation (3.3:B) for the phase α we have

$$U_1 = T \qquad U_2 = y_\alpha \qquad U_3 = \mu_w \qquad U_4 = \mu_a \, . \tag{3.3:M}$$

The double sum may be simplified since:

$$\sum_{j=1}^{4} U_{ij}\ \delta X_j = \sum_{j=1}^{4} \frac{\partial U_i}{\partial X_j} \cdot \delta X_j = \delta U_i \qquad (3.3\text{:N})$$

Here δU_i is the first-order variation in U_i .

We now have, returning to the usual notation:

$$\delta U_\alpha = T\delta S_\alpha + y_\alpha\ \delta Y_\alpha + \mu_w\ \delta N_w^\alpha + \mu_a\ \delta N_a^\alpha \qquad (3.3\text{:O})$$

$$\delta^2 U_\alpha = T\delta^2 S_\alpha + y_\alpha\ \delta^2 Y_\alpha + \mu_w\ \delta^2 N_w^\alpha + \mu_a\ \delta^2 N_a^\alpha +$$

$$+ \frac{1}{2}\{\delta T_\alpha \cdot \delta S_\alpha + \delta y_\alpha \cdot \delta Y_\alpha + \delta\mu_w^\alpha \cdot \delta N_w^\alpha + \delta\mu_a^\alpha \cdot \delta N_a^\alpha\} \qquad (3.3\text{:P})$$

Here for example δT_α is the induced first-order change in the temperature of the phase α . For a solid phase we have only the terms involving S_α .

The second part of (3.3:L or P) is the second-order change in U_α in the variation:

$$X_i \rightarrow X_i + \delta X_i \qquad (3.3\text{:Q})$$

Let us denote this part $\delta^2 U'_\alpha$. Then from (3.3:L and P) we have

$$\delta^2 U'_\alpha = \frac{1}{2} \sum_{i=1}^{4} \sum_{j=1}^{4} \frac{\partial^2 U_\alpha}{\partial X_i\ \partial X_j}\ \delta X_i \cdot \delta X_j =$$

$$= \frac{1}{2}\{\delta T_\alpha \cdot \delta S_\alpha + \delta y_\alpha \cdot \delta Y_\alpha + \delta\mu_w^\alpha \cdot \delta N_w^\alpha + \delta\mu_a^\alpha \cdot \delta N_a^\alpha\} \qquad (3.3\text{:R})$$

Any phase α must be internally stable, that is stable for any internal variation between different parts of it. This leads to the important conclusion that $\delta^2 U'_\alpha$ is non-negative for all values of $\delta X_1 = \delta S_\alpha$, $\delta X_2 = \delta Y_\alpha$, $\delta X_3 = \delta N_w^\alpha$ and $\delta X_4 = \delta N_a^\alpha$:

$$\delta^2 U'_\alpha \geq 0 \qquad (3.3\text{:S})$$

This will be used in paragraph 3.4.

Consider in order to show this two equal parts A and B of a phase α. Consider an arbitrary variation where the quantities dX_i, $i = 1,2,3,4$, are transferred from part B to part A:

$$X_i^A \rightarrow X_i^A + dX_i \qquad X_i^B \rightarrow X_i^B - dX_i \quad (i=1,2,3,4) \tag{3.3:T}$$

Then we have for part A:

$$\delta U_\alpha^A = \sum_{i=1}^{4} U_i \, dX_i \tag{3.3:U}$$

$$\delta^2 U_\alpha^A = \sum_{i=1}^{4} \sum_{j=1}^{4} U_{ij} \, dX_i \, dX_j$$

The coefficients U_i and U_{ij} are of cause the same for both cases since these are of equal size. For part B we have the same formulas with $-dX_i$ instead of dX_i. Thus the first-order variations cancel out and the second-order variations are equal:

$$\delta^2 U_\alpha^A = \delta^2 U_\alpha^B \tag{3.3:V}$$

Stability requires that

$$\delta^2 U_\alpha = \delta^2 U_\alpha^A + \delta^2 U_\alpha^B = 2 \cdot \delta^2 U_\alpha^A \geq 0 \tag{3.3:W}$$

Thus $\delta^2 U_\alpha^A$ is non-negative for all variations and we have proved formula (3.3:S).

3.4. Stability of a meniscus region.

Consider a region around a water meniscus S in a pore:

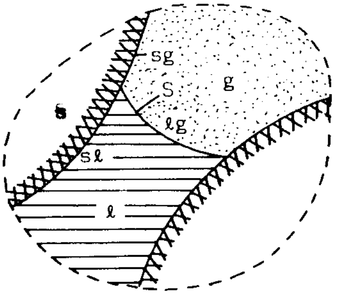


Figure 3.4:I. A water meniscus S in a pore surrounded by a certain region. The internal stability of this system is studied in section 3.4.

We will in this section study the internal stability of this thermodynamical system, which consists of a water meniscus in a pore and a certain surrounding region. Internal stability refers to the case, when the system is regarded as completely isolated. The system consists of a solid phase s , a gas phase g and a liquid phase ℓ . Between these there are three surface phases: solid-liquid sℓ , solid-gas sg , and liquid-gas ℓg .

The stability of this isolated system requires that the total energy is minimal relative to any small internal variation with constant total entropy. These variations are transfer of entropy or heat between the six phases, transfer of air and water between the five pore phases and displacements of the water meniscus S. Deformations of the solid part will not be considered, since the solid is assumed rigid. The total entropy and masses of the system are constant in the variation. The outside boundary of the total system is fixed.

The system is thermodynamically stable if:

$$\Delta U = \sum_{\alpha} \Delta U_{\alpha} \geq 0 \qquad \alpha = s,\ell,g,s\ell,sg,\ell g \qquad (3.4:A)$$

for all possible small variations of these types. The first-order terms of ΔU must vanish, since they are linear in the variations. This gives the conditions for thermodynamical equilibrium. Stability then requires that the second-order variation in the total energy is non-negative. Thus we have the stability requirements:

$$\delta U = \sum_{\alpha} \delta U_{\alpha} = 0 \tag{3.4:B}$$

$$\delta^2 U = \sum_{\alpha} \delta^2 U_{\alpha} \geq 0 \tag{3.4:C}$$

The second-order terms dominate over terms of higher order. Thus there is stability, if $\delta^2 U$ is strictly positive for all variations. The stability will be determined by terms of higher order, if $\delta^2 U$ becomes zero for some variation. This special case will not be considered. Excluding this possibility we have stability, if $\delta^2 U$ is positive for all variations and instability, if there exists a variation for which $\delta^2 U$ is negative.

3.4.1. First-order variation in energy.

We will first in this section study the first-order variation δU . We will again get the results of section 2.2. on force equilibrium. The derivation here will give a better motivation of the interpretation of the quantity $\gamma_{sg} - \gamma_{s\ell}$ as a force along the pore wall acting on the boundary Γ of S. The approach of this section will be used in subsequent sections.

By adding the expressions for δU_{α} in formula (3.3:D) for the six phases we get the total first-order variation in the energy:

$$\delta U = \sum_{\alpha} \delta U_{\alpha} = T\delta S + \mu_w \delta N_w + \mu_a \delta N_a - p_g \delta V_g - p_\ell \delta V_\ell + \gamma_{sg} \delta A_{sg} + \gamma_{s\ell} \delta A_{s\ell} + \gamma_{\ell g} \delta A_{\ell g} \quad . \tag{3.4.1:A}$$

Here δS is the sum of the first-order changes in entropy for the six phases, while δN_w and δN_a are the changes in the total amounts of water and air. For the considered isolated system these changes are zero: $\delta S = 0$, $\delta N_w = 0$, and $\delta N_a = 0$.

Since the outer boundary of the total region is fixed and the solid is rigid, we have:

$$\delta V_g = - \delta V_\ell \qquad \delta A_{s\ell} = - \delta A_{sg} \quad . \tag{3.4.1:B}$$

Thus the first-order change in the energy is given by:

$$\delta U = \gamma_{\ell g}\, \delta A_{\ell g} + (\gamma_{sg} - \gamma_{s\ell})\delta A_{sg} + (p_g - p_\ell)\delta V_\ell \quad . \tag{3.4.1:C}$$

The first term $\gamma_{\ell g}\ \delta A_{\ell g}$ represents the work required to increase the area of the liquid-gas surface by an amount $\delta A_{\ell g}$ against the surface tension $\gamma_{\ell g}$. The second term $(\gamma_{sg} - \gamma_{s\ell})\delta A_{sg}$ can be interpreted as the work required to increase the area of solid-gas surface by an amount δA_{sg} at the expense of the solid-liquid surface against a force $\gamma_{sg} - \gamma_{s\ell}$. Finally, $(p_g - p_\ell)\delta V_\ell$ is the work required to increase the liquid volume by an amount δV_ℓ at the expense of the gas volume against the pressure difference $p_g - p_\ell$.

The meniscus S is displaced to a slightly different position in the considered variation. The displacement of each point on the surface S is given by a vector $d\bar{r}$. See figure 3.4.1:I below.

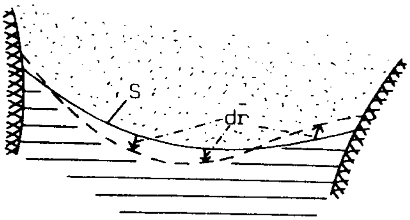


Figure 3.4.1:I A displacement of the water meniscus S. The displacement is for each point on S given by a vector $d\bar{r}$.

Let the surface S be given in parametric form by $\bar{r} = \bar{r}(u,v)$, where the parameters u and v vary in a certain region in the (u,v)-plane. Then the displaced meniscus is given by $\bar{r} = \bar{r}(u,v) + d\bar{r}(u,v)$. The displaced meniscus must be a reasonable physical surface, which fits to the given pore walls. The function $d\bar{r}(u,v)$ is of course continuous. We will assume that $d\bar{r}(u,v)$ is twice continuously differentiable. We also assume that the derivatives of $d\bar{r}(u,v)$ are of the same order of magnitude as the small quantity $d\bar{r}$ itself. The only exception from these assumptions is when, in a few arguments in the following, the displaced surface consists of two smooth parts. The normal to the displaced surface will have a discontinuity along the curve, where these two parts meet. In these cases we thus allow well-behaved discontinuities in the derivates $d\bar{r}_u$ and $d\bar{r}_v$ along simple curves on S .

The first-order change of liquid volume V_ℓ is:

$$\delta V_\ell = \iint_S d\bar{r} \cdot \bar{n} \, dS = \iint_S \delta n \, dS \quad . \qquad (3.4.1{:}D)$$

Here $\delta n = d\bar{r}\cdot\bar{n}$ is the first order displacement of S in the normal direction $\bar{n}$.

The first-order change of solid-gas area A_{sg} is given by:

$$A_{sg} = - \oint_\Gamma d\bar{r} \cdot \bar{m}' \, ds = - \oint_\Gamma \delta m' \, ds \quad . \qquad (3.4.1{:}E)$$

Here Γ denotes the closed boundary curve of the meniscus S along the pore wall. The unit vector $\bar{m}'$ is perpendicular to Γ , tangent to the pore wall ,and $\bar{m}'$ points into the gas side. See figure 3.4.1:II. The quantity $\delta m' = d\bar{r}\cdot\bar{m}'$ gives the first-order displacement along the pore wall in the direction of $\bar{m}'$.

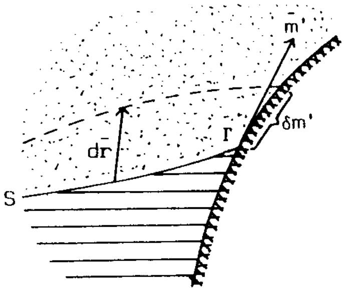


Figure 3.4.1:II Cross-section perpendicular to Γ showing a meniscus S meeting the pore wall. The vector $d\bar{r}$ gives the displacement of S. The first-order displacement along the pore wall perpendicular to Γ (in the direction of $\bar{m}'$) is given by $\delta m'$.

The first order change $\delta A_{\ell g}$ in the area of the meniscus is a bit more difficult to obtain. We will derive the expression using the work of the forces that act on S in the displacement. This method is very convenient and it will be used later in deriving second-order variations in section 3.4.9.

The work done on the meniscus in the displacement $d\bar{r}$ is in the first order $\gamma_{\ell g}\delta A_{\ell g}$. The surface tension $\gamma_{\ell g}$ of the curved surface with mean curvature κ gives rise to a net force $2\gamma_{\ell g}\kappa\bar{n}$ per unit area. See formula 2.2.:E and figure 2.2:IV. In order to balance this force and the surface tension along the boundary we must apply a force $-2\gamma_{\ell g}\kappa\bar{n}$ per unit area acting over the surface S and a force $\gamma_{\ell g}\bar{m}$ per unit length acting on the boundary Γ . The displacement work is also given by the work done by these balancing forces in the displacement $d\bar{r}$:

$$\gamma_{\ell g}\,\delta A_{\ell g} = \iint_S d\bar{r}\cdot(-2\gamma_{\ell g}\kappa\,\bar{n})dS + \oint_\Gamma d\bar{r}\cdot(\gamma_{\ell g}\,\bar{m})\,ds \qquad (3.4.1:F)$$

or

$$\delta A_{\ell g} = - \iint_S 2\,\kappa\, d\bar{r}\cdot\bar{n}\; dS + \oint_\Gamma d\bar{r}\cdot\bar{m}\; ds \quad . \qquad (3.4.1:G)$$

The displacement at the boundary Γ is in the first order parallel to the pore wall. The component in the direction of $\bar{m}'$ is $\delta m'$. The other component in the direction of Γ does not contribute to the integrand $d\bar{r}\cdot\bar{m}$ of the line integral:

$$d\bar{r}\cdot\bar{m} = \delta m'\bar{m}'\cdot\bar{m} = \delta m' \cos(\theta') \quad . \qquad (3.4.1:H)$$

Here θ' denotes the angle of contact (on the liquid side) between the pore wall and the meniscus S at the considered point on Γ.

Thus we have:

$$\delta A_{\ell g} = - \iint_S 2\kappa\cdot\delta n\, dS + \oint_\Gamma \cos(\theta')\delta m'\; ds$$

$$\delta n = d\bar{r}\cdot\bar{n} \qquad \delta m' = d\bar{r}\cdot\bar{m}' \quad . \qquad (3.4.1:I)$$

This formula for the first-order variation of the area of a surface in a displacement $d\bar{r}$ is well-known. It originates from Gauss 8). A derivation of the formula using ordinary methods of differential geometry is given in 9a).

The geometrical interpretation of formula 3.4.1:I is straight-forward. The line integral represents the increase in area due to a displacement of the surface in the outward tangent direction $\bar{m}$. See figure 3.4.1:III below. The change of the area of a surface element dS in the normal displacement δn is according to formula 3.4.1:I given by $-2\,\kappa\,\delta n\, dS = -(\frac{\delta n}{R_1} + \frac{\delta n}{R_2})dS$. Here R_1 and R_2 are the radii of curvature in two perpendicular directions on S. Let ds_1 and ds_2 be two line elements in these two directions on the surface. Then the area of the corresponding surface element is $dS = ds_1 \cdot ds_2$. The area after the normal displacement is

$$ds_1(1 - \frac{\delta n}{R_1})\ ds_2(1 - \frac{\delta n}{R_2}) \simeq dS(1 - \frac{\delta n}{R_1} - \frac{\delta n}{R_2}) \qquad (3.4.1:J)$$

see figure 3.4.1:III. Thus the surface integral of formula 3.4.1:I does indeed give the increase in area of S in the normal displacement δn .

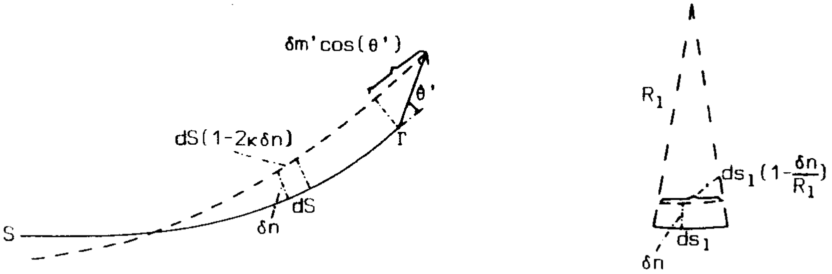


Figure 3.4.1:III The figure illustrates formula 3.4.1:I for the change in area of a surface S in a displacement.

Other contributions to the change of area are of higher order in $d\bar{r}$. For example the tilting of a surface element on S gives a contribution to the change in area proportional to the second power of the angle of tilting. The tilting angle is givén by the derivates $d\bar{r}_u$ and $d\bar{r}_v$. Thus the tilting gives second-order terms in $d\bar{r}$ and its derivatives.

The first-order variation of the energy of the membrane region is now from formulas 3.4.1:C,D,E and I:

$$\delta U = \iint_S (p_g - p_\ell - 2\kappa\gamma_{\ell g})\delta n\, dS + \gamma_{\ell g} \oint_\Gamma (\cos\theta' - \frac{\gamma_{sg} - \gamma_{s\ell}}{\gamma_{\ell g}})\delta m' ds \qquad (3.4.1:K)$$

The variations δn and $\delta m'$ may be chosen at will. Then from the equilibrium requirement that δU is zero (formula 3.4:B), we get again:

$$p_g - p_\ell = 2\kappa\gamma_{\ell g} \quad . \qquad (3.4.1:L)$$

We also get:

$$\cos\theta' = \frac{\gamma_{sg}-\gamma_{s\ell}}{\gamma_{\ell g}} = \cos\theta \quad . \qquad (3.4.1:M)$$

Thus the angle of contact θ' between the pore wall and the surface S must be equal to the contact angle θ determined by the thermodynamical quantity $(\gamma_{sg} - \gamma_{s\ell})/\gamma_{\ell g}$. The contact angle θ depends on the kind of material in the pore wall. It may thus be different for different parts of the pore wall. It will also in general be a function of the thermodynamical state of the system.

3.4.2 The expression $\Delta A_{\ell g} + \cos(\theta)\Delta A_{sg} + 2\kappa\ \Delta V_\ell$.

From formula 3.4.1:C and the equilibrium conditions 3.4.1:L and M we have:

$$\delta U = \gamma_{\ell g}\ \{\delta A_{\ell g} + \cos(\theta)\delta A_{sg} + 2\kappa\ \delta V_\ell\} \quad . \qquad (3.4.2:A)$$

This linear combination of the changes of the two areas and the volume within the brackets is of particular interest in the equilibrium and stability investigations. We will meet the same combination in the expressions for the second-order variation of the energy, $\delta^2 U$, in section 3.4.4. As a preliminary we will study this combination in this section.

It is convenient to introduce a special notation. Consider any water surface or meniscus S in a pore. Let κ' denote the mean curvature and θ' the angle of contact at the pore wall. If S is a non-equilibrium meniscus, then κ' and θ' will vary throughout S and Γ respectively. Let κ and θ be two constants. Then for a displacement $d\bar{r}$ of S we define:

$$T = T[d\bar{r}] = \Delta A_{\ell g} + \cos(\theta)\, \Delta A_{sg} + 2\kappa\, \Delta V_{\ell} \quad . \tag{3.4.2:B}$$

The physical meaning of T is the following. The first term $\Delta A_{\ell g}$ is the work required to increase the area $A_{\ell g}$ against a surface tension of unit strength. The second term $\cos(\theta)\Delta A_{sg}$ is the work required to increase the area A_{sg} against a force $\cos(\theta)$. Finally the third term $2\kappa\, \Delta V_{\ell}$ is the work required to increase the volume V_{ℓ} against a pressure difference 2κ.

The expansion of T in increasing orders of $d\bar{r}$ is:

$$T = \delta T + \delta^2 T + \dots \quad , \tag{3.4.2:C}$$

where

$$\delta T = \delta A_{\ell g} + \cos(\theta)\delta A_{sg} + 2\kappa\ \delta V_{\ell} \tag{3.4.2:D}$$

$$\delta^2 T = \delta^2 A_{\ell g} + \cos(\theta)\delta^2 A_{sg} + 2\kappa\ \delta^2 V_{\ell} \quad . \tag{3.4.2:E}$$

The formula 3.4.2:A reads

$$\delta U = \gamma_{\ell g}\ \ \delta T \quad . \tag{3.4.2:F}$$

From formulas 3.4.1:I,E and D we get the first-order variation of T :

$$\delta T = - \iint_S 2(\kappa' - \kappa)\delta n\, dS + \oint_\Gamma (\cos\theta' - \cos\theta)\delta m'\, ds$$

$$\delta n = d\bar{r}\cdot\bar{n} \qquad\qquad \delta m' = d\bar{r}\cdot\bar{m}' \quad . \tag{3.4.2:G}$$

For a meniscus in equilibrium with $\kappa = \kappa'$ and $\theta = \theta'$ we have $\delta T = 0$ or:

$$\delta A_{\ell g} + \cos(\theta)\delta A_{sg} + 2\kappa\ \delta V_{\ell} = 0 \quad . \tag{3.4.2:H}$$

This nice formula is valid for any displacement $d\bar{r}$ of a meniscus which is in equilibrium; that is for any meniscus of constant mean curvature κ and of constant angle of contact θ. The formula is an immediate consequence of the Gaussian formula 3.4.1:I for an equilibrium meniscus. This is pointed out in 10).

Let us now consider a continuous sequence of displacements S_ε enumerated by a parameter ε :

$$S_\varepsilon : \quad \bar{r} = \bar{r}(u,v,\varepsilon) \qquad (u,v) \in \Omega \quad . \tag{3.4.2:I}$$

The undisplaced surface S is given by $\varepsilon = 0$:

$$S = S_0 : \quad \bar{r} = \bar{r}(u,v,0) \qquad (u,v) \in \Omega \quad . \tag{3.4.2:J}$$

Now T will be a function of ε : $T = T(\varepsilon)$.

Consider first the displacement from S_ε to $S_{\varepsilon+d\varepsilon}$. Here we have $d\bar{r} = \frac{d\bar{r}}{\partial\varepsilon} d\varepsilon$. Formula 3.4.2:G gives:

$$\frac{dT}{d\varepsilon} = - \iint_{S_\varepsilon} 2(\kappa' - \kappa) \frac{\partial\bar{r}}{\partial\varepsilon}\cdot\bar{n}\ dS + \oint_{\Gamma_\varepsilon} (\cos\theta' - \cos\theta) \frac{\partial\bar{r}}{\partial\varepsilon} \cdot \bar{m}'\ ds \tag{3.4.2:K}$$

By integration we get T as a function of the parameter:

$$T(\varepsilon_0) = \int_0^{\varepsilon_0} \{- \iint_{S_\varepsilon} 2(\kappa' - \kappa) \frac{\partial\bar{r}}{\partial\varepsilon} \cdot \bar{n}\ dS + \oint_{\Gamma_\varepsilon} (\cos\theta' - \cos\theta) \frac{\partial\bar{r}}{\partial\varepsilon} \cdot \bar{m}'\ ds\} d\varepsilon \quad . \tag{3.4.2:L}$$

We note that $\frac{\partial \bar{r}}{\partial \varepsilon} \cdot \bar{n}\, dS\, d\varepsilon$ is a volume element in the pore space which is swept by the sequence S_ε . Moreover $\frac{\partial \bar{r}}{\partial \varepsilon} \cdot m'\, ds\, d\varepsilon$ is a surface element on the pore wall between Γ_0 and Γ_{ε_0} . The volume and surface elements are positive or negative depending on whether the displacement in that region is in the positive direction, that is into the gas side, or in the negative direction. A complication is that the sequence S_ε may sweep back and forth in the pore space for increasing ε . But for a monotonous sequence S_ε , where for each u and v the displacement is in the positive or in the negative direction for all ε , we have:

$$T(\varepsilon_0) = - \iiint_{S_0 \to S_{\varepsilon_0}} 2(\kappa' - \kappa)\eta\, dV + \iint_{\Gamma_0 \to \Gamma_{\varepsilon_0}} (\cos\theta' - \cos\theta)\eta\, dS \qquad (3.4.2{:}M)$$

$$\eta = \eta(u,v) = \mathrm{sign}(\varepsilon_0 \frac{\partial \bar{r}}{\partial \varepsilon} \cdot \bar{n}) \quad .$$

Here $S_0 \to S_{\varepsilon_0}$ signifies the pore space between S_0 and S_{ε_0} , while $\Gamma_0 \to \Gamma_{\varepsilon_0}$ is the pore wall between Γ_0 and Γ_{ε_0} .

3.4.3 The second-order variation of the energy.

By adding the expressions 3.3:P for the six phases of the meniscus region we get the second-order variation of the energy:

$$\delta^2 U = \sum_\alpha \delta^2 U_\alpha =$$

$$= T\, \delta^2 S + \mu_w\, \delta^2 N_w + \mu_a\, \delta^2 N_a +$$

$$+ \gamma_{\ell g}\, \delta^2 A_{\ell g} + \gamma_{sg}\, \delta^2 A_{sg} + \gamma_{s\ell}\, \delta^2 A_{s\ell} - p_g\, \delta^2 V_g - p_\ell \delta^2 V_\ell +$$

$$+ \sum_\alpha \delta^2 U'_\alpha \quad . \qquad (3.4.3{:}A)$$

Here $\delta^2 U'_\alpha$ is defined by formula 3.3:R. The quantity $\delta^2 S$ is the sum of the second-order variations in entropies for the six phases, while $\delta^2 N_w$ and $\delta^2 N_a$ are the second-order changes in the total amount of water and air. For the considered isolated system these changes are zero: $\delta^2 S = 0$, $\delta^2 N_w = 0$ and $\delta^2 N_a = 0$. Since the outer boundary of the total region is fixed and the solid is rigid, we have:

$$\delta^2 V_g = - \delta^2 V_\ell \qquad \delta^2 A_{s\ell} = - \delta^2 A_{sg} \quad . \tag{3.4.3:B}$$

Then with formulas 3.4.1:L and M we obtain:

$$\delta^2 U = \gamma_{\ell g} \, \delta^2 T + \delta^2 U' \tag{3.4.:C}$$

where

$$\delta^2 T = \delta^2 A_{\ell g} + \cos(\theta) \delta^2 A_{sg} + 2\kappa \, \delta^2 V_\ell \quad , \tag{3.4.3:D}$$

$$\delta^2 U' = \sum_\alpha \delta^2 U'_\alpha \tag{3.4.3:E}$$

$(\alpha = s, \ell, g, s\ell, sg, \ell g)$

$$\delta^2 U'_\alpha = \frac{1}{2} \sum_{i=1}^{4} \sum_{j=1}^{4} \frac{\partial^2 U_\alpha}{\partial X_i \partial X_j} \delta X_i \, \delta X_j \tag{3.4.3:F}$$

In formula 3.4.3:F we have used the notations of paragraph 3.3: $X_1 = S_\alpha$, $X_2 = V_\alpha$ or A_α , $X_3 = N_w^\alpha$ and $X_4 = N_a^\alpha$. For the solid phase $\alpha = s$ there is only the entropy term $(i=j=1)$.

The formula above for $\delta^2 U$ is the starting point for the mathematical analysis of the stability. The second-order variation $\delta^2 U$ is divided into two parts.

The first part, $\gamma_{\ell g} \, \delta^2 T$, is (apart from the factor $\gamma_{\ell g}$) a geometric quantity depending on the displacement $d\bar{r}$ of the meniscus S with the constant mean curvature κ and the constant contact angle θ. It does not depend on the thermodynamical states and properties of the various phases of the considered system. It only depends on the shape of the surface S and on the shape of the pore wall in the vicinity of the boundary curve Γ.

The second part δ^2U', the sum over $\delta^2U'_\alpha$, depends on the considered variation as well as on the thermodynamical properties of the six phases. From formula 3.3:S we have that each term $\delta^2U'_\alpha$ is non-negative for any variation. We note from formula 3.4.3:F above that the second part involves only products of first-order variations.

Paragraphs 3.4.4-6 below deal with the first geometrical part of δ^2U and 3.4.7 with the second phase-dependent part. In paragraph 3.4.8 the results on the stability of a meniscus region are summarized.

The contact angle θ depends on the type of pore wall. The general case, when the contact angle θ is any given varying function over the pore walls, is discussed in section 3.4.9. We only note that formula 3.4.1:K is still valid. In this case $(\gamma_{sg} - \gamma_{s\ell})/\gamma_{\ell g} = \cos(\theta)$ is a given function along the boundary curve Γ. Formula 3.4.2:H is replaced by:

$$\delta A_{\ell g} - \oint_\Gamma \cos(\theta(s))\ \delta m'\ ds + 2\kappa\ \delta V_\ell = 0 \quad . \qquad (3.4.3:G)$$

3.4.4 A formula for δ^2T.

The second order variation δ^2T in a displacement $d\bar{r}$ of an equilibrium meniscus S is according to formula 3.4.3:D given by

$$\delta^2 T = \delta^2 A_{\ell g} + \cos(\theta)\ \delta^2 A_{sg} + 2\kappa\ \delta^2 V_\ell \quad . \qquad (3.4.4{:}A)$$

It is an arduous task to express the variations $\delta^2 A_{\ell g}$, $\delta^2 A_{sg}$ and $\delta^2 V_\ell$ in $d\bar{r}$. The expressions become complicated and intractable. I have not found much on this in the literature. But the second-order variation of the area of a surface in the special case of a normal displacement $d\bar{r} = dn\ \bar{n}$ is given in Blaschke [9b)]. In our notations:

$$\delta^2 A_{\ell g} = \frac{1}{2} \iint_S \{\nabla(dn)\cdot\nabla(dn) + 2K(dn)^2\} dS$$

$$d\bar{r} = dn\ \bar{n} \quad . \qquad (3.4.4{:}B)$$

Here $K = \kappa_1\ \kappa_2$ is the Gaussian curvature for each point on S . See appendix 1. The differential operator ∇ is the gradient on the surface S . This operator is discussed in the following section 3.4.5 and in the appendix 1 which gives the elements of differential geometry.

It is much easier to derive $\delta^2 T$ directly from the formulas in paragraph 3.4.2. There, a sequence of displacements S_ε was considered (formula 3.4.2:I):

$$S_\varepsilon :\ \bar{r}(u,v,\varepsilon) \qquad (u,v) \in \Omega \quad . \qquad (3.4.4{:}D)$$

Formula 3.4.2:L is applicable:

$$T[d\bar{r}] = T(\varepsilon_0) = \int_0^{\varepsilon_0} \{ -\iint_{S_\varepsilon} 2(\kappa' - \kappa)\frac{\partial \bar{r}}{\partial \varepsilon}\cdot\bar{n}\ dS + \oint_{\Gamma_\varepsilon} (\cos\theta' - \cos\theta)\frac{\partial \bar{r}}{\partial \varepsilon}\cdot\bar{m}'\ ds\} d\varepsilon \quad . \qquad (3.4.4{:}E)$$

When ε is zero, we have that $\kappa' = \kappa$ and $\theta' = \theta$. Thus the integrands of the surface integral and of the line integral are of the first order in ε .

Now let $\delta\kappa'$ and $\delta\theta'$ be the first order variations in mean curvature and angle of contact in the displacement $d\bar{r}$:

$$\kappa'(u,v,\varepsilon_0) - \kappa = \kappa'(u,v,\varepsilon_0) - \kappa'(u,v,0) = \delta\kappa' + \dots \quad (3.4.4{:}F)$$

$$\theta'(u,v,\varepsilon_0) - \theta = \theta'(u,v,\varepsilon_0) - \theta'(u,v,0) = \delta\theta' + \dots \quad (3.4.4{:}G)$$

Then for the integrand of the surface integral in 3.4.4:E we have:

$$2(\kappa' - \kappa)\frac{\partial\bar{r}}{\partial\varepsilon} \cdot \bar{n}\, dS = 2(\kappa'(u,v,\varepsilon) - \kappa'(u,v,o))dS(u,v,\varepsilon) \times$$

$$\times \frac{\partial\bar{r}(u,v,\varepsilon)}{\partial\varepsilon} \cdot \bar{n}(u,v,\varepsilon) = 2\,\frac{\delta\kappa'}{\varepsilon_0}\,\varepsilon\,\frac{d\bar{r}}{\varepsilon_0} \cdot \bar{n}(u,v,0)\, dS(u,v,o) + \dots$$

$$(3.4.4{:}H)$$

In the lower line only the first-order term is written out. Here $\kappa'(u,v,\varepsilon)$ is the mean curvature of S_ε in the point given by (u,v) and so on. The quantities $dS(u,v,\varepsilon)$ and $dS(u,v,0)$ are the areas of corresponding surface elements on S_ε and S_0 . For the integrand of the line integral in 3.4.4:E we have in the same way:

$$(\cos\theta' - \cos\theta)\frac{\partial\bar{r}}{\partial\varepsilon}\cdot\bar{m}'\, ds =$$

$$= (\cos(\theta'(u,v,\varepsilon)) - \cos(\theta'(u,v,0)))\frac{\partial\bar{r}(u,v,\varepsilon)}{\partial\varepsilon} \cdot \bar{m}'(u,v,\varepsilon)ds(u,v,\varepsilon) =$$

$$= -\sin(\theta)\,\frac{\delta\theta'}{\varepsilon_0}\,\varepsilon\,\frac{d\bar{r}}{\varepsilon_0} \cdot \bar{m}'(u,v,0)\, ds(u,v,0) + \dots \qquad (3.4.4{:}I)$$

Here $ds(u,v,\varepsilon)$ and $ds(u,v,0)$ are the lengths of corresponding line elements on Γ_ε and Γ_0 .

Inserting 3.4.4:H and I in 3.4.4:E we get:

$$T[d\bar{r}] = \int_0^{\varepsilon_0} \{ - \iint_{S_\varepsilon} [\frac{2\varepsilon}{\varepsilon_0^2} \delta\kappa' \, d\bar{r} \cdot \bar{n}(u,v,0) \, dS(u,v,0) + \ldots] +$$

$$+ \oint_{\Gamma_\varepsilon} [- \frac{\varepsilon}{\varepsilon_0^2} \sin(\theta) \, \delta\theta' \, d\bar{r} \cdot \bar{m}'(u,v,0) ds(u,v,0) + \ldots] \} d\varepsilon$$

$$= - \iint_{S_0} \delta\kappa' \, d\bar{r} \cdot \bar{n} \, dS - \frac{1}{2} \oint_{\Gamma_0} \sin(\theta) \, \delta\theta' \, d\bar{r} \cdot \bar{m}' \, ds + \ldots \qquad (3.4.4:J)$$

On the last line above we have the second-order terms of $T[d\bar{r}]$. The first order terms are zero for our equilibrium meniscus.

With the usual notations

$$d\bar{r} \cdot \bar{n} = \delta n \qquad \sin(\theta) \, d\bar{r} \cdot \bar{m}' = \sin(\theta) \, \delta m' = \delta n \qquad (3.4.4:K)$$

we have the fundamental formula for the second-order variation of an equilibrium meniscus:

$$\delta^2 T = - \iint_S \delta\kappa' \, \delta n \, dS - \frac{1}{2} \oint_\Gamma \delta\theta' \, \delta n \, ds \quad . \qquad (3.4.4:L)$$

Here $\delta n = d\bar{r} \cdot \bar{n}$ is the first-order displacement in the normal direction. The quantity $\delta\kappa'$ denotes the first-order variation in the mean curvature for each point on S , while $\delta\theta'$ is the first order variation in angle of contact. These quantities are illustrated in figure 3.4.4:I below.

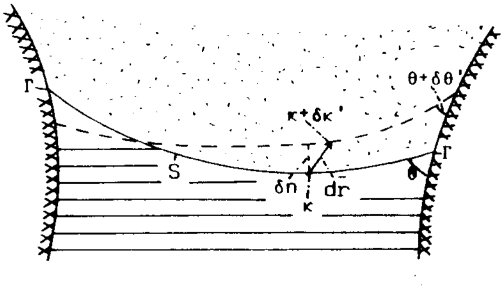


Figure 3.4.4:I The figure shows the notations of formula 3.4.4:L for $\delta^2 T$. The equilibrium meniscus S with boundary Γ is displaced to a new position in the displacement $d\bar{r}$. The mean curvature is then changed from κ to κ + δκ' + ... , while the angle of contact is changed from θ to θ + δθ'+...

It is possible to derive the fundamental formula 3.4.4:L above by considering the work done by the forces acting on the meniscus during the displacement $d\bar{r}$. This very instructive derivation is made in section 3.4.9 for the more general case, when the angle of contact θ may vary over the pore wall.

3.4.5 The variation δκ' of the mean curvature.

There is in reference 9c) an expression for the first-order variation of the mean curvature in the case of a normal displacement $d\bar{r} = dn\,\bar{n}$:

$$2\delta\kappa' = \nabla \cdot \nabla(dn) + (4\kappa^2 - 2K)dn \quad . \qquad (3.4.5:A)$$

Here ∇ is the gradient operator associated with the surface S . For a surface given by $\bar{r} = \bar{r}(u,v)$ the gradient operator ∇ is defined through:

$$\nabla = \frac{1}{EG-F^2}\{\bar{r}_u(G\frac{\partial}{\partial u} - F\frac{\partial}{\partial v}) + \bar{r}_v(E\frac{\partial}{\partial v} - F\frac{\partial}{\partial u})\} \qquad (3.4.5:B)$$

where

$$E = \bar{r}_u \cdot \bar{r}_u \qquad F = \bar{r}_u \cdot \bar{r}_v \qquad G = \bar{r}_v \cdot \bar{r}_v \quad . \qquad (3.4.5:C)$$

The operator $\nabla \cdot \nabla$ is identical with the operator Δ of reference 9c) through formula A1:O in the appendix on differential geometry.

Let κ_1 and κ_2 denote the two principal radii of curvature. See appendix A1. Then with formulas A1:Q and A1:R we have:

$$4\kappa^2 - 2K = 4(\frac{\kappa_1+\kappa_2}{2})^2 - 2\kappa_1\kappa_2 = \kappa_1^2 + \kappa_2^2 \quad . \qquad (3.4.5:D)$$

The gradient operator ∇ for a surface S is discussed in some detail in appendix A1. We only note that the gradient operator has the following important property. Let $\psi = \psi(u,v)$ be a function defined on S . Then $\nabla\psi$ for a point on S is a vector lying in the tangent plane to S in the point:

$$\nabla\psi = \frac{1}{EG-F^2}\{\bar{r}_u(G\frac{\partial\psi}{\partial u} - F\frac{\partial\psi}{\partial v}) + \bar{r}_v(E\frac{\partial\psi}{\partial v} - F\frac{\partial\psi}{\partial u})\}. \qquad (3.4.5:E)$$

Let $d\bar{t}$ be an infinitesimal vector between two adjacent points on S and $d\psi$ the difference in ψ between the two points. Then we have

$$d\psi = d\bar{t} \cdot \nabla\psi \quad . \qquad (3.4.5:F)$$

The second term in formula 3.4.5:A is not difficult to interpret. Let $R_1 = 1/\kappa_1$ and $R_2 = 1/\kappa_2$ be the principal radii of curvature to S . Then the normal displacement dn dimishes these radii to $R_1 - dn$ and $R_2 - dn$. Thus we get the following contribution to the increase of the mean curvature:

$$\frac{1}{2}\left\{\frac{1}{R_1-dn}-\frac{1}{R_1}+\frac{1}{R_2-dn}-\frac{1}{R_2}\right\}\approx\frac{1}{2}\left\{\frac{dn}{R_1^2}+\frac{dn}{R_2^2}\right\}=\frac{1}{2}(\kappa_1^2+\kappa_2^2)dn \quad .$$

(3.4.5:G)

The first term of 3.4.5:A, $\nabla\cdot\nabla(dn)$, is a bit more difficult to interpret. It gives the change in mean curvature due to the fact that $dn = dn(u,v)$ is a varying function over S .

We need the generalization of formula 3.4.5:A to an arbitrary displacement $d\bar{r}$:

$$d\bar{r} = \delta n\ \bar{n} + d\bar{t} \qquad (\delta n = d\bar{r}\cdot\bar{n}) \quad . \qquad (3.4.5:H)$$

Here $d\bar{t}$ is the component of $d\bar{r}$ that is tangent to the surface S . A direct calculation of $\delta\kappa$ in the general case is rather laborious. We will therefore instead use the following method.

Let P be a point on the surface S and P' the corresponding point after the displacement. Let P_n be the point on the displaced surface that lies on the normal to S at P :

P: $\bar{r}(u,v)$

P': $\bar{r}(u,v) + d\bar{r} =$

$= \bar{r}(u,v) + \delta n\bar{n} + d\bar{t}$

P_n: $\bar{r}(u,v) + (\delta n + \dots)\bar{n}$

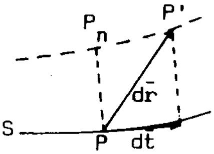


Figure 3.4.5:I The figure shows a point P on a meniscus S and the points P' and P_n on the displaced meniscus.

Then from formula 3.4.5:A we get, writing out the first-order terms:

$$\kappa'(P_n) - \kappa(P) = \frac{1}{2}\{\nabla\cdot\nabla(\delta n) + (\kappa_1^2+\kappa_2^2)\delta n\} + \dots \qquad (3.4.5:I)$$

We now need the increase in mean curvature from P_n to P' on the displaced surface. The vector from P_n to P' is in the first order $d\bar{t}$. Let κ' denote the curvature and ∇' the gradient operator for the displaced surface. Then from formula 3.4.5:F we have:

$$\kappa'(P') - \kappa'(P_n) = d\bar{t} \cdot \nabla'(\kappa') + \ldots =$$

$$= d\bar{t} \cdot (\nabla + \ldots)(\kappa + \ldots) + \ldots = d\bar{t} \cdot \nabla\kappa + \ldots \quad . \tag{3.4.5:J}$$

We have used that in the zeroth order $\nabla = \nabla'$ and $\kappa = \kappa'$.

By adding formulas 3.4.5:I and J we get the formula for the first-order variation in an arbitrary displacement:

$$\delta\kappa' = \frac{1}{2}\{\nabla \cdot \nabla(\delta n) + (\kappa_1^2 + \kappa_2^2)\delta n\} + d\bar{t} \cdot \nabla\kappa$$

$$d\bar{r} = \delta n\,\bar{n} + d\bar{t} \quad . \tag{3.4.5:K}$$

For a meniscus in equilibrium the mean curvature κ is constant. Then $\nabla\kappa$ vanishes and we have:

$$\delta\kappa' = \frac{1}{2}\{\nabla \cdot \nabla(\delta n) + (\kappa_1^2 + \kappa_2^2)\delta n\} \quad . \tag{3.4.5:L}$$

(κ constant)

3.4.6 The variation $\delta\theta'$ in angle of contact.

The contact angle θ between a meniscus S and the pore wall at a point on the boundary curve Γ is given by:

$$\cos(\theta) = \bar{n} \cdot \bar{n}_S \quad . \tag{3.4.6:A}$$

Here $\bar{n}_S$ is the unit normal to the solid pore wall directed into the pore volume. Let $\bar{m}_\Gamma$ denote the unit tangent vector of the boundary curve Γ . Figure 3.4.6:I below shows the various unit vectors used in this section.

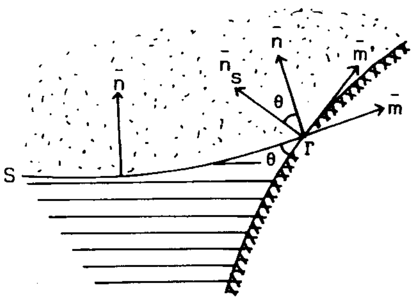


Figure 3.4.6:I The figure shows the different unit vectors used in the calculation of $\delta\theta'$.

From the figure 3.4.6:I we have:

$$\bar{m}' = \cos(\theta)\ \bar{m} + \sin(\theta)\ \bar{n} \qquad (3.4.6:B)$$

$$\bar{n}_s = -\sin(\theta)\ \bar{m} + \cos(\theta)\ \bar{n} \qquad (3.4.6:C)$$

$$\bar{n} = \sin(\theta)\ \bar{m}' + \cos(\theta)\ \bar{n}_s \quad . \qquad (3.4.6:D)$$

The angle of contact θ' between the displaced surface S' and the pore wall is given by

$$\cos(\theta') = \cos(\theta + \delta\theta' + \ldots) = (\bar{n} + \delta\bar{n} + \ldots)\cdot(\bar{n}_s + \delta\bar{n}_s + \ldots)$$

$$(3.4.6:E)$$

where $\delta\theta'$, $\delta\bar{n}$ and $\delta\bar{n}_s$ are the first-order variations of θ' , $\bar{n}$ and $\bar{n}_s$ in the displacement $d\bar{r}$. The first-order terms of the equation above give:

$$-\sin(\theta)\delta\theta' = \bar{n}\cdot\delta\bar{n}_s + \bar{n}_s\cdot\delta\bar{n} \quad . \qquad (3.4.6:F)$$

The displacement $d\bar{r}$ of a point on the boundary Γ to a new position on the pore wall may be written:

$$d\bar{r} = \delta m' \, \bar{m}' + \delta m_\Gamma \, \bar{m}_\Gamma + \ldots \quad . \qquad (3.4.6:G)$$

Here $\delta m'$ and δm_Γ are the first-order displacements in the directions of $\bar{m}'$ and $\bar{m}_\Gamma$ respectively. The quantity $\delta\bar{n}_s$ is the change of the normal $\bar{n}_s$ in this displacement along the pore wall. Then from formula 3.4.5:F we have:

$$\delta\bar{n}_s = (d\bar{r} \cdot \nabla_s)\bar{n}_s = [(\delta m' \, \bar{m}' + \delta m_\Gamma \bar{m}_\Gamma) \cdot \nabla_s] n_s \quad . \qquad (3.4.6:H)$$

We have here applied formula 3.4.5:F on each component of $\bar{n}_s$. The symbol ∇_s is the gradient operator for the surface of the pore wall.

With formulas 3.4.6:B and G the displacement of a point on the boundary may be written:

$$d\bar{r} = \delta n \, \bar{n} + \delta\bar{t} + \ldots \quad ,$$
$$\delta\bar{t} = \delta m' \cos(\theta)\bar{m} + \delta m_\Gamma \bar{m}_\Gamma \quad . \qquad (3.4.6:I)$$

The displacement $\delta\bar{t}$ is tangent to the meniscus S.

The quantity $\delta\bar{n}$ denotes the change of the unit normal of the meniscus S in this displacement. The problem of getting $\delta\bar{n}$ for the displacement 3.4.6:I is analogous to the problem of calculating $\delta\kappa'$ in the preceding section for a displacement $d\bar{r} = \delta n \, \bar{n} + \delta\bar{t}$. The total change $\delta\bar{n}$ is the sum of a change $\delta\bar{n}^1$ in the tangent displacement $\delta\bar{t}$ and a change $\delta\bar{n}^2$ in the normal displacement $\delta n \, \bar{n}$.

The change $\delta\bar{n}^1$ in $\bar{n}$ due to the displacement $\delta\bar{t}$ is in the same way as above for $\delta\bar{n}_s$:

$$\delta\bar{n}^1 = (\delta\bar{t} \cdot \nabla)\bar{n} = [(\delta m' \cos(\theta)\bar{m} + \delta m_\Gamma \bar{m}_\Gamma) \cdot \nabla] \bar{n} \quad . \qquad (3.4.6:J)$$

A formula for the change in $\bar{n}$ in a displacement is given in reference 12a):

$$\begin{aligned} \delta\bar{n}^2 &= - \bar{n} \times [\nabla \times (\delta n \ \bar{n})] = \\ &= - \bar{n} \times [\nabla(\delta n) \times \bar{n}] = \\ &= - \nabla(\delta n) \quad . \end{aligned} \qquad (3.4.6:K)$$

On the second line we have used a formula from 12b).

In conclusion we have the following formula for the first-order variation in $\bar{n}$ in an arbitrary displacement:

$$\begin{aligned} \delta\bar{n} &= - \nabla(\delta n) + (\delta\bar{t} \cdot \nabla)\bar{n} \\ d\bar{r} &= \delta n \cdot \bar{n} + \delta\bar{t} \quad . \end{aligned} \qquad (3.4.6:L)$$

Using 3.4.6:C,D,H,J and K in 3.4.6:F we get:

$$\begin{aligned} - \sin(\theta) \bullet \delta\theta' &= \bar{n}_s \cdot [\delta m_\Gamma \ \bar{m}_\Gamma \cdot \nabla]\bar{n} + \\ &+ (- \sin(\theta)\bar{m} + \cos(\theta)\bar{n}) \bullet \{ - \nabla(\delta n) + [\delta m' \cos(\theta)\bar{m} \bullet \nabla]\bar{n}\} + \\ &+ (\sin(\theta)\bar{m}' + \cos(\theta)\bar{n}_s) \bullet [\delta m'\bar{m}' \cdot \nabla_s]\bar{n}_s + \bar{n} \cdot [\delta m_\Gamma \bar{m}_\Gamma \bullet \nabla_s]\bar{n}_s \end{aligned} \quad (3.4.6:M)$$

Let m_Γ denote the arc length along Γ . Then we have from formula 3.4.5:F:

$$[\bar{m}_\Gamma \bullet \nabla_s]\bar{n}_s = \frac{\partial\bar{n}_s}{\partial m_\Gamma} \qquad [\bar{m}_\Gamma \bullet \nabla]\bar{n} = \frac{\partial\bar{n}}{\partial m_\Gamma} \quad . \qquad (3.4.6:N)$$

Let κ_s denote the curvature of the pore wall of the boundary curve Γ in the direction of $\bar{m}'$, that is perpendicular to Γ . Then from formula A1:P in appendix 1 we have:

$$\kappa_s = - \bar{m}' \bullet [(\bar{m}' \bullet \nabla_s)\bar{n}_s] \quad . \qquad (3.4.6:O)$$

Let κ_m denote the curvature of the meniscus S at Γ in the direction of $\bar{m}$, that is perpendicular to Γ. Then in the same way we have:

$$\kappa_m = - \bar{m} \cdot [(\bar{m} \cdot \nabla)\bar{n}] \quad . \qquad (3.4.6:P)$$

Since $\bar{n}$ is a unit vector, we have

$$0 = (\bar{m} \cdot \nabla)(\bar{n} \cdot \bar{n}) = 2\bar{n} \cdot [(\bar{m} \cdot \nabla)\bar{n}] \quad . \qquad (3.4.6:Q)$$

In the same way we have for $\bar{n}_s$:

$$0 = \bar{n}_s \cdot [(\bar{m}' \cdot \nabla_s)\bar{n}_s] \quad . \qquad (3.4.6:R)$$

Inserting 3.4.6:N-R in 3.4.6:M we get:

$$- \sin(\theta)\delta\theta' = \sin(\theta)\delta m'(- \kappa_s) + \delta m_\Gamma \, \bar{n} \cdot \frac{\partial \bar{n}_s}{\partial m_\Gamma} +$$

$$+ \sin(\theta)\bar{m} \cdot \nabla(\delta n) - \sin(\theta)\delta m' \cos(\theta)(- \kappa_m) + \delta m_\Gamma \bar{n}_s \cdot \frac{\partial \bar{n}}{\partial m_\Gamma} \quad .$$

$$(3.4.6:S)$$

With the use of formula 3.4.6:A and $\delta m' = \delta n/\sin(\theta)$ we get the fundamental formula for the first-order change in angle of contact θ' :

$$\delta\theta' = \delta m_\Gamma \frac{\partial\theta}{\partial m_\Gamma} + \delta n \frac{\kappa_s - \kappa_m \cos(\theta)}{\sin(\theta)} - \bar{m} \cdot \nabla(\delta n) \quad . \qquad (3.4.6:T)$$

The first term, $\delta m_\Gamma \frac{\partial\theta}{\partial m_\Gamma}$, gives the change in θ' due to the displacement δm_Γ in the direction of Γ . For a meniscus, where the contact angle θ is constant along the boundary curve Γ , $\frac{\partial\theta}{\partial m_\Gamma}$ is zero and this term vanishes. Then we have:

$$\delta\theta' = \delta n \frac{\kappa_s - \kappa_m \cos(\theta)}{\sin(\theta)} - \bar{m} \cdot \nabla(\delta n) \quad . \qquad (3.4.6:U)$$

(θ constant)

3.4.7 The second part δ^2U' of the variation of energy.

The change δ^2U in energy for a displacement $d\bar{r}$ of a meniscus in an isolated meniscus region is given by formulas 3.4.3:C-F. We have in the preceding sections studied the first part δ^2T of the second-order variation of the energy. The second part δ^2U' of formula 3.4.3:C depends on the thermodynamical properties of the six phases of the meniscus region. From formulas 3.4.3:E,F and formula 3.3:R we have:

$$\delta^2U' = \sum_{\alpha} \delta^2U'_{\alpha} \quad , \tag{3.4.7:A}$$

$$\delta^2U'_{\alpha} = \frac{1}{2} \sum_{i=1}^{4} \sum_{j=1}^{4} \frac{\delta^2U_{\alpha}}{\partial X_i \partial X_j} \delta X_i \; \delta X_j =$$

$$= \frac{1}{2}\{\delta T_{\alpha} \; \delta S_{\alpha} + \delta y_{\alpha} \; \delta Y_{\alpha} + \delta\mu_w^{\alpha} \; \delta N_w^{\alpha} + \delta u_a^{\alpha} \; \delta N_a^{\alpha}\} \quad . \tag{3.4.7:B}$$

Here we have used the notations of paragraph 3.3

The displacement $d\bar{r}$ determines the change δV_{ℓ} of liquid volume and the change $\delta A_{s\ell}$ of solid-liquid area. Then we have for the isolated meniscus region using formula 3.4.2:H:

$$\delta V_g = - \delta V_{\ell} \qquad \delta A_{sg} = - \delta A_{s\ell} \qquad \delta A_{\ell g} = \cos(\theta)\delta A_{s\ell} - 2\kappa \; \delta V_{\ell} \tag{3.4.7:C}$$

δV_{ℓ} and $\delta A_{s\ell}$ may have any values. Then δV_g , δA_{sg} and $\delta A_{\ell g}$ are given from these formulas.

We will in this section study the dependance of δ^2U' on the variations of entropies and masses for a given displacement $d\bar{r}$. In our study of stability we are interested in those variations which give the smallest possible value for δ^2U' and thus for δ^2U .

The six changes of entropies are only subject to the condition of isolation:

$$\sum_{\alpha} \delta S_{\alpha} = 0 \qquad (3.4.7:D)$$

$$(\alpha = s, \ell, g, s\ell, sg, \ell g)$$

For the five variations of amounts of water and the five variations of amounts of air we have:

$$\sum_{\alpha} \delta N_{w}^{\alpha} = 0 \qquad \sum_{\alpha} \delta N_{a}^{\alpha} = 0 \qquad (3.4.7:E)$$

$$(\alpha = \ell, g, s\ell, sg, \ell g)$$

In the quadratic form 3.4.7:A,B we now have fifteen (2+5+4+4) independent variables δV_{ℓ} , $\delta A_{s\ell}$, δS_{s} , ..., $\delta N_{a}^{\ell g}$. In the variation we get certain induced changes of the temperatures, δT_{α} , and chemical potentials, $\delta\mu_{w}^{\alpha}$ and $\delta\mu_{a}^{\alpha}$, in the different phases α . Consider for given $d\bar{r}$ and thus for given δV_{ℓ} and $\delta A_{s\ell}$ any possible variation in entropies and masses. The phases α are mutually stable for variations of entropy and masses. This follows from the internal stability of the phases using formula 3.3:S. Suppose now that, after the considered variation, heat or entropy is transferred between the phases so that we get the same temperature in all phases. Then this will diminish the energy, since thermal equilibrium is established. In the same way the energy will diminish, when water and air are transferred between the phases, so that we get the same chemical potentials in all phases.

Thus for given δV_{ℓ} and $\delta A_{s\ell}$ the smallest value of $\delta^2 U'$ is given for a variation such that the new temperatures and chemical potentials are the same in all phases:

$$\delta T_\alpha = \delta T \qquad (\alpha = s, \ell, g, s\ell, sg, \ell g)$$

$$\delta\mu_w^\alpha = \delta\mu_w \qquad (\alpha = \ell, g, s\ell, sg, \ell g) \qquad (3.4.7{:}F)$$

$$\delta\mu_a^\alpha = \delta\mu_a \qquad \text{– " –}$$

This gives thirteen (5+4+4) relations between the variations. Then we have only two independent variations δV_ℓ and δA_ℓ left. Inserting 3.4.7:F in 3.4.7:A and B and using 3.4.7:D-E we get for this smallest $\delta^2 U'$ for given δV_ℓ and $\delta A_{s\ell}$:

$$\delta^2 U' = \frac{1}{2} \sum_\alpha \delta y_\alpha \cdot \delta Y_\alpha =$$

$$= \frac{1}{2} \{- \delta p_g \, \delta V_g - \delta p_\ell \, \delta V_\ell + \delta\gamma_{s\ell} \delta A_{s\ell} + \delta\gamma_{sg} \delta A_{sg} + \delta\gamma_{\ell g} \delta A_{\ell g}\}$$

(3.4.7:G)

Using 3.4.7:C we get

$$2\delta^2 U' = [\delta(p_g - p_\ell) - 2\kappa \, \delta\gamma_{\ell g}]\delta V_\ell + [\cos(\theta)\delta\gamma_{\ell g} - \delta(\gamma_{sg} - \gamma_{s\ell})]\delta A_{s\ell}$$

(3.4.7:H)

This variation giving the smallest change for $\delta^2 U'$ for given δV_ℓ and $\delta A_{s\ell}$ is of a rather special type. The meniscus of the isolated region is conceived to be displaced to a new position giving the prescribed δV_ℓ and $\delta A_{s\ell}$. This new position is normally no equilibrium position. Then the meniscus is kept fixed, and thermal and chemical equilibrium between the six phases is established. Then $\delta(p_g - p_\ell)$ in formula 3.4.7:H is the change of the pressure difference over the meniscus for the state thus established. The quantity $\delta\gamma_{\ell g}$ is the change of surface tension of the meniscus, and $\delta(\gamma_{sg} - \gamma_{s\ell})$ is the change of $\gamma_{sg} - \gamma_{s\ell}$. These three changes will depend linearly on the on the prescribed values δV_ℓ and $\delta A_{s\ell}$, since we are dealing with first-order changes. For example for the change δp_g in gas pressure we will have:

$$\delta p_g = K_V\ \delta V_\ell + K_A\ \delta A_{s\ell} \quad . \tag{3.4.7:I}$$

The coefficients K_V and K_A will be functions of the thermodynamical variables of the different phases.

Thus we get for the combination of changes in formula 3.4.7:H expressions of the following type:

$$\delta(p_g - p_\ell) - 2\kappa\ \delta\gamma_{\ell g} = \gamma_{\ell g}\{\beta_{VV}\ \delta V_\ell + \beta'_{VA}\ \sin(\theta)\delta A_{s\ell}\}$$

$$\cos(\theta)\delta\gamma_{\ell g} - \delta(\gamma_{sg} - \gamma_{s\ell}) = \gamma_{\ell g}\{\beta''_{VA}\ \sin(\theta)\delta V_\ell + \beta_{AA}\ \sin^2(\theta)\delta A_{s\ell}\} \tag{3.4.7:J}$$

The factors $\gamma_{\ell g}$ and $\sin(\theta)$ are introduced for future convenience.

Inserting these expressions in 3.4.7:H we get:

$$\delta^2 U' = \frac{\gamma_{\ell g}}{2}\{\beta_{VV}(\delta V_\ell)^2 + 2\ \beta_{VA}\ \delta V_\ell\ (\sin(\theta)\delta A_{s\ell}) + $$

$$+ \beta_{AA}(\sin(\theta)\delta A_{s\ell})^2\} \quad , \tag{3.4.7:K}$$

where

$$\delta V_\ell = \iint_S \delta n\ dS \qquad \sin(\theta)\delta A_{s\ell} = \oint_\Gamma \delta n\ ds \tag{3.4.7:L}$$

and

$$\beta_{VA} = \frac{\beta'_{VA} + \beta''_{VA}}{2} \quad . \tag{3.4.7:M}$$

Formula 3.4.7:K will be used in the mathematical analysis of stability in section 3.5.

From formula 3.3:S we have that $\delta^2 U'_\alpha$ is non-negative for any variation. Then this is also true for the sum $\delta^2 U'$. Thus the quadratic form 3.4.7:K is non-negative and the coefficients will satisfy:

$$\beta_{VV} \geq 0 \qquad \beta_{AA} \geq 0 \qquad \beta_{VV}\,\beta_{AA} \geq (\beta_{VA})^2 \ . \qquad (3.4.7:N)$$

If we make the pore region surrounding the meniscus larger and larger, then the changes $\delta(p_g - p_\ell)$, $\delta\gamma_{\ell g}$, and $\delta(\gamma_{sg} - \gamma_{s\ell})$ of intensive variables for given δV_ℓ and $\delta A_{s\ell}$ will become smaller and smaller. Thus we have the important conclusion that, in the limit of an infinite pore region around the meniscus, the coefficients β_{VV}, β_{VA}, and β_{AA} will be zero.

The coefficients β_{VV}, β_{VA} and β_{AA} depend on the thermodynamical variables of the six phases in a rather complex way. A calculation of the coefficients would require a detailed knowledge of the thermodynamical properties of the bulk phases and surface phases. We will not discuss this problem any further. A very simple example of the type of calculations necessary to get the coefficients is given in section 3.5.1.

3.4.8 Stability of a meniscus region.

In this section we will summarize the results of the previous sections. We have considered a displacement $d\bar{r}$ of an equilibrium meniscus in an isolated meniscus region. See figures 3.4:I and 3.4.1:I. The second-order variation of the energy is according to formula 3.4.3:C:

$$\delta^2 U = \gamma_{\ell g}\,\delta^2 T + \delta^2 U' \quad . \qquad (3.4.8:A)$$

The first term is given by formula 3.4.4:L:

$$\delta^2 T = -\iint_S \delta\kappa' \, \delta n \, dS - \frac{1}{2}\oint_\Gamma \delta\theta' \, \delta n \, ds \quad . \tag{3.4.8:B}$$

Here $\delta n = d\bar{r} \cdot \bar{n}$ is the first order displacement in the normal direction.

The change $\delta\kappa'$ of mean curvature is from formula 3.4.5:L:

$$2\delta\kappa' = \nabla \cdot \nabla(\delta n) + (\kappa_1^2 + \kappa_2^2)\delta n \quad . \tag{3.4.8:C}$$

The change $\delta\theta'$ in angle of contact is from formula 3.4.6:U:

$$\delta\theta' = \delta n \, \frac{\kappa_s - \kappa_m \cos(\theta)}{\sin(\theta)} - \bar{m} \cdot \nabla(\delta n) \quad . \tag{3.4.8:D}$$

It is here assumed that the contact angle θ is constant over the pore wall and that $0 < \theta < \pi$. The case of varying contact angle θ over the pore wall is treated in the following section 3.4.9. The modifications required, when $\theta = 0$ or $\theta = \pi$, are discussed at the end of this section.

From formula 3.4.8:B-D we have:

$$2\delta^2 T = -\iint_S [\nabla \cdot \nabla(\delta n) + (\kappa_1^2 + \kappa_2^2)\delta n]\delta n \, dS +$$

$$+ \oint_\Gamma [\frac{\kappa_m \cos(\theta) - \kappa_s}{\sin(\theta)} \delta n + \bar{m} \cdot \nabla(\delta n)]\delta n \, ds \quad . \tag{3.4.8:E}$$

This formula may be simplified by the use of formula A1:U in appendix 1. We then get the following fundamental formula:

$$2\delta^2 T = \iint_S [\nabla(\delta n) \cdot \nabla(\delta n) - (\kappa_1^2 + \kappa_2^2)(\delta n)^2] \, dS +$$

$$+ \oint_\Gamma \frac{\kappa_m \cos(\theta) - \kappa_s}{\sin(\theta)} (\delta n)^2 \, ds \quad . \tag{3.4.8:F}$$

The second part $\delta^2 U'$ of the second-order change in energy in formula 3.4.8:A depends on the changes in entropies and masses. The smallest possible value of $\delta^2 U'$ for a given displacement $d\bar{r}$ is from formula 3.4.7:K of the following type:

$$\delta^2 U' = \frac{\gamma_{\ell g}}{2} \{\beta_{VV}(\delta V_\ell)^2 + 2\ \beta_{VA}\ \delta V_\ell (\sin(\theta)\ \delta A_{s\ell}) + + \beta_{AA}(\sin(\theta)\ \delta A_{s\ell})^2\} \quad . \qquad (3.4.8{:}G)$$

where

$$\delta V_\ell = \iint_S \delta n\ dS \qquad \sin(\theta)\delta A_{s\ell} = \oint_\Gamma \delta n\ ds \quad . \qquad (3.4.8{:}H)$$

We will from now on only consider this variation in entropies and masses that gives the smallest $\delta^2 U'$ for given $d\bar{r}$.

Finally, we now have from 3.4.8:A,F and G the (smallest) second-order variation in energy in a displacement $d\bar{r}$ with first-order normal component δn :

$$\delta^2 U = \frac{\gamma_{\ell g}}{2} \{ \iint_S [\nabla(\delta n)\cdot\nabla(\delta n) - (\kappa_1^2 + \kappa_2^2)(\delta n)^2] dS + + \oint_\Gamma \frac{\kappa_m \cos(\theta) - \kappa_s}{\sin(\theta)} (\delta n)^2\ ds + \beta_{VV}(\iint \delta n\ dS)^2 + + 2\ \beta_{VA}(\iint_S \delta n\ dS \oint_\Gamma \delta n\ ds) + \beta_{AA}(\oint_\Gamma \delta n\ ds)^2\} . \quad (3.4.8{:}I)$$

In this fundamental formula $\delta n = \delta n(u,v)$ is any function over the surface S . Stability requires that this expression is non-negative for all δn .

The second part $\delta^2 U'$ of $\delta^2 U$ in 3.4.8:A is non-negative for any variation. Thus if $\delta^2 T$ is positive for all variations, then this is also true for $\delta^2 U$, and we have stability. This stability criterion with $\delta^2 T$ given by formula 3.4.2:E is stated by Gibbs [13]. The second part $\delta^2 U'$ is zero for displacements δn with $\delta V_\ell = 0$ and $\delta A_{s\ell} = 0$. Thus if there is a displacement δn with $\delta V_\ell = 0$, $\delta A_{s\ell} = 0$ and $\delta^2 T < 0$, then $\delta^2 U$ is negative and we have instability. When neither of these two possibilities occur, the stability investigation requires a study of both $\delta^2 T$ and $\delta^2 U'$.

It is appropriate to introduce the following terminology. A meniscus S is called strongly stable if

$$\delta^2 T > 0 \qquad \text{for all} \quad \delta n \quad . \tag{3.4.8:J}$$

(The case $\delta n \equiv 0$ is of course excluded.)
The meniscus S is strongly unstable if there exists a displacement δn such that

$$\delta^2 T < 0 \qquad \delta V_\ell = 0 \qquad \delta A_{s\ell} = 0 \quad . \tag{3.4.8:K}$$

Finally the meniscus S is called weakly stable if the following two conditions are fulfilled:

i. There exists a displacement δn with $\delta^2 T < 0$

ii. $\delta^2 T > 0$ for all displacements with $\delta V_\ell = 0$ and $\delta A_{s\ell} = 0$. (3.4.8:L)

These two conditions are essentially the negation of 3.4.8:J and K. The remaining possibilities with $\delta^2 T = 0$ for some variation in the cases 3.4.8:J-L are more complicated. The stability may be governed by terms of higher order than two. We will not study these more complicated special cases.

With this terminology we have that, if a meniscus S is strongly stable, then S together with any surrounding meniscus region is stable. If, in the other extreme, a meniscus is strongly unstable, then any surrounding meniscus region is unstable. Finally, if the meniscus is weakly stable then the stability of the meniscus region will depend on the surrounding region, that is on β_{VV} , β_{VA} and β_{AA} .

Thermodynamically the region around the meniscus acts on the meniscus through δ^2U' as a restoring force in the displacement. When the meniscus is strongly stable, we have stability even without the use of these restoring effects of the different phases in the meniscus region. When the meniscus is strongly unstable, there is a displacement with $\delta^2T < 0$ such that δV_ℓ and $\delta A_{s\ell} = 0$. In this displacement the different phases are unaffected. Consequently there is no restoring force, and we certainly have instability.

When the meniscus is weakly stable, the stability of the meniscus region will depend on the strength of the restoring forces from the phases of the region. Let us first consider the case when the surrounding pore volume of the meniscus region is very large. Then, for a given displacement, for example the change in gas pressure, δp_g will be very small. The restoring forces of the phases are very small. Mathematically this means that the coefficients β_{VV} , β_{VA} and β_{AA} are very small, and δ^2U' is very close to zero. Thus the meniscus region will be unstable for a sufficiently large surrounding. Suppose now that we diminish the surrounding region. Then the restoring forces and consequently δ^2U' will increase for a given displacement (except for displacements with $\delta V_\ell = 0$ and $\delta A_{s\ell} = 0$ where $\delta^2U' = 0$). By making the surrounding region sufficiently small we can increase

δ^2U' as much as we choose. The meniscus region will be stable if it is sufficiently small. In conclusion we have instability for a weakly stable meniscus together with a sufficiently large surrounding, but stability for the meniscus together with a sufficiently small surrounding.

Thus, coarsely speaking, a weakly stable meniscus has to fluctaute cooperatively with a surrounding of a certain size in order to reach a state of lower total energy. The probability for the required fluctuation will decrease with increasing size of these surroundings.

Modifications when $\theta = 0$ and $\theta = \pi$. We have in this section assumed that $\sin(\theta)$ is not zero. The modifications required, when the contact angle θ is equal to 0 or π , are straight-forward.

For the displacement $\delta m' = d\bar{r} \cdot \bar{m}'$ in the $\bar{m}'$-direction we have that $\delta m' \sin(\theta) = \delta n$. See figure 3.4.1:II. Thus the normal displacement δn is zero at the boundary Γ , when $\sin(\theta)$ is zero:

$$\delta n \Big|_{\Gamma} = 0 \qquad (\theta=0,\pi) \quad . \qquad (3.4.8:M)$$

There are no restrictions on the displacement $\delta m'$ along the pore wall. The quantity $\delta n/\sin(\theta)$ is to be replaced by $\delta m'$ in the different formulas:

$$\left.\frac{\delta n}{\sin(\theta)}\right|_{\Gamma} \rightarrow \delta m' \quad (\theta=0,\pi) \quad . \qquad (3.4.8:N)$$

Then the line integral in expression 3.4.8:F for δ^2T vanishes:

$$2\delta^2T = \iint_S [\nabla(\delta n) \cdot \nabla(\delta n) - (\kappa_1^2 + \kappa_2^2)(\delta n)^2]dS \quad . \qquad (3.4.8:O)$$

$$(\theta=0,\pi)$$

Formula 3.4.7:H for $\delta^2 U'$ is still valid. But in the linear expressions 3.4.7:J we must omit the factors $\sin(\theta)$.

$$\delta(p_g - p_\ell) - 2\kappa\ \delta\gamma_{\ell g} = \gamma_{\ell g}\{\beta_{VV}\ \delta V_\ell + \beta'_{VA}\ \delta A_{s\ell}\}$$

$$\cos(\theta)\delta\gamma_{\ell g} - \delta(\gamma_{sg} - \gamma_{s\ell}) = \gamma_{\ell g}\{\beta''_{VA}\ \delta V_\ell + \beta_{AA}\ \delta A_{s\ell}\} \qquad (3.4.8:P)$$

Then we get for $\delta^2 U'$:

$$\delta^2 U' = \frac{\gamma_{\ell g}}{2}\ \{(\beta_{VV} - \frac{\beta_{VA}^2}{\beta_{AA}})(\delta V_\ell)^2 + \beta_{AA}(\delta A_{s\ell} + \frac{\beta_{VA}}{\beta_{AA}}\ \delta V_\ell)^2\} \qquad (3.4.8:Q)$$

The change $\delta A_{s\ell}$ is given by

$$\delta A_{s\ell} = \oint_\Gamma \delta m'\ ds \quad . \qquad (3.4.8:R)$$

The displacement $\delta m'$ and thereby $\delta A_{s\ell}$ may be chosen independently of δn . Then from 3.4.8:Q the smallest value of $\delta^2 U'$ for given δn is:

$$\delta^2 U' = \frac{\gamma_{\ell g}}{2}\ \beta^o_{VV}(\delta V_\ell)^2$$

where

$$\beta^o_{VV} = \beta_{VV} - \frac{\beta_{VA}^2}{\beta_{AA}} \quad . \qquad (3.4.8:T)$$

Formula 3.4.8:I for the total change in energy is replaced by

$$\delta^2 U = \frac{\gamma_{\ell g}}{2}\ \{\iint_S [\nabla(\delta n)\ \nabla(\delta n) - (\kappa_1^2 + \kappa_2^2)(\delta n)^2]dS + \beta^o_{VV}(\iint_S \delta n\ dS)^2\}$$

$$(\theta = 0, \pi) \qquad (3.4.8:U)$$

where δn is any function over S which is zero on the boundary Γ .

3.4.9 Alternative derivation of $\delta^2 U$ for a more general situation

There is an alternative, very instructive way to derive the change in energy $\delta^2 U$ by considering the work done by the forces that act on the meniscus in the imagined displacement $d\bar{r}$.

We have hitherto assumed that the contact angle θ is constant throughout the pore wall. We will in this section remove this restriction and allow θ to vary over the pore wall. The contact angle θ is also for each point on the walls a function of the thermodynamical state. The given function θ over the pore walls refers to the contact angles at the intitial equilibrium state of the meniscus region. The function θ will be discontinuous along a curve, where two different kinds of pore walls meet.

We assume that θ is continuously differentiable over the pore wall, except along some simple curves, where θ may be discontinuous. We will also allow corners and edges on the pore walls along some curves. Thus we have that the contact angle θ is a smooth function over smooth pore walls except for some curves, where the contact angle θ or the unit normal to the pore wall have discontinuities.

Consider now a displacement $d\bar{r}$ of a meniscus in an isolated meniscus region. This equilibrium meniscus S is displaced to a new surface S' in the pore. The forces acting on S balance. But on S' there are unbalanced forces. In the gas and liquid phases there are after the displacement the pressures $p_g + \Delta p_g$ and $p_\ell + \Delta p_\ell$. The surface tension of the meniscus is $\gamma_{\ell g} + \Delta\gamma_{\ell g}$, and the mean curvature at a point on S' is $\kappa + \Delta\kappa'$. The pressures and the surface tension give a net force on the meniscus.

See section 2.2 and especially formulas 2.2:C,E and figures 2.2:III,IV. This net force acting on a surface element dS' of the displaced surface S' is directed in the normal direction $\bar{n}'$. The force is:

$$\bar{F}_{dS'} = (-p_g-\Delta p_g + p_\ell+\Delta p_\ell + 2(\gamma_{\ell g}+\Delta\gamma_{\ell g})(\kappa+\Delta\kappa'))\bar{n}'\ dS' =$$

$$= (-p_g+p_\ell + 2\gamma_{\ell g}\kappa - \delta p_g+\delta p_\ell + 2\kappa\delta\gamma_{\ell g} + 2\gamma_{\ell g}\delta\kappa' + \ldots)(\bar{n} + \ldots)(dS + \ldots) =$$

$$= 2\gamma_{\ell g}\ \delta\kappa'\ \bar{n}\ dS + (-\ \delta(p_g-p_\ell) + 2\kappa\delta\gamma_{\ell g})\bar{n}\ dS + \ldots \qquad (3.4.9:A)$$

The zero-order terms vanish because of the force equilibrium condition (formula 2.2:D). The last line gives the first-order terms of the force. Here dS and dS' are corresponding surface elements on S and S' . The first term of the last line is the force due to a change $\delta\kappa'$ in mean curvature and the second term is the force due to changes in the thermodynamical variables p_g , p_ℓ and $\gamma_{\ell g}$ in the vicinity of the surface element.

At the boundary Γ' of S' there is a net force acting along the pore wall. Let $\bar{m}''$ (corresponding to $\bar{m}'$ at Γ) be the unit vector which is tangential to the pore wall, perpendicular to Γ' , and points in the direction from liquid to gas. Let $\theta' = \theta + \delta\theta' + \ldots$ be the angle of contact. Then the force on a line element ds' along the pore wall due to the surface tension $\gamma_{\ell g} + \Delta\gamma_{\ell g}$ is:

$$-\ (\gamma_{\ell g} + \Delta\gamma_{\ell g})\ \cos(\theta')\bar{m}''\ ds' \quad . \qquad (3.4.9:B)$$

The difference $\gamma_{sg}-\gamma_{s\ell}$ may be interpreted as a force per unit length acting on Γ in the direction of $\bar{m}'$. Then the following force acts on the corresponding displaced line element ds' of Γ' :

$$[\gamma_{sg}-\gamma_{s\ell} + \Delta(\gamma_{sg}-\gamma_{s\ell})]\bar{m}'' \, ds' \quad . \qquad (3.4.9{:}C)$$

The quantity $\Delta(\gamma_{sg}-\gamma_{s\ell})$ is the change of $\gamma_{sg}-\gamma_{s\ell}$ in the displacement $d\bar{r}$ of a point on the boundary Γ . This change has two different causes. Firstly, there is a change due to the displacement from a point on the pore wall with contact angle θ to a new point with contact angle $\theta + \Delta\theta$. These two values are the contact angles in the initial thermodynamical state of the meniscus region. This first part of the change is then from formula 3.4.1:M:

$$\Delta^{I}(\gamma_{sg}-\gamma_{s\ell}) = \gamma_{\ell g} \cos(\theta + \Delta\theta) - \gamma_{\ell g} \cos(\theta) \quad . \qquad (3.4.9{:}D)$$

Secondly the displacement $d\bar{r}$ induces a change in the thermodynamical states of the phases of the meniscus region and thus a change in $\gamma_{sg}-\gamma_{s\ell}$. Let us denote the first-order term $\delta^{II}(\gamma_{sg}-\gamma_{s\ell})$:

$$\Delta^{II}(\gamma_{sg}-\gamma_{s\ell}) = \delta^{II}(\gamma_{sg}-\gamma_{s\ell}) + \ldots \quad . \qquad (3.4.9{:}E)$$

From 3.4.9:B-E we get the net force along the pore wall on a line element ds' of Γ' :

$$\bar{F}_{ds'} = [-(\gamma_{\ell g}+\Delta\gamma_{\ell g})\cos(\theta') + \gamma_{sg}-\gamma_{s\ell} + \Delta^{I}(\gamma_{sg}-\gamma_{s\ell}) + \Delta^{II}(\gamma_{sg}-\gamma_{s\ell})]\,\bar{m}''\,ds' =$$

$$= [-(\gamma_{\ell g}+\delta\gamma_{\ell g} + \ldots)\cos(\theta+\delta\theta' + \ldots) + \gamma_{sg}-\gamma_{s\ell} + \gamma_{\ell g}\cos(\theta+\delta\theta+\ldots) -$$

$$- \gamma_{\ell g} \cos(\theta) + \delta^{II}(\gamma_{sg}-\gamma_{s\ell})+\ldots]\,(\bar{m}'+\ldots)(ds+\ldots) =$$

$$= \gamma_{\ell g} \sin(\theta)(\delta\theta' - \delta\theta)\bar{m}' \, ds + [\delta^{II}(\gamma_{sg} - \gamma_{s\ell}) - \delta\gamma_{g\ell}\cos(\theta)]\bar{m}' \, ds + \ldots \tag{3.4.9:F}$$

Here we have again used formula 3.4.1:M. The last line gives the first-order terms of the net force. The quantity $\delta\theta'$ denotes the first-order change in angle of contact and $\delta\theta$ the difference in contact angle between corresponding points on Γ' and Γ in the initial thermodynamical state. Thus the first term of the last line gives the force due to a change in angle of contact $\delta\theta'$ in the displacement and the force due to the difference $\delta\theta$ in contact angle between corresponding points in the displacement on the pore wall. The second term gives the force due to induced changes in the values of the thermodynamical variables γ_{sg}, $\gamma_{s\ell}$ and $\gamma_{\ell g}$ in the vicinity of the considered line element.

The change $\delta\theta'$ in angle of contact is studied in section 3.4.6. From formula 3.4.6:T we have:

$$\delta\theta' = \delta m_\Gamma \frac{\partial\theta}{\partial m_\Gamma} + \delta n \frac{\kappa_s - \kappa_m \cos(\theta)}{\sin(\theta)} - \bar{m} \cdot \nabla(\delta n) \quad . \tag{3.4.9:G}$$

Here $\delta m_\Gamma = d\bar{r} \cdot \bar{m}_\Gamma$ is the displacement along the boundary curve Γ, while $\frac{\partial\theta}{\partial m_\Gamma}$ is the rate of increase in θ in this direction.

The displacement $d\bar{r}$ of a point on the boundary Γ to a new position on the pore wall may according to formula 3.4.6:G be written:

$$d\bar{r} = \delta m' \, \bar{m}' + \delta m_\Gamma \, \bar{m}_\Gamma + \ldots \quad . \tag{3.4.9:H}$$

Here δm_Γ and $\delta m'$ are the displacements along Γ and perpendicular to Γ in the direction of $\bar{m}'$ on the pore wall. Thus the change $\delta\theta$ in contact angle is:

$$\delta\theta = \delta m_{\Gamma} \frac{\partial\theta}{\partial m_{\Gamma}} + \delta m' \frac{\partial\theta}{\partial m'} \quad . \qquad (3.4.9:I)$$

Here $\frac{\partial\theta}{\partial m'}$ is the rate of increase in θ in the direction of $\bar{m}'$, that is perpendicular to Γ along the pore wall.

From 3.4.9:G and I we get:

$$\delta\theta' - \delta\theta = \delta n \, \frac{\kappa_s - \kappa_m \cos(\theta) - \frac{\partial\theta}{\partial m'}}{\sin(\theta)} - \bar{m} \cdot \nabla(\delta n) \quad . \qquad (3.4.9:J)$$

We note that the change of θ along Γ does not appear in this formula.

Now in order to keep the displaced meniscus S' in its non-equilibrium position the extraneous forces $-\bar{F}_{dS'}$ and $-\bar{F}_{ds'}$ are needed for each surface and line element.

Let us now consider a continuous sequence of increasing displacements $td\bar{r}$, where t goes from zero to one. Then the extraneous forces needed to keep the meniscus in position will in the first-order increase linearly with t from zero for $t=0$ to $-\bar{F}_{dS'}$ and $-\bar{F}_{ds'}$ for $t=1$. In order to perform the displacement $d\bar{r}$ we must exert these linearly increasing forces on the meniscus during the increasing sequence of displacements. The work done on the meniscus from these extraneous forces are:

$$W_{S\to S'} = \int_{o}^{1} \Big[\iint_{S} (-\, t\, \bar{F}_{dS'} + \ldots) \cdot d\bar{r}\, dt + \oint_{\Gamma} (-\, t\, \bar{F}_{ds'} + \ldots) \cdot d\bar{r}\, dt\Big] =$$

$$= -\frac{1}{2} \Big[\iint_{S} \bar{F}_{dS'} \cdot d\bar{r} + \oint_{\Gamma} \bar{F}_{ds'} \cdot d\bar{r}\Big] + \ldots \quad . \qquad (3.4.9:K)$$

The second line gives the work done up to the second order, since $\bar{F}_{dS'}$ and $\bar{F}_{ds'}$, given by 3.4.9:A and F, contain only first-order and higher terms.

Thus the displacement $d\bar{r}$ may be performed by doing the work $W_{S\to S'}$ on the meniscus region. Otherwise the region is isolated from the surroundings. Then the increase in energy is equal to the work done on the system:

$$\Delta U = W_{S\to S'} \quad . \tag{3.4.9:L}$$

The first-order terms of this equation vanish. The second-order terms give with the use of 3.4.9:A,F and K:

$$\delta^2 U = \frac{\gamma_{\ell g}}{2}\{-\iint_S 2\delta\kappa'\delta n\, dS - \oint_\Gamma (\delta\theta'-\delta\theta)\delta n\, ds\} + \tag{3.4.9:M}$$
$$+\frac{1}{2}\{\iint_S [\delta(p_g-p_\ell) - 2\kappa\delta\gamma_{\ell g}]\delta n\, dS + \oint_\Gamma [\delta\gamma_{\ell g}\cos(\theta) - \delta^{\mathrm{II}}(\gamma_{sg}-\gamma_{s\ell})]\delta m'\, ds\}$$

The work needed to perform the total displacement depends on the sequence of thermodynamical states in the six phases and in different parts of these during the displacement. The state within the six phases may deviate more or less from internal equilibrium, and there may be smaller or greater deviations from thermal and chemical equilibrium between the phases. The necessary work will increase, when these deviations from equilibrium increase. We get the smallest possible value on the work needed, when the six phases are in internal equilibrium and when the phases are in mutual thermal and chemical equilibrium during the complete sequence of displacements.

Thus we will consider the case, when the six phases of the meniscus region are in internal and mutual equilibrium during the displacement, except for the forces on the meniscus, which are balanced by the extraneous forces. Then the temperature and chemical potentials for water and air have constant values throughout the meniscus region. We have the type of situation considered in section 3.4.7, where $\delta^2 U'$ was studied. The second line of 3.4.9:M above corresponds to formula 3.4.7:H for the change in energy $\delta^2 U'$ due to induced changes in pressures and γ:s.

We have allowed discontinuities in the contact angle θ and in the direction of the pore wall normal along simple curves on the pore walls. This gives two possible complications. Firstly the boundary Γ may intersect such a curve of discontinuity. Secondly a segment of the boundary Γ may follow such a curve. The conditions for force equilibrium in these two situations are discussed in section 2.2 on pages 28-35.

Let us first consider a point where Γ intersects a curve of discontinuity at a non-zero angle. The orientation of the surface S at the point of intersection at the boundary of S must satisfy condition 2.2:L,M. The upper line of formula 3.4.9:K is of course still valid. The force $\bar{F}_{ds'}$ will have a discontinuity at the sequence of intersection points during the displacement. But still $\bar{F}_{ds'}$ is of the first order. The extension of the part of the boundary affected by the discontinuity during the displacement is also of the first order. Then the contribution to the work from the discontinuity is of the third order in $d\bar{r}$. Thus the intersection of a curve of discontinuity does not affect the second-order terms of our stability analysis.

Consider next a segment of the boundary Γ where Γ follows a curve of discontinuity. Let θ_c denote the angle of contact on the liquid side between the pore wall and the meniscus S .

Then θ_c must satisfy the inequalitities 2.2.:O on page 31. Let θ_c satisfy strict inequalities: $\theta_1 < \theta_c < \theta_2 - \alpha$. The quantities θ_1 , θ_2 and α are defined in figure 2.2:VIII on page 31. We have from the discussion on page 31 that the restoring force per unit length of the displaced boundary will be finite. The required work in a displacement of the boundary segment will be positive and of the first order in $d\bar{r}$. But all other contributions to the energy change ΔU are of second order. Thus any displacement, where a segment of Γ that follows a curve of discontinuity is displaced, leads to a state of higher total energy. The system will be stable relative to this kind of displacements. In the following analysis we only have to consider displacements for which the boundary Γ is kept fixed along those segments of the boundary where it follows a curve of discontinuity.

We also have to consider the special case, when θ_c is equal to θ_1 or $\theta_2 - \alpha$ in formula 2.2:O. Then we have the ordinary situation of the continuous case for displacements of the boundary to the side of the pore wall that corresponds to the equality in formula 2.2:O. A displacement to the other side (corresponding to the inequality in formula 2.2:O) will be stopped by a finite restoring force.

The first line of 3.4.9:M corresponds to $\gamma_{\ell g}\,\delta^2 T$ in the previous case for constant θ . We will still use this notation. From formulas 3.4.8:A and B we see that the only difference is that $\delta\theta'$ is replaced by $\delta\theta' - \delta\theta$. Comparing 3.4.9:J and 3.4.8:D we see that the term $\frac{\partial\theta}{\partial m'}$ is to be added to $\kappa_m \cos(\theta) - \kappa_s$, when θ is variable. Instead of formula 3.4.8:F we now have:

$$2\delta^2 T = \iint_S [\nabla(\delta n) \cdot \nabla(\delta n) - (\kappa_1^2 + \kappa_2^2)(\delta n)^2] dS +$$

$$+ \oint_\Gamma \frac{\kappa_m \cos(\theta) - \kappa_s + \frac{\partial\theta}{\partial m'}}{\sin(\theta)} (\delta n)^2 \, ds \quad . \qquad (3.4.9:N)$$

The second line of 3.5.9:M is more complicated. Let us first consider the case, when the pore wall consists of a certain number of regions of different types. For each region there is a constant contact angle. The boundary curve Γ will pass through different regions of the pore wall. The boundary curve is then divided into a number of segments Γ_i, each with a constant contact angle θ_i. The displacement $\delta m'$ is zero for any segment of the boundary, where it follows a curve of discontinuity.

In the earlier case of constant θ throughout the pore wall studied in section 3.4.7 the changes $\delta(p_g - p_\ell) - 2\kappa\,\delta\gamma_{\ell g}$ and $\cos(\theta)\delta\gamma_{\ell g} - \delta^{II}(\gamma_{sg} - \gamma_{s\ell})$ were given by linear combinations of δV_ℓ and $\delta A_{s\ell}$ according to formula 3.4.7:J. Let $\delta A^i_{s\ell}$ denote the increase in area covered by liquid for the part of the pore wall with the contact angle θ_i:

$$\delta A^i_{s\ell} = \int_{\Gamma_i} \delta m' \, ds = \int_{\Gamma_i} \frac{\delta n}{\sin(\theta_i)} \, ds \quad . \qquad (3.4.9:O)$$

Now $\delta(p_g - p_\ell) - 2\kappa\,\delta\gamma_{\ell g}$ and $\cos(\theta)\delta\gamma_{\ell g} - \delta^{II}(\gamma_{sg} - \gamma_{s\ell})$ will depend linearly on δV_ℓ and all $\delta A^i_{s\ell}$. The change $\delta^{II}(\gamma_{sg} - \gamma_{s\ell})$ is of course in general different for the different types of pore wall. Then we get expressions of the following type:

$$\delta(p_g - p_\ell) - 2\kappa\,\delta\gamma_{\ell g} = \gamma_{\ell g}\{\beta_{VV}\,\delta V_\ell + \sum_i \beta'_{Vi}\,\sin(\theta_i)\delta A^i_{s\ell}\}$$

$$\cos(\theta_i)\delta\gamma_{\ell g} - \delta^{II}(\gamma_{sg} - \gamma_{s\ell})\Big|_{\Gamma_i} = \gamma_{\ell g}\{\beta''_{Vi}\,\sin(\theta_i)\delta V_\ell +$$

$$+ \sum_j \beta_{ij}\,\sin(\theta_i)\,\sin(\theta_j)\delta A^j_{s\ell}\} \quad . \qquad (3.4.9{:}P)$$

The factors $\gamma_{\ell g}$ and $\sin(\theta_i)$ are introduced for future convenience. The various β coefficients will depend on the thermodynamical variables of all bulk and surface phases of the system.

Formula 3.4.9:M may now be written:

$$\delta^2 U = \gamma_{\ell g}\,\delta^2 T + \delta^2 U' \quad , \qquad (3.4.9{:}Q)$$

where $\delta^2 T$ is given by formula 3.4.9:N. The only difference from the previous formulas 3.4.8:E or F is that θ has different values θ_i on each segment Γ_i of Γ.

The second part $\delta^2 U'$ is given by formulas 3.4.9:M and P:

$$\delta^2 U' = \frac{\gamma_{\ell g}}{2}\{\beta_{VV}(\delta V_\ell)^2 + 2\sum_i \beta_{Vi}\,\sin(\theta_i)\delta A^i_{s\ell}\,\delta V_\ell +$$

$$+ \sum_i\sum_j \beta_{ij}\,\sin(\theta_i)\,\sin(\theta_j)\delta A^i_{s\ell}\,\delta A^i_{s\ell}\} \quad , \qquad (3.4.9{:}R)$$

where

$$\beta_{Vi} = \frac{1}{2}(\beta'_{Vi} + \beta''_{Vi})$$

$$\delta V_\ell = \iint_S \delta n\,dS \qquad \sin(\theta_i)\delta A^i_{s\ell} = \int_{\Gamma_i} \delta n\,dS \qquad (3.4.9{:}S)$$

We have again as a consequence of formula 3.3:S that $\delta^2 U'$ is non-negative.

The generalization to the case of a continuously varying contact angle θ is now straight-forward. The first part $\delta^2 T$ in $\delta^2 U$ of formula 3.4.9:Q is given by formula 3.4.9:N. The second part $\delta^2 U'$ is given by an expression of the following type:

$$\delta^2 U' = \frac{\gamma_{\ell g}}{2} \{\beta_{VV}(\delta V_\ell)^2 + 2\delta V_\ell \oint_\Gamma \beta_{VA}(s)\delta n \, ds +$$

$$+ \oint_\Gamma \oint_\Gamma \beta_{AA}(s,s') \, \delta n(s) \, \delta n(s') ds \, ds' \quad . \qquad (3.4.9:T)$$

This general case is of course from an experimental and practical point of view extremely complicated. The formula is given for the sake of completeness.

We will end this section by giving the exact definition of T in the general case of varying contact angle θ. The definition of formula 3.4.2:B is replaced by:

$$T = T[d\bar{r}] = \Delta A_{\ell g} + \iint_{\Gamma \to \Gamma'} (-\eta) \cos(\theta) dS + 2\kappa \, \Delta V_\ell \quad . \qquad (3.4.9:U)$$

Here $\Delta A_{\ell g}$ is the increase in area of the meniscus, and ΔV_ℓ is the increase in liquid volume in the displacement $d\bar{r}$. The surface integral is taken over the part of the pore wall between the initial boundary curve Γ and the boundary curve Γ' after the displacement. The factor η is equal to -1 on that part which is changed from solid-liquid to solid-gas, while η is equal to $+1$ on the other part which is changed from solid-gas to solid-liquid.

Formula 3.4.2:G for the first order variation δT is still valid. From this we get that formula 3.4.2:M is still valid. Then the line of argument in section 3.4.4 starting with formula 3.4.4:D is also valid. The only modification starting in formula 3.4.4:I is to replace $\delta\theta'$ by $\delta\theta'-\delta\theta$, since θ may now vary. Thus, in accordance with the upper line of 3.4.9:M, we have instead of 3.4.4:L:

$$2\delta^2 T = -\iint_S 2\delta\kappa'\ \delta n\ dS - \oint_\Gamma (\delta\theta' - \delta\theta)\delta n\ ds \quad . \qquad (3.4.9:V)$$

The quantity $\gamma_{\ell g} T$ is the work necessary to achieve the displacement of the meniscus, if all phases were to remain in their initial thermodynamical state.

3.5 Mathematical analysis of the stability of a water meniscus.

3.5.1 Introduction

We will in this section 3.5 analyse the mathematical side of the stability of a water meniscus S with boundary Γ in a pore. We will study the stability of the meniscus together with an isolated surrounding meniscus region. See figure 3.4:I. The surface S has a constant mean curvature κ. There is given a contact angle θ depending on the character of the pore wall. The angle of contact θ' between S and the pore wall (on the liquid side) is equal to the prescribed contact angle θ.

We assume that θ is constant over the pore wall. If the pore wall consists of regions of different types, then we get a certain contact angle for each region. When the character of the pore wall changes continuously, we get a continuously varying contact angle over the pore wall. The modifications necessary in these two cases are given at the end of this introductory section.

The pore wall may in general have corners and edges, where the unit normal of the wall has a discontinuity. We assume that the pore wall is smooth in the vicinity of the boundary curve Γ. The boundary curve may in fact intersect corners and edges on the pore wall, if the equilibrium condition 2.2:L-M is fulfilled. The case when the boundary curve follows a corner line is touched upon on page 101.

The surface S is given in parametric form by $\bar{r} = \bar{r}(u,v)$, where the parameters u and v vary over a given domain of the (u,v)-plane. Let ψ be a sufficiently regular function defined on S : $\psi = \psi(u,v)$. Then we define the functional J for the meniscus S through:

$$J[\psi] = \iint_S [\nabla\psi \cdot \nabla\psi - (\kappa_1^2 + \kappa_2^2)\psi^2]dS + \oint_\Gamma \sigma\,\psi^2\,ds \quad . \qquad (3.5.1:A)$$

Here the function σ, defined along Γ, is given by:

$$\sigma = \frac{\kappa_m \cos(\theta) - \kappa_s}{\sin(\theta)} \quad . \qquad (3.5.1:B)$$

The symbol ∇ denotes the gradient operator on the surface. It is defined by 3.4.5:B and C. The quantities κ_1 and κ_2 are the principal curvatures of S. See appendix 1 on differential geometry. The quantities κ_m and κ_s are the curvatures of S and of the pore wall at Γ in the direction perpendicular to Γ. (The gas side defines the positive sides of the surfaces.)

From formula 3.4.8:F on page 77 we have for a small displacement of S with normal component $\delta n\ \bar{n}$:

$$J[\delta n] = 2\ \delta^2 T \quad . \tag{3.5.1:C}$$

Let S_ψ and Γ_ψ be defined by

$$S_\psi = \iint\limits_S \psi dS \qquad \Gamma_\psi = \oint\limits_\Gamma \psi ds \quad . \tag{3.5.1:D}$$

Then $S_{\delta n}$ will give the increase δV_ℓ in liquid volume, while $\Gamma_{\delta n}/\sin(\theta)$ gives the increase $\delta A_{s\ell}$ in the part of the pore wall which is covered by liquid.

We define the functional $I[\psi]$ through

$$I[\psi] = \beta_{VV}(S_\psi)^2 + 2\,\beta_{VA}\ S_\psi\ \Gamma_\psi + \beta_{AA}(\Gamma_\psi)^2 \quad . \tag{3.5.1:E}$$

The coefficients β_{VV} , β_{VA} , and β_{AA} depend on the thermodynamical characteristics of the region surrounding the meniscus S . The functional $I[\psi]$ is a positive semi-definite quadratic form in S_ψ and Γ_ψ (formula 3.4.7:N on page 76).

From formulas 3.4.8:G and H on page 78 we have for a displacement with normal component $\delta n\ \bar{n}$:

$$\delta^2 U' = \frac{\gamma_{\ell g}}{2}\ I[\delta n] \quad . \tag{3.5.1:F}$$

Let J_t denote the sum of J and I :

$$J_t[\psi] = J[\psi] + I[\psi] \quad . \tag{3.5.1:G}$$

Then the total change in energy for the meniscus region in a displacement with normal component $\delta n\ \bar{n}$ is according to formulas 3.4.8:A, 3.5.1:C and F:

$$\delta^2 U = \frac{\gamma_{\ell g}}{2} J_t[\delta n] \quad . \qquad (3.5.1:H)$$

The physical meaning of $\gamma_{\ell g}\ \delta^2 T$ and $\delta^2 U'$ has been discussed at length in sections 3.4.2, 3 and 7. We have a displacement with normal component $\delta n\ \bar{n}$. Then $\gamma_{\ell g}\ \delta^2 T = \frac{\gamma_{\ell g}}{2} J[\delta n]$ is the work necessary to displace the meniscus against the surface tension $\gamma_{\ell g}$, the pressure difference $p_g - p_\ell$, and the force $\gamma_{sg} - \gamma_{s\ell} = \gamma_{\ell g} \cos(\theta)$ at the pore wall. The quantity $\frac{\gamma_{\ell g}}{2} J[\psi]$ gives the work of the displacement, when these forces retain their values of the initial equilibrium state. But during the displacement these forces will change. The second part $\frac{\gamma_{\ell g}}{2} I[\delta n] = \delta^2 U'$ gives the work necessary to overcome these induced additional forces from the changes $\delta\gamma_{\ell g}$, $\delta(p_g - p_\ell)$ and $\delta(\gamma_{sg} - \gamma_{s\ell})$.

The analogy between our water meniscus and a stretched membrane is very illuminating. In this analogy the membrane is stretched along the surface S , and it is attached to the pore wall at the boundary Γ . The tension of the infinitely flexible membrane is $\gamma_{\ell g}$. The fluids above and below the membrane have the pressures p_g and p_ℓ. The membrane is linked to the pore wall but is is free to move along the wall. The force from the membrane at the boundary Γ in the normal direction of the pore wall is balanced by the linkage device. At the boundary Γ there is a force $\gamma_{\ell g} \cos(\theta) (= \gamma_{sg} - \gamma_{s\ell})$ per unit length acting along the pore wall perpendicular to Γ . See figure 3.5.1:I

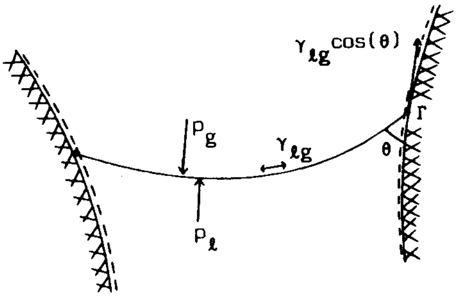


Figure 3.5.1:I The figure illustrates the analogy between the water meniscus and a stretched membrane with a tension $\gamma_{\ell g}$. The boundary of the membrane is kept attached to the pore wall, but it may move along the wall. There is a pressure difference $p_g - p_\ell$ over the membrane. A force $\gamma_{\ell g}\cos(\theta)$ per unit length acts on the boundary.

The work needed to overcome these forces in a displacement of the membrane from a position S to a new position S' is:

$$W_{S\to S'} = \gamma_{\ell g}\, \Delta A_{\ell g} + \gamma_{\ell g}\, \cos(\theta)\Delta A_{sg} + (p_g - p_\ell)\Delta V_\ell \,. \qquad (3.5.1:I)$$

Here $\Delta A_{\ell g}$ is the increase in membrane area, ΔA_{sg} the increase in pore wall area above the membrane (solid-gas area), and ΔV_ℓ the increase in the pore volume below the membrane (liquid volume). The quantity $\frac{\gamma_{\ell g}}{2} J[\delta n]$ gives this work up to the second order for a displacement with normal component δn. Inserting the equilibrium condition $p_g - p_\ell = 2\gamma_{\ell g}\kappa$ we get the geometrical interpretation of $J[\delta n]$:

$$\frac{1}{2} J[\delta n] = \delta^2 A_{\ell g} + \cos(\theta)\delta^2 A_{sg} + 2\kappa\,\delta^2 V_\ell \quad . \qquad (3.5.1:J)$$

If the forces are unchanged during the displacement, then $\frac{\gamma_{\ell g}}{2} J[\delta n]$ gives the total change in energy of the membrane region. But for example the pressures p_g and p_ℓ may change due to changes in gas and liquid volumes. The tension $\gamma_{\ell g}$ in the membrane may depend on the area of the membrane. Then $\gamma_{\ell g}$ will change during the displacement. The work necessary to overcome additional forces of such types is given by $\frac{\gamma_{\ell g}}{2} I[\delta n]$. Consider as an example a case where the pressures p_g and p_ℓ change because of a volume change $\delta V_g = - \delta V_\ell$ in the displacement. The work $\delta^2 U'$ necessary to overcome these forces is:

$$\delta^2 U' = \frac{1}{2}\{ - \delta p_g \cdot \delta V_g - \delta p_\ell \cdot \delta V_\ell \} \quad . \qquad (3.5.1:K)$$

Let k_g and k_ℓ denote appropriate compressibilities for the two fluids:

$$k_g = - \frac{1}{V_g} \cdot \frac{\partial V_g}{\partial p_g} \qquad k_\ell = - \frac{1}{V_\ell} \cdot \frac{\partial V_\ell}{\partial p_\ell} \quad . \qquad (3.5.1:L)$$

Here V_g and V_ℓ are the volumes of the two fluids. The total pore volume is constant: $\delta V_g = - \delta V_\ell$. Then from formulas 3.5.1:F,K,L and E we get for this example:

$$I[\delta n] = \frac{1}{\gamma_{\ell g}} \{\frac{1}{k_g V_g} + \frac{1}{k_\ell V_\ell}\} (\delta V_\ell)^2 = \beta_{VV}(S_{\delta n})^2 \quad . \qquad (3.5.1:N)$$

This is a special case of 3.5.1:E.

The function σ is defined along the boundary Γ by formula 3.5.1:B. A slightly different analogy between the meniscus and a stretched membrane gives an instructive physical interpretation of σ . We have again an elastic membrane S with a tension $\gamma_{\ell g}$ between two fluids with the pressures p_g and p_ℓ . The old pore wall is replaced by a new one in the vicinity of the boundary curve Γ . The new wall is generated by straight lines having the direction of the normal $\bar{n}$ to S at Γ . See figure 3.5.1:II. The new wall is attributed a constant contact angle $\theta = \frac{\pi}{2}$. The membrane is attached to the wall, but it is free to move along the pore wall. In this new situation both terms $\kappa_m \cos(\theta)$ and κ_s of formula 3.5.1:B for σ will vanish. Let us now imagine that we have along Γ springs with a spring constant $\gamma_{\ell g}\, \sigma$ per unit length of Γ acting on the boundary of the membrane. See figure 3.5.1:II.

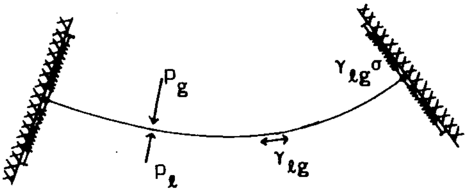


Figure 3.5.1:II The figure illustrates an analogy between the water meniscus and a stretched membrane. The conditions at the boundary of the meniscus, which are contained in the function σ , correspond to springs that act on the boundary of the membrane. The spring constant is $\gamma_{\ell g}\, \sigma$ per unit length along the boundary curve.

The restoring force on a line element ds of the boundary curve Γ is equal to $x\, \gamma_{\ell g}\, \sigma\, ds$, where x is the displacement perpendicular to Γ along the plane pore wall. The boundary function σ may assume negative values.

Consider now a small normal displacement $d\bar{r} = \delta n\, \bar{n}$ of the membrane. Then the energy stored in the springs is equal to:

$$\frac{\gamma_{\ell g}}{2} \oint_{\Gamma} \sigma(\delta n)^2 \, ds \quad . \tag{3.5.1:O}$$

The energy of the displacement of the membrane against the forces shown in figure 3.5.1:II is then given by $\frac{\gamma_{\ell g}}{2} J[\delta n]$, where J is given by formula 3.5.1:A.

We will in our analysis include the possibility that $\sigma(s)$ may become infinite: $-\infty \leq \sigma(s) \leq +\infty$. We have instability when $\sigma(s) = -\infty$ on a finite segment of the boundary Γ . There is an infinitely strong restoring force, when $\sigma(s) = +\infty$ on a segment of the boundary. The membrane will be kept fixed in its original position along such a segment of the boundary. Thus we will always have:

$$\psi = 0 \quad \text{on those parts of } \Gamma \text{, where } \sigma = +\infty \quad . \tag{3.5.1:P}$$

The situation with $\sigma = +\infty$ may be realized, when the boundary Γ follows an edge on the pore wall. Compare figure 2.2:VIII on page 31. (The situation $\theta_1 = \theta_2$, $\alpha < 0$ and $\theta_1 < \theta_c < \theta_2 - \alpha$ gives $\sigma = +\infty$, while $\theta_1 = \theta_2$ and $\alpha > 0$ gives $\sigma = -\infty$.)

The given formulas must be modified, when the contact angle θ equals 0 or π since $\sin(\theta)$ appears in the denominator. Then we have instead:

$$J[\psi] = \iint_S [\nabla\psi \cdot \nabla\psi - (\kappa_1^2 + \kappa_2^2)\psi^2] dS \qquad (\theta = 0,\pi) \tag{3.5.1:Q}$$

$$I[\psi] = \beta'_{VV}(S_\psi)^2 \qquad (\theta = 0,\pi) \tag{3.5.1:R}$$

At the boundary Γ , ψ must be zero:

$$\psi\big|_\Gamma = 0 \quad . \qquad (\theta = 0,\pi) \tag{3.5.1:S}$$

We will finally give the modifications for the general case, when the contact angle θ is any function over the pore walls. The contact angle θ and the unit normal to the pore wall may even be discontinuous along some curves on the pore walls. The intricacies, when the boundary Γ follows a curve of discontinuity, are discussed on pages 89-90.

Formula 3.5.1:A for $J[\psi]$ is still valid in this general case. In formula 3.5.1:B for the boundary function σ one term is to be added:

$$\sigma = \frac{\kappa_m \cos(\theta) - \kappa_s + \frac{\partial\theta}{\partial m'}}{\sin(\theta)} \quad . \qquad (3.5.1:T)$$

The additional term $\frac{\partial\theta}{\partial m'}$ is the rate of increase in θ in the direction $\bar{m}'$. See for example figure 3.4.1:II on page 52.

The modifications for $I[\psi]$ are more drastic. Let us first consider the case, when the pore wall consists of a number of regions with a constant contact angle for each region. The boundary curve Γ is divided into a number of segments Γ_i with the constant contact angles θ_i . Then we define:

$$\Gamma_\psi^i = \int_{\Gamma_i} \psi \, ds \quad . \qquad (3.5.1:U)$$

The functional $I[\psi]$ is now given by:

$$I[\psi] = \beta_{VV}(S_\psi)^2 + 2\sum_i \beta_{Vi} S_\psi \Gamma_\psi^i + \sum_i \sum_j \beta_{ij} \Gamma_\psi^i \Gamma_\psi^j \, . \quad (3.5.1:V)$$

Here I is a positive semi-definite quadratic form in the variables $\Gamma_\psi^1, \Gamma_\psi^2, \ldots,$ and S_ψ .

In the general case, when θ varies over the pore wall, we have

$$I[\psi] = \beta_{VV}(S_\psi)^2 + 2\, S_\psi \oint_\Gamma \beta_{VA}(s)\ \psi(s)\ ds + \oint_\Gamma \oint_\Gamma \beta_{AA}(s,s')\ \psi(s)\ \psi(s')ds\ ds' \quad . \qquad (3.5.1{:}W)$$

The functional $I[\psi]$ is positive semi-definite.

In conclusion of this introduction we note that the mathematical theory of stability presented in section 3.5 is inspired by the methods of reference 19). The comparison of the stability in certain related situations in section 3.5.2 has a counterpart in 19a) for similar problems. The eigenvalue methods used in section 3.5.5 are similar to the methods in 19b).

3.5.2 Some general conclusions. Strong and weak stability.

The meniscus region is stable, if $\delta^2U > 0$ for all displacements, and it is unstable if there is a displacement with $\delta^2U < 0$. There remains the possibility that δ^2U is equal to zero for some displacement, although it never becomes negative. In this case the stability will depend on terms of higher order than two. We will not study this special case.

Thus from 3.5.1:H we have stability if for all ψ

$$J_t[\psi] > 0 \quad . \qquad (3.5.2{:}A)$$

(The case $\psi \equiv 0$ is of course excluded.) We have instability if there exists a ψ such that

$$J_t[\psi] < 0 \quad . \qquad (3.5.2{:}B)$$

The remaining more special possibilities will not be considered.

Now J_t is the sum of J and I , where I is nonnegative. We have on page 79 in section 3.4.8 introduced the following terminology.

The meniscus is strongly stable if

$$J[\psi] > 0 \quad \text{for all } \psi \quad . \tag{3.5.2:C}$$

(The case $\psi \equiv 0$ is of course excluded.)

The meniscus is weakly stable if

i. There is a ψ with $J[\psi] < 0$

(3.5.2:D)

ii. $J[\psi] > 0$ for all ψ such that $S_\psi = 0$, $\Gamma_\psi = 0$.

Finally the meniscus is strongly unstable if

there is a ψ such that $J[\psi] < 0$, $S_\psi = 0$, $\Gamma_\psi = 0$.

(3.5.2:E)

The case 3.5.2:D for weak stability is essentially the complement to the other possibilities. The remaining more special possibilities will not be considered.

We note again that strong stability for J implies the stability of J_t , and that strong instability for J implies the instability of J_t . In the intermediate case of weak stability we have to study the sum $J+I = J_t$ in order to decide on stability.

The function σ , defined along the boundary Γ is allowed to become infinite:

$$- \infty \leq \sigma(s) \leq + \infty \quad . \tag{3.5.2:F}$$

Here s is the arc length along the boundary curve Γ . It is clear that there is a strong instability, if $\sigma = -\infty$ for a segment of the boundary. The meniscus may be stable when $\sigma = -\infty$ just for some isolated points on the boundary. In the following stability investigations we need only to consider the functions σ , where $-\infty < \sigma(s) \leq +\infty$.

In the subsequent sections we will often study a family of stability problems. The following general observations on the stability performance for related cases will prove useful. Consider first a certain meniscus S with a certain surrounding region. Let us compare two cases I and II with different boundary functions $\sigma_I(s)$ and $\sigma_{II}(s)$. Let J_I and J_{II} denote the corresponding functionals. Suppose we have

$$\sigma_I(s) \geq \sigma_{II}(s) \quad \text{on} \quad \Gamma \quad . \qquad (3.5.2:G)$$

Then from formula 3.5.1:A we have for any ψ:

$$J_I[\psi] \geq J_{II}[\psi] \quad . \qquad (3.5.2:H)$$

From this we may draw the following conclusions. Strong stability in case II implies strong stability in case I. Weak stability in case II implies weak or strong stability in case I. Conversely, weak stability in case I implies weak stability or strong instability in case II. Strong instability in case I implies strong instability in case II. The functional $I[\psi]$ is the same in the two cases. Thus stability in case II implies stability in case I, while instability in case I implies instability in case II.

We might say that case I has better stability than case II. We will use this terminology in the following, when two related stability problems are compared. Thus a case I has better stability than a case II if all implications of the preceding paragraph hold true. When the implications for J on strong stability, weak stability, and strong instability above hold true, we will say that J has better stability in case I than in case II.

Let us next compare two situations I and II, where the meniscus S_{II} consists of a certain part of the meniscus S_I. We may also say that S_I is an extension of S_{II}. The smaller meniscus S_{II} has a boundary that partly coincides with the boundary of S_I, and partly lies in the interior of S_I. The surface S_{II} may also lie completely in the interior of S_I. Let Γ'_{II} denote the part of the boundary of S_{II} that coincides with Γ_I and let Γ''_{II} be the rest of Γ_{II}. See figure 3.5.2:I below.

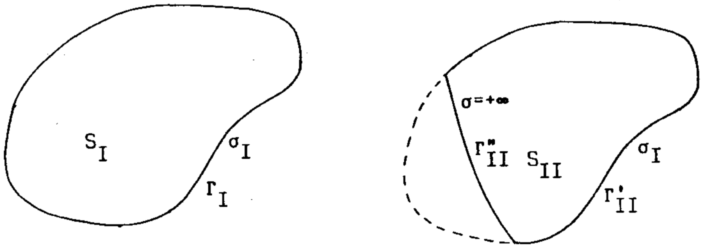


Figure 3.5.2:I Comparison of a meniscus S_I with a part S_{II} of it. The right case has better stability.

Let σ_I be the boundary function for case I. For case II we choose the following boundary function:

$$\sigma_{II} = \begin{cases} \sigma_I & \text{on } \Gamma'_{II} \\ +\infty & \text{on } \Gamma''_{II} \end{cases} . \qquad (3.5.2:I)$$

Thus at the new boundary Γ''_{II} the meniscus is kept fixed. Then there is better stability for J in case II than in case I.

Consider in order to show this any function ψ_{II} for stability problem II. The function ψ_{II} is defined on S_{II}, and it is zero on Γ''_{II}. Put:

$$\psi_I = \begin{cases} \psi_{II} & \text{on} \quad S_{II} \\ 0 & \text{on} \quad S_I - S_{II} \end{cases} \quad . \qquad (3.5.2{:}J)$$

The function ψ_I is defined and continuous on S_I. The gradient $\nabla\psi_I$ has a finite jump at Γ''_{II}. Anyhow $J_I[\psi_I]$ is well-defined. It is clear that $J_I[\psi_I] = J_{II}[\psi_{II}]$. Thus for any function on S_{II} giving a certain value for J_{II} we can get a function on S_I with the same value for J_I. Then certainly J_{II} must have better stability than J_I.

Let us finally compare two cases I and II with the same meniscus and boundary function but with different surrounding regions. See figure 3.4:I on page 48. The functional J is the same in the two cases. But we have different functionals I_I and I_{II}. The functional $I[\psi]$ represents the work necessary to overcome induced changes in pressures and surface tensions. For a displacement given by a certain ψ the induced changes and this work will be smaller, when the region is extended. Let case II have a larger surrounding region. This region consists of the region of case I and an additional part. Then for any ψ we will have:

$$I_I[\psi] \geq I_{II}[\psi] \quad . \qquad (3.5.2{:}K)$$

It is then clear that case I will have better stability than case II.

To sum up, we have shown that the stability is improved when the boundary function σ is increased. We have also shown that the stability is improved, when the surrounding region is diminished. Finally, we have shown that the stability of a meniscus is improved when a part of it is cut away, while the new parts of the boundary are kept fixed. Conversely, the stability deteriorates when the meniscus is extended beyond a part of the boundary with $\sigma = +\infty$, whatever boundary function we choose for the new part. Especially we note that when a meniscus with $\sigma = +\infty$ along the entire boundary is extended, then the stability will deteriorate for any choice of boundary function on the new parts of the boundary. For future reference we will give two simple corollaries to this.

Suppose for a certain meniscus S that there is a function ϕ $(\phi \not\equiv 0)$ that satisfies:

$$J[\phi] = 0 \qquad \phi\Big|_{\Gamma} = 0 \quad . \tag{3.5.2:L}$$

Then there is not strong stability for S or any extension of it. This holds true for any choice of boundary function σ and for any extension of S .

To prove this we have only to note that because of 3.5.2:L there is not strong stability for S with the boundary condition $\sigma = +\infty$.

We also have the following obvious corollary .

Suppose that there exists, for a certain meniscus S , a function ϕ $(\phi \not\equiv 0)$ which satisfies:

$$J[\phi] = 0$$

$$\phi\big|_{\Gamma} = 0 \qquad (3.5.2:M)$$

$$S_{\phi} = 0$$

Then there is not weak (or strong) stability for S or any extension of it. This is true for any choice of boundary function σ and for any extension of S .

3.5.3 Formulas for $J[\psi]$. A criterion for strong stability.

Let ϕ and ψ be two functions defined on S . Then as a generalization of formula 3.5.1:A for $J[\psi]$ we define:

$$J[\phi,\psi] = \iint_S \{\nabla\phi\cdot\nabla\psi - (\kappa_1^2+\kappa_2^2)\phi\psi\}dS + \oint_{\Gamma} \sigma\,\phi\,\psi\,ds \;. \qquad (3.5.3:A)$$

Then we have that $J[\psi] = J[\psi,\psi]$. The function $J[\phi,\psi]$ is linear in ϕ and in ψ . It is symmetric:

$$J[\phi,\psi] = J[\psi,\phi] \quad . \qquad (3.5.3:B)$$

From formula A1:U in appendix 1 we have:

$$\iint_S \nabla\phi\cdot\nabla\psi \, dS = - \iint_S \phi\nabla\cdot\nabla\psi \, dS + \oint_\Gamma \phi \, \bar{m}\cdot\nabla\psi \, ds \quad . \qquad (3.5.3:C)$$

Here ∇ denotes the gradient operator on the surface S given by formulas 3.4.5:B and C on page 65. The unit vector $\bar{m}$ is the outward tangent vector to S at the boundary Γ. See figure 2.2:II on page 19.

Let us now introduce the differential operator L :

$$L(\psi) = - \{\nabla\cdot\nabla\psi + (\kappa_1^2 + \kappa_2^2)\psi\} \quad . \qquad (3.5.3:D)$$

We will also use the notation:

$$L_\Gamma(\psi) = \sigma\,\psi + \bar{m}\cdot\nabla\psi \quad . \qquad (3.5.3:E)$$

The expression $L_\Gamma(\psi)$ is defined on the boundary curve Γ for all points where σ is finite.

From formula 3.4.5:L on page 67 we have

$$L(\delta n) = - 2\,\delta\,\kappa' \quad . \qquad (3.5.3:F)$$

Formula 3.4.6:U on page 71 gives:

$$L_\Gamma(\delta n) = - \delta\,\theta' \quad . \qquad (3.5.3:G)$$

Here $\delta\kappa'$ denotes the change in mean curvature and $\delta\theta'$ the change in angle of contact in a displacement $d\bar{r}$ with normal component $\delta n\,\bar{n}$.

With these notations we get from 3.5.3:A and C:

$$J[\phi,\psi] = \iint_S \phi\, L(\psi)dS + \oint_\Gamma \phi\, L_\Gamma(\psi)ds \quad . \qquad (3.5.3:H)$$

We may change the order between ϕ and ψ in this formula, since J is symmetric. This gives the analogue of the so-called Green's second formula. Formulas 3.5.3:A and H give the analogue of Green's first formula.

From the different expression for $J[\phi,\psi]$ we get, putting $\phi = \psi$:

$$J[\psi] = J[\psi,\psi] = \iint_S \psi\, L(\psi)dS + \oint_\Gamma \psi\, L_\Gamma(\psi)ds =$$

$$= - \iint_S \psi[\nabla\cdot\nabla\psi + (\kappa_1^2+\kappa_2^2)\psi]dS + \oint \psi(\sigma\psi + \bar{m}\cdot\nabla\psi)ds =$$

$$= \iint_S [\nabla\psi\cdot\nabla\psi - (\kappa_1^2+\kappa_2^2)\psi^2]dS + \oint_\Gamma \sigma\,\psi^2\, ds \ . \qquad (3.5.3{:}I)$$

When $\sigma = +\infty$ for a part of the boundary, then ψ must be zero on this part. The line integral of $\sigma\psi^2$ over this part has to be omitted in the above formulas.

From the linearity of L and L_Γ and from the symmetry of J we get the sum of two functions:

$$J[\phi+\psi] = J[\phi] + J[\psi] + 2J[\phi,\psi] \ . \qquad (3.5.3{:}J)$$

For the product of two arbitrary functions we have the following important relation:

$$J[\psi\phi] = \iint_S \psi^2\, \phi\, L(\phi)dS + \oint_\Gamma \psi^2\, \phi\, L_\Gamma(\phi)ds + \iint_S \phi^2\, \nabla\psi\cdot\nabla\psi\, dS \qquad (3.5.3{:}K)$$

The proof is as follows. We start from formula 3.5.1:A and expand the gradient $\nabla(\phi\psi)$. The integrand of the surface integral becomes:

$$\psi^2\, \nabla\phi\cdot\nabla\phi + 2\,\psi\phi\, \nabla\psi\cdot\nabla\phi + \phi^2\, \nabla\psi\cdot\nabla\psi - (\kappa_1^2+\kappa_2^2)\psi^2\phi^2 \ . \qquad (3.5.3{:}L)$$

The first two terms may with the use of A1:K and N be written:

$$\psi^2\, \nabla\phi\cdot\nabla\phi + \phi\nabla(\psi^2)\cdot\nabla\phi = \nabla\cdot(\psi^2\phi\, \nabla\phi) - \psi^2\phi\, \nabla\cdot\nabla\phi \ . \qquad (3.5.3{:}M)$$

The surface integral of the divergence term in 3.5.3:M above may be transformed into a line integral along Γ. From formula A1:S in the appendix 1 on differential geometry with $\bar{w} = \psi^2\phi\nabla\phi$ and thus $\bar{w}\cdot\bar{n} = 0$ we have:

$$\iint_S \nabla\cdot(\psi^2\phi\nabla\phi)dS = \oint_\Gamma \psi^2\phi\ \bar{m}\cdot\nabla\phi\ ds \quad . \qquad (3.5.3:N)$$

Then from 3.5.3:L-N we have:

$$J[\psi\phi] = -\iint_S \psi^2\ \phi\ \{\nabla\cdot\nabla\phi + (\kappa_1^2+\kappa_2^2)\phi\}dS + $$

$$+ \iint_S \phi^2\ \nabla\psi\cdot\nabla\psi\ dS + \oint_\Gamma \psi^2\phi\{\bar{m}\cdot\nabla\phi + \sigma\phi\}ds \quad . \qquad (3.5.3:O)$$

This is the given formula 3.5.3:K using the definitions of L and L_Γ.

Formula 3.5.3:K for $J[\psi\phi]$ gives a very useful criterion for strong stability:

Let ϕ be a function defined on S satisfying:

i. $L(\phi) \geq 0$ on S

ii. $L_\Gamma(\phi) \geq 0$ on Γ (3.5.3:P)

iii. $\phi > 0$ on S

We also assume that $L(\phi)$ and $L_\Gamma(\phi)$ are not both identically zero on S and Γ respectively. Then we have strong stability.

In order to prove this we must show that $J[\psi]$ is positive for all ψ. (The case $\psi \equiv 0$ is of course excluded.) Since ϕ is strictly positive on the whole of S, we have, using the product formula 3.5.3:K:

$$J[\psi] = J[\frac{\psi}{\phi}\cdot\phi] = \iint_S (\frac{\psi}{\phi})^2\,\phi L(\phi)dS + \oint_\Gamma (\frac{\psi}{\phi})^2\,\phi L_\Gamma(\phi)ds +$$

$$+ \iint_S \phi^2\,\nabla(\frac{\psi}{\phi})\cdot\nabla(\frac{\psi}{\phi})dS \quad . \qquad (3.5.3{:}Q)$$

All integrands are non-negative. Thus $J[\psi]$ is non-negative. The third term vanishes when $\frac{\psi}{\phi}$ is a constant. In this case, the sum of the first two terms is strictly positive, since we have assumed that $L(\phi)$ and $L_\Gamma(\phi)$ are not both identically zero. Thus $J[\psi]$ is actually strictly positive, and we have strong stability.

When $\sigma = +\infty$ on a part Γ' of Γ, we may allow ϕ to be zero on this part of the boundary. We then only have to consider functions ψ which are zero on Γ'. Then $\frac{\psi}{\phi}$ is in the normal case a nice function and the theorem is still valid.

There is a nice alternative proof of the above theorem 3.5.3:P. Let $S_{+\phi}$ denote the displaced surface in a displacement of S with normal component $\varepsilon\phi$, where ε is a small positive quantity. The surface $S_{+\phi}$ lies above S, since ϕ is strictly positive. In the same way we have a surface $S_{-\phi}$ completely below S from a displacement with normal component $-\varepsilon\phi$. The meniscus S lies between $S_{+\phi}$ and $S_{-\phi}$. See figure 3.5.3:I.

The mean curvature of $S_{+\phi}$ is from formula 3.5.3:F $\kappa - 0.5\,L(\varepsilon\phi) = \kappa - 0.5\,\varepsilon L(\phi)$. We have assumed that $L(\phi)$ is non-negative. Thus the mean curvature of $S_{+\phi}$ is everywhere less than the mean curvature κ of S. At the boundary of $S_{+\phi}$ we have from 3.5.3:G that $\delta\theta' = -L_\Gamma(\varepsilon\phi)$. We have assumed that $L_\Gamma(\phi)$ is non-negative. Thus the angle of contact θ' of $S_{+\phi}$ is less than the prescribed contact angle θ. In the same way we have that the mean curvature of $S_{-\phi}$ is everywhere greater than the mean curvature κ of S, and that the angle of contact θ' of $S_{-\phi}$ is greater than the prescribed contact angle θ.

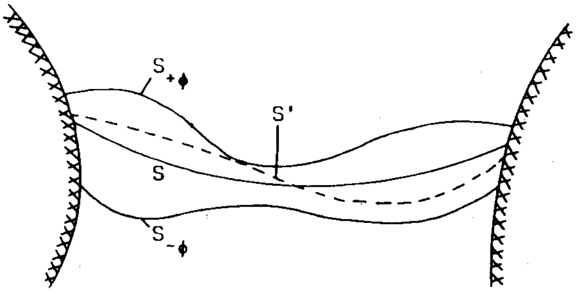


Figure 3.5.3:I The figures shows the meniscus S and the surfaces $S_{+\phi}$ and $S_{-\phi}$ above respectively below S. A displaced surface S' cannot penetrate the confining surfaces $S_{+\phi}$ and $S_{-\phi}$.

Consider now any displacement $d\bar{r}$ of S. Let us imagine this displacement as a continuous sequence of displacements $\eta\, d\bar{r}$, where η increases from zero to one and if necessary above one. When η is sufficiently small, the displaced surface will lie completely between $S_{+\phi}$ and $S_{-\phi}$. For a certain value of η the displaced surface touches $S_{+\phi}$ or $S_{-\phi}$ somewhere for the first time. We will denote this surface S'. See figure 3.5.3:I. This first point of contact between S' and $S_{+\phi}$ or $S_{-\phi}$ will lie either at the boundary on the pore wall or in the interior of S'.

Let us first look at the case when the point of contact is an interior point on $S_{+\phi}$ as in the figure 3.5.3:I above. The surfaces $S_{+\phi}$ and S' have the same tangent plane at the point of contact. The mean curvature of S' in this point will be smaller than that of $S_{+\phi}$, since S' lies below $S_{+\phi}$. But the mean curvature of $S_{+\phi}$ is everywhere smaller than the mean curvature κ of S. Thus the mean curvature of S' at the point of contact is smaller than (or equal to) κ.

The forces acting on the meniscus are the pressure difference p_g-p_ℓ and the surface tension $\gamma_{\ell g}$. The magnitude of these forces are unchanged during the displacement, since we are studying $J[\psi]$. (The induced changes in pressures and surface tension are contained in $I[\psi]$.) The equation for force equilibrium is $p_g-p_\ell = 2\,\gamma_{\ell g}\,\kappa$. We have shown that the mean curvature of S' is smaller than κ at the point of contact. Thus we get a net restoring force on S' at the point of contact pushing the displaced meniscus back in the $-\bar{n}$ direction.

Let us next consider the case when the point of contact lies on the boundary of $S_{+\phi}$ and S' at the pore wall. The boundary curves of $S_{+\phi}$ and S' will be tangential at the contact point. The surface S' lies below $S_{+\phi}$. Thus the angle of contact for S' at the contact point will be smaller than that of $S_{+\phi}$. But the angle of contact for $S_{+\phi}$ is everywhere smaller than the prescribed contact angle. Then the angle of contact for S' at the contact point will be smaller than the prescribed contact angle θ in this point.

At the boundary of a meniscus there is a force $\gamma_{sg}-\gamma_{s\ell}$ ($= \gamma_{\ell g}\cos\theta$) acting in the direction of $\bar{m}'$. See section 2.2 and especially figure 2.2:VI on page 28. From the surface tension $\gamma_{\ell g}$ we get a force $\gamma_{\ell g}\cos(\theta')$ acting in the opposite direction.

Here θ' is the angle of contact. When θ' is equal to the contact angle θ, there is force equilibrium. When θ' is smaller than θ, we get a net force in the direction of $-\bar{m}'$. Thus we get a net restoring force on the boundary of S' at the point of contact pushing the displaced meniscus back in the $-\bar{m}'$ direction.

In conclusion we have that, when a displaced meniscus touches $S_{+\phi}$, it will experience a restoring force at the point of contact pushing the meniscus back. The displaced meniscus cannot penetrate the surface $S_{+\phi}$.

Consider now the case when the point of contact lies on $S_{-\phi}$ instead of on $S_{+\phi}$. Following the same line of argument we get again a restoring force at the point of contact pushing the displaced meniscus back. The displaced meniscus cannot pass the surface $S_{-\phi}$. The meniscus is entrapped between $S_{+\phi}$ and $S_{-\phi}$. Then we certainly have strong stability.

The third condition of 3.5.3:P requiring that ϕ is strictly positive is necessary, since we divide by ϕ. Let us now allow the function ϕ to be zero along some curves on S. Formula 3.5.3:Q will still be valid, if $\frac{\psi}{\phi}$ is a sufficiently well-behaved function on S. We must then restrict the functions ψ to those which are zero at the points where ϕ is zero. Coarsely speaking, ψ must have a zero of the same kind as ϕ at the points where ϕ is zero. We get the following corollary to 3.5.3:P:

Let ϕ be a function defined on S satisfying:

i. $\phi L(\phi) \geq 0$ on S

(3.5.3:R)

ii. $\phi L_\Gamma(\phi)\ \_\ 0$ on Γ

Let ψ be any function on S such that $\frac{\psi}{\phi}$ is sufficiently well-behaved. This implies that ψ must be zero where ϕ is zero. Then we have that $J[\psi]$ is non-negative: $J[\psi] \geq 0$.

A standard technique for studying the behaviour of quadratic functionals is a method using so-called conjugate points. See reference 14). The method is there only developed in the one-dimensional case. In this method the quotient between the argument function ψ and a certain function ϕ is studied. The analysis of the product $J[\phi\psi]$ has been inspired by this. The technique is extended to the two-dimensional case for functions which are zero at the boundary in reference 15). This is very similar to our approach.

The stability of various special surfaces will be studied in sections 3.5.7-10. It will turn out to be rather simple to find appropriate functions ϕ for criterion 3.5.3:P on strong stability. This criterion is the simplest and most direct method that I have been able to find. The problem of deciding between weak stability and strong instability will be more difficult.

3.5.4 Formulas for $J_t[\psi]$

From formulas 3.5.1:H,A,E, and D we define the bilinear functional J_t representing the total energy:

$$J_t[\phi,\psi] = J[\phi,\psi] + I[\phi,\psi] =$$

$$= \iint_S \{\nabla\phi\cdot\nabla\psi - (\kappa_1^2+\kappa_2^2)\phi\psi\}dS + \oint_\Gamma \sigma\,\phi\,\psi\,ds +$$

$$+ \beta_{VV}\,S_\phi\,S_\psi + \beta_{VA}\,S_\phi\,\Gamma_\psi + \beta_{VA}\,S_\psi\,\Gamma_\phi + \beta_{AA}\,\Gamma_\phi\Gamma_\psi \quad , \tag{3.5.4:A}$$

where

$$S_\phi = \iint_S \phi \, dS \qquad \Gamma_\phi = \oint_\Gamma \phi \, ds \quad . \qquad (3.5.4\text{:B})$$

We have $J_t[\psi] = J_t[\psi,\psi]$. The functional J_t is linear in ϕ and in ψ . It is symmetric:

$$J_t[\phi,\psi] = J_t[\psi,\phi] \quad . \qquad (3.5.4\text{:C})$$

We will use the notations:

$$L_t(\psi) = L(\psi) + \beta_{VV} S_\psi + \beta'_{VA} \Gamma_\psi \quad , \qquad (3.5.4\text{:D})$$

$$L_\Gamma^t(\psi) = L_\Gamma(\psi) + \beta''_{VA} S_\psi + \beta_{AA} \Gamma_\psi \quad . \qquad (3.5.4\text{:E})$$

The expression $L_t(\psi)$ is defined on S , while $L_\Gamma^t(\psi)$ is defined on the boundary curve Γ . The coefficients β'_{VA} and β''_{VA} are defined on page 75.

From formulas 3.5.3:F,G and from formula 3.4.7:J on page 75 we get the physical meaning of L_t and L_Γ^t :

$$\gamma_{\ell g} L_t(\delta n) = - 2 \gamma_{\ell g} \delta\kappa' + \delta(p_g - p_\ell) - 2\kappa\delta\gamma_{\ell g} =$$

$$= \delta(p_g - p_\ell - 2\kappa\gamma_{\ell g}) \quad , \qquad (3.5.4\text{:F})$$

$$\sin(\theta)\gamma_{\ell g} L_\Gamma^t(\delta n) = - \gamma_{\ell g} \sin(\theta)\delta\theta' + \cos(\theta)\delta\gamma_{\ell g} - \delta(\gamma_{sg} - \gamma_{s\ell}) =$$

$$= \delta(\gamma_{\ell g} \cos(\theta') - \gamma_{sg} + \gamma_{s\ell}) \quad . \qquad (3.5.4\text{:G})$$

The operator L_t represents the restoring force per unit area on the displaced meniscus, while L_Γ^t represents the restoring force per unit length acting on the boundary curve along the pore wall.

The analogue of the addition formula 3.5.3:J is:

$$J_t[\phi+\psi] = J_t[\phi] + J_t[\psi] + 2\,J_t[\phi,\psi]$$

I have not been able to find any analogue to the theorem of formula 3.5.3:P for the stability of J_t .

3.5.5 Stability criteria using eigenvalue methods.

Eigenvalue methods provide a powerful technique for the study of the behaviour of quadratic functionals. This technique is described in reference 16). In this section the method is applied to our functionals J and J_t .

We will use the following notations

$$J'[\psi] = \frac{J[\psi]}{\iint\limits_S \psi^2 dS} \qquad J_t'[\psi] = \frac{J_t[\psi]}{\iint\limits_S \psi^2 dS} \quad . \tag{3.5.5:A}$$

The case $\psi \equiv 0$ is excluded, so that the integral in the denominators is strictly positive. J' and J_t' are not changed when ψ is multiplied by a constant:

$$J'[\alpha\psi] = J'[\psi] \qquad J_t'[\alpha\psi] = J_t'[\psi] \quad . \tag{3.5.5:B}$$

We now assume that $J'[\psi]$ has a minimum λ_0 for $\psi = \psi_0$. Then for any ψ we have

$$J[\psi_0+\varepsilon\psi'] \geq \lambda_0 \iint\limits_S (\psi_0+\varepsilon\psi')^2 \, dS \quad . \tag{3.5.5:D}$$

We apply the addition formula 3.5.3:J. The terms of the above inequality that do not contain ε cancel out. The first-order terms in ε must also vanish, since the inequality shall hold true for both positive and negative ε . Thus we must have

$$2\varepsilon \; J[\psi',\psi_0] = 2\varepsilon \; \lambda_0 \iint_S \psi_0\psi' \, dS \qquad (3.5.5:E)$$

or with formula 3.5.3:H

$$\iint_S \psi'\{L(\psi_0) - \lambda_0\psi_0\}dS + \oint_\Gamma \psi' \, L_\Gamma(\psi_0)ds = 0 \quad . \qquad (3.5.5:F)$$

Here ψ' is any function on S and on Γ . Then the minimal function ψ_0 must satisfy:

$$\begin{aligned} L(\psi_0) &= \lambda_0\psi_0 \\ L_\Gamma(\psi_0) &= 0 \quad . \end{aligned} \qquad (3.5.5:G)$$

The minimum of $J'[\psi]$ is thus given by the smallest eigenvalue of the eigenvalue problem:

$$\begin{aligned} L(\psi) &= \lambda\psi \\ L_\Gamma(\psi) &= 0 \quad . \end{aligned} \qquad (3.5.5:H)$$

We note that, if $\sigma = +\infty$ on a part of the boundary, then for this part the boundary condition $L_\Gamma(\psi) = 0$ is replaced by the condition $\psi = 0$. In conclusion we have that J is strongly stable, if and only if the smallest eigenvalue for the eigenvalue problem 3.5.5:H is positive.

J is weakly stable if $J[\psi]$ and thence $J'[\psi]$ are positive for all ψ with $S_\psi = 0$ and $\Gamma_\psi = 0$. We assume that $J'[\psi]$ with the subsidiary conditions $S_\psi = 0$ and $\Gamma_\psi = 0$ has a smallest value λ_1 for $\psi = \psi_1$:

$$J'[\psi] \geq J'[\psi_1] = \lambda_1 \quad \text{for } \psi \text{ such that } S_\psi = 0 \, , \Gamma_\psi = 0. \qquad (3.5.5:I)$$

Put $\psi = \psi_1 + \varepsilon\psi'$. We get as in the preceding case, following formulas 3.5.5:D-F:

$$\iint_S \psi'\{L(\psi_1) - \lambda_1\psi_1\}dS + \oint \psi' L_\Gamma(\psi_1)ds = 0 \quad , \qquad (3.5.5:J)$$

where ψ' is any function satisfying

$$S_{\psi'} = \iint_S \psi' \, dS = 0 \qquad \Gamma_{\psi'} = \oint_\Gamma \psi' \, ds = 0 \quad . \qquad (3.5.5:K)$$

From 3.5.5:J and K we can now only conclude that $L(\psi_1) - \lambda_1\psi_1$ is constant over S , and that $L_\Gamma(\psi_1)$ is constant along Γ . The minimal function ψ_1 must then satisfy:

$$\begin{aligned} L(\psi_1) &= \lambda_1\psi_1 + A_1 & S_{\psi_1} &= 0 \\ L_\Gamma(\psi_1) &= B_1 & \Gamma_{\psi_1} &= 0 \end{aligned} \qquad (3.5.5:L)$$

Here A_1 and B_1 are two constants. We note that, if $\sigma = +\infty$ on a part of the boundary, then for this part the boundary condition $L_\Gamma(\psi) = B_1$ is replaced by the condition $\psi = 0$.

Thus the study of weak stability or the minimum of $J'[\psi]$ with the subsidiary conditions $S_\psi = 0$ and $\Gamma_\psi = 0$ give rise to the following problem of eigenvalue type. The minimal function ψ shall for some constants A and B satisfy:

$$\begin{aligned} L(\psi) &= \lambda\psi + A & S_\psi &= 0 \\ L_\Gamma(\psi) &= B & \Gamma_\psi &= 0 \end{aligned} \qquad (3.5.5:M)$$

The smallest λ for any A and B , for which there is a nonzero solution ψ , gives the minimum of $J'[\psi]$ with subsidiary conditions $S_\psi = 0$ and $\Gamma_\psi = 0$.

In conclusion we have (when J is not strongly stable) that J is weakly stable if and only if the smallest λ of problem 3.5.5:M is positive.

A meniscus region is stable if $J_t[\psi]$ is positive for all ψ ($\neq 0$). Let λ_t be the minimum of $J_t'[\psi]$ assumed for $\psi = \psi_t$. Following the same line of argument as for the minimum of $J'[\psi]$ in formulas 3.5.5:C to G we get that ψ_t must satisfy:

$$\begin{aligned} L_t(\psi_t) &= \lambda_t \psi_t \\ L_\Gamma^t(\psi_t) &= 0 \end{aligned} \qquad (3.5.5:N)$$

Then the minimum of $J_t'[\psi]$ is given by the smallest eigenvalue for the eigenvalue problem:

$$\begin{aligned} L_t(\psi) &= \lambda\psi \\ L_\Gamma^t(\psi) &= 0 \end{aligned} \qquad (3.5.5:O)$$

We note again that the boundary condition $L_\Gamma^t(\psi) = 0$ is replaced by the condition $\psi = 0$ for a part of the boundary where $\sigma = +\infty$. We have stability if and only if the smallest eigenvalue for problem 3.5.5:O is positive.

The first eigenvalue problem 3.5.5:H for strong stability is the simplest one to solve. The problems 3.5.5:M for weak stability and 3.5.5:O for stability are more difficult. In the following section another method to handle weak stability and stability is developed.

3.5.6 Stability criteria using meniscus solutions.

We have an equilibrium water meniscus S in a certain surrounding region. The mean curvature κ is constant, and the angle of contact θ' is equal to the contact angle θ. The system is in a certain thermodynamical state given by some thermodynamical variables. When these variables are changed infinitesimally, the meniscus S is displaced to a new equilibrium position S'. Normally S' lies infinitely close to S. Let then $\varepsilon\psi$, where ε is infinitesimal and ψ a function over S, be the normal component of this displacement.

The change in mean curvature $\delta\kappa'$ is constant over S, since S' also has constant mean curvature. Formula 3.5.3:F gives:

$$L(\varepsilon\psi) = -2\delta\kappa' = \text{const.} \qquad (3.5.6:A)$$

When the state is changed, the contact angle θ changes to a new value. The change $\delta\theta'$ in angle of contact in the displacement must be equal to this change in θ, since S' is an equilibrium meniscus. Thus from formula 3.5.3:G we get:

$$L_\Gamma(\varepsilon\psi) = -\delta\theta' = \text{const.} \qquad (3.5.6:B)$$

From 3.5.6:A and B we have that ψ must satisfy:

$$\begin{aligned} L(\psi) &= C \\ L_\Gamma(\psi) &= C' \quad , \end{aligned} \qquad (3.5.6:C)$$

where C and C' are two constants. Functions satisfying 3.5.6:C represent a displacement of a meniscus to a new equilibrium meniscus in another thermodynamical state. We will call functions ψ satisfying 3.5.6:C <u>meniscus solutions</u>. On parts of of Γ where $\sigma = +\infty$ the boundary condition $L_\Gamma(\psi) = C'$ is as usual replaced by the condition $\psi = 0$.

Meniscus solutions will be of great significance in the stability investigations. Suppose for a given stability problem that we are able to find two linearly independent (that is non-proportional) meniscus solutions ϕ_a and ϕ_b . We will in this section investigate consequences of this assumption.

Thus we assume that we have two linearly independent meniscus solutions ϕ_a and ϕ_b :

$$\begin{array}{ll} L(\phi_a) = C_a & L(\phi_b) = C_b \\ L_\Gamma(\phi_a) = C'_a & L_\Gamma(\phi_b) = C'_b \end{array} \tag{3.5.6:D}$$

There are restrictions on the constants. Applying formulas 3.5.3:B and H on $J[\phi_a,\phi_b]$ we immediately get:

$$C_a\, S_{\phi_b} + C'_a\, \Gamma_{\phi_b} = C_b\, S_{\phi_a} + C'_b\, \Gamma_{\phi_a} \quad . \tag{3.5.6:E}$$

Consider now a certain type of stability problem, for example the stability of a cylindrical surface for different heights of the cylinder and different boundary conditions. The situation is characterized by a set of parameters. A major problem in the stability investigations is to find those values of the parameters which give the boundary or limit between weak stability and strong instability.

From section 3.5.5 we have that there is weak stability if the smallest λ_1 of problem 3.5.5:L is positive, and strong instability if the smallest λ_1 is negative. Thus at the boundary between weak stability and strong instability the smallest λ_1

of 3.5.5:L is zero. The minimal function ψ_1 will then satisfy:

$$L(\psi_1) = A_1 \qquad S_{\psi_1} = 0$$
$$L_\Gamma(\psi_1) = B_1 \qquad \Gamma_{\psi_1} = 0 \tag{3.5.6:F}$$

Thus ψ_1 is a meniscus solution. We may apply formula 3.5.6:E on the two meniscus solutions ψ_1 and ϕ_a, and on ψ_1 and ϕ_b. Then we get:

$$A_1 S_{\phi_a} + B_1 \Gamma_{\phi_a} = 0$$
$$A_1 S_{\phi_b} + B_1 \Gamma_{\phi_b} = 0 \tag{3.5.6:G}$$

This is an equation system for A_1 and B_1. Either we have

$$A_1 = 0 \qquad B_1 = 0 \tag{3.5.6:H}$$

or that the determinant is zero:

$$S_{\phi_a} \Gamma_{\phi_b} - S_{\phi_b} \Gamma_{\phi_a} = 0 \quad . \tag{3.5.6:I}$$

Thus we have got the following criterion for the limit between weak stability and strong instability.

We have two linearly independent meniscus solutions ϕ_a and ϕ_b. Then for values of the parameters of the stability problem at the transition between weak stability and strong instability we must have either that

$$S_{\phi_a} \Gamma_{\phi_b} - S_{\phi_b} \Gamma_{\phi_a} = 0 \tag{3.5.6:J}$$

or that there is a non-zero solution ψ to

$$L(\psi) = 0 \qquad S_\psi = 0$$
$$L_\Gamma(\psi) = 0 \qquad \Gamma_\psi = 0 \tag{3.5.6:K}$$

This criterion will be simpler to use than criterion 3.5.5:L on weak stability.

Let us now turn to the question of stability of J_t . The functional J_t is stable, if J is strongly stable, and unstable if J is strongly unstable. The remaining problem is then to investigate the stability of J_t , when J is weakly stable.

The functional J_t is the sum of J and I , where I is a quadratic form in S_ψ and Γ_ψ (formula 3.5.1:E). Let us put:

$$S_\psi = x \qquad \Gamma_\psi = y \quad . \tag{3.5.6:L}$$

We will first study the minimum of $J[\psi]$ with the subsidiary conditions $S_\psi = x$ and $\Gamma_\psi = y$ for any x and y .

We have assumed that J is weakly stable. We also assume that we have two linearly independent meniscus solutions ϕ_a and ϕ_b . If the determinant $S_{\phi_a}\Gamma_{\phi_b} - S_{\phi_b}\Gamma_{\phi_a}$ were zero, then we could form a non-zero linear combination ϕ of ϕ_a and ϕ_b with $S_\phi = 0$ and $\Gamma_\phi = 0$. It is easy to see from formula 3.5.3:I that then $J[\phi]$ is zero, and we would not have weak stability. Thus $S_{\phi_a}\Gamma_{\phi_b} - S_{\phi_b}\Gamma_{\phi_a}$ is different from zero. We can form, from linear combinations of ϕ_a and ϕ_b , two new meniscus solutions ϕ_V and ϕ_A which have the following properties:

$$\begin{aligned} L(\phi_V) &= D_{VV} & S_{\phi_V} &= 1 \\ L_\Gamma(\phi_V) &= D_{VA} & \Gamma_{\phi_V} &= 0 \end{aligned} \tag{3.5.6:M}$$

$$\begin{aligned} L(\phi_A) &= D_{AV}(=D_{VA}) & S_{\phi_A} &= 0 \\ L_\Gamma(\phi_A) &= D_{AA} & \Gamma_{\phi_A} &= 1 \end{aligned} \tag{3.5.6:N}$$

Here D_{VV} , D_{VA} , D_{AV} and D_{AA} are constants. Formula 3.5.6:E gives that D_{AV} and D_{VA} are equal. As usual the boundary conditions are replaced by the conditions $\phi_V = 0$ and $\phi_A = 0$ on those parts of the boundary where $\sigma = +\infty$. The case when $\sigma = +\infty$ on the entire boundary is treated below.

Let now ψ be any function satisfying $S_\psi = x$ and $\Gamma_\psi = y$ and put:

$$\psi' = \psi - x\,\phi_V - y\,\phi_A \quad . \tag{3.5.6:O}$$

Then $S_{\psi'} = 0$ and $\Gamma_{\psi'} = 0$ and we have:

$$J[\psi', x\,\phi_V + y\,\phi_A] = \iint_S \psi'(xD_{VV} + yD_{VA})dS + \oint_\Gamma \psi'(xD_{VA} + yD_{AA})ds = 0 \ . \tag{3.5.6:P}$$

Thus we have from the addition formula 2.5.3:J:

$$J[\psi] = J[\psi' + x\phi_V + y\phi_A] = J[\psi'] + J[x\phi_V + y\phi_A] \ . \tag{3.5.6:Q}$$

The quantity $J[\psi']$ is non-negative, since J is weakly stable. Thus $J[x\phi_V + y\phi_A]$ is the minimum of $J[\psi]$ with the subsidiary conditions $S_\psi = x$ and $\Gamma_\psi = y$. From formulas 3.5.6:M and N we have for the minimum value:

$$J[x\phi_V + y\phi_A] = \iint_S (x\phi_V + y\phi_A)(xD_{VV} + yD_{VA})dS + \oint (x\phi_V + y\phi_A)(xD_{VA} + yD_{AA})ds = D_{VV}\,x^2 + 2\,D_{VA}\,xy + D_{AA}\,y^2 \tag{3.5.6:R}$$

We have proved the following theorem.

Let J be weakly stable. There exist two meniscus solutions ϕ_V and ϕ_A satisfying 3.5.6:M and N. Then the minimum of $J[\psi]$ with the subsidiary conditions $S_\psi = x$ and $\Gamma_\psi = y$ is $D_{VV}\, x^2 + 2D_{VA}\, xy + D_{AA}\, y^2$ .The minimum is assumed for $\psi = x\phi_V + y\,\phi_A$.

For $J_t[\psi]$ we now have:

$$J_t[\psi] = J[\psi] + I[\psi] \geq (D_{VV} + \beta_{VV})x^2 + 2(D_{VA} + \beta_{VA})xy +$$

$$+ (D_{AA} + \beta_{VV})y^2 \quad , \qquad (3.5.6:S)$$

where $x = S_\psi$ and $y = \Gamma_\psi$.

For J_t we have arrived at the following theorem. Let J be weakly stable. There exist two meniscus solutions ϕ_V and ϕ_A that satisfy 3.5.6:M and N. Then J_t is stable precisely when the quadratic form in 3.5.6:S is positive definite, that is precisely when:

$$D_{VV} + \beta_{VV} > 0$$

$$(D_{VV} + \beta_{VV})(D_{AA} + \beta_{AA}) > (D_{VA} + \beta_{VA})^2 \qquad (3.5.6:T)$$

The functions ϕ_V and ϕ_A will be called fundamental meniscus solutions. They are uniquely determined, when J is weakly or strongly stable. Consider in order to prove this two meniscus solutions $\psi = \phi_V$ and $\psi = \phi_V'$ with $S_\psi = 1$ and $\Gamma_\psi = 0$. Then the difference $\phi = \phi_V - \phi_V'$ is a meniscus function with $S_\phi = 0$ and $\Gamma_\phi = 0$. Then from formula 3.5.3:I $J[\phi]$ is zero, and ϕ must vanish on S , since J is weakly stable.

The left side of 3.5.6:J is equal to $+1$ for $\phi_a = \phi_V$ and $\phi_b = \phi_A$. This gives the following theorem from the criterion of formulas 3.5.6:J and K.

There exist two fundamental meniscus solutions ϕ_V and ϕ_A. Then for values of the parameters of the stability problem on the limit between weak stability and strong instability there is a non-zero solution to the following problem:

$$\begin{aligned} &L(\psi) = 0 \qquad && S_\psi = 0 \\ &L_\Gamma(\psi) = 0 && \Gamma_\psi = 0 \end{aligned} \tag{3.5.6:U}$$

Let us finally consider the special case, when the meniscus is kept fixed along the entire boundary, that is when $\sigma = +\infty$ on Γ. Then the functions ψ must vanish on Γ. The function ϕ_A drops out. We then need one meniscus solution ϕ_V, which satisfies

$$\begin{aligned} &L(\phi_V) = D_{VV} \qquad && S_{\phi_V} = 1 \\ &\phi_V\Big|_\Gamma = 0 \end{aligned} \tag{3.5.6:V}$$

Instead of the theorem of formula 3.5.6:U we now have the following stability criterion.

There exists a fundamental meniscus solution ϕ_V. Then for values of the parameters of the stability problem on the boundary between weak stability and strong instability there is a non-zero solution to the following problem:

$$\begin{aligned} &L(\psi) = 0 \qquad && S_\psi = 0 \\ &\psi\Big|_\Gamma = 0 \end{aligned} \tag{3.5.6:W}$$

Consider now, in the region of weak stability, the minimum of $J[\psi]$ with the subsidiary condition $S_\psi = x$. The minimum is assumed for $\psi = x \cdot \phi_V$. Instead of 3.5.6:S we now have for any ψ, that vanishes on Γ :

$$J_t[\psi] \geq J[x\phi_V] + I[\psi] = (D_{VV} + \beta_{VV})x^2 \quad . \qquad (3.5.6{:}A')$$

Thus J_t is stable precisely when:

$$D_{VV} + \beta_{VV} > 0 \quad . \qquad (3.5.6{:}B')$$

We will end this section with some remarks on how to construct meniscus solutions. Suppose that we have completely solved the eigenvalue problem 3.5.5:H. Let ψ_i be the eigenfunctions and λ_i the eigenvalues:

$$\left.\begin{array}{l} L(\psi_i) = \lambda_i \psi_i \\ L_\Gamma(\psi_i) = 0 \end{array}\right. \quad i=1,2,\ldots \qquad (3.5.6{:}C')$$

The functions ψ_i are chosen so that they form an orthonormal set:

$$\iint_S \psi_i \; \psi_j \; dS = \begin{cases} 1 & i=j \\ 0 & i \neq j \end{cases} \qquad (3.5.6{:}D')$$

We postulate that the set of functions is complete, so that the constant $\psi = 1$ can be expanded in the series:

$$1 = \sum_i \alpha_i \; \psi_i \quad \text{on} \quad S \quad . \qquad (3.5.6{:}E')$$

The coefficient α_i is equal to S_{ψ_i} because of 3.5.6:D'. Then we get the following meniscus solution:

$$\phi_a = \sum_i \frac{S_{\psi_i}}{\lambda_i} \psi_i \quad . \qquad (3.5.6{:}F')$$

Here

$$\left.\begin{array}{l} L(\phi_a) = 1 \\ L_\Gamma(\phi_a) = 0 \end{array}\right. \qquad (3.5.6{:}G')$$

The terms with $S_{\psi_i} = 0$ vanish in the sum 3.5.6:F'. The function ϕ_a is defined if, for all i with non-zero S_{ψ_i}, λ_i is different from zero. (We postulate suitable convergence of the series.)

In the special case when $\sigma = +\infty$ along Γ we have instead of 3.5.6:C':

$$\left.\begin{array}{l} L(\psi_i) = \lambda_i \psi_i \\ \psi_i \Big|_{\Gamma} = 0 \end{array}\right. \qquad i=1,2,\ldots \quad . \tag{3.5.6:H'}$$

Then we have the following fundamental meniscus solution:

$$\phi_V = \frac{1}{\sum\limits_i \frac{1}{\lambda_i}(S_{\psi_i})^2} \sum_i \frac{1}{\lambda_i} S_{\psi_i} \psi_i \quad . \tag{3.5.6:I'}$$

Here the sum in the denominator must of course be different from zero. For the constant D_{VV} we get:

$$D_{VV} = \frac{1}{\sum\limits_i \frac{1}{\lambda_i}(S_{\psi_i})^2} \quad . \tag{3.5.6:J'}$$

The functions ψ_i must be orthonormal. An application of these formulas i given in section 3.5.10.

Suppose next that we have found all solutions of $L(\psi) = 0$ (without any boundary conditions). Let ψ_i^0 denote these functions:

$$L(\psi_i^0) = 0 \qquad i=1,2,\ldots \quad . \tag{3.5.6:K'}$$

If the functions $L_\Gamma(\psi_i^0)$, $i=1,2,\ldots$, form a complete set on the boundary Γ, then the constant $\phi=1$ can be expanded on Γ :

$$1 = \sum_i \alpha_i^0 L_\Gamma(\psi_i^0) \quad \text{on } \Gamma . \tag{3.5.6:L'}$$

We get a second meniscus solution:

$$\phi_b = \sum_i \alpha_i^0 \psi_i^0 \quad . \tag{3.5.6:M'}$$

Here

$$\begin{aligned} L(\phi_b) &= 0 \\ L_\Gamma(\phi_b) &= 1 \end{aligned} \tag{3.5.6:N'}$$

3.5.7 Stability of a cylindrical meniscus.

We will in sections 3.5.7-10 apply the preceding theory in some different cases. The surface S must have constant mean curvature. There are very few simple surfaces of this kind. The simplest ones are a part of a plane, a part of a cylinder, and a part of a sphere. Reference 16) discusses rotationally symmetric surfaces of constant mean curvature.

In this section we will study the stability of a cylindrical meniscus in a pore. In the following section 3.5.8 we will study the stability of a spherical cap. The stability of a symmetric spherical zone is studied in section 3.5.9. Finally we will investigate the stability of a rectangular cylindrical meniscus in section 3.5.10.

The cylindrical meniscus S is given in parametric form by

$$S: \quad \bar{r}(\varphi, z) = (R\cos\varphi,\ R\sin\varphi, z) \qquad \begin{array}{l} -\frac{L}{2} \le z \le \frac{L}{2} \\ -\pi \le \varphi \le \pi \end{array} \tag{3.5.7:A}$$

The radius of the cylinder is R, and the height is L. The boundary Γ consists of two parts:

$$\begin{aligned} \Gamma_+ &: \quad \bar{r}(\varphi,\tfrac{L}{2}) \\ & \qquad\qquad -\pi \leq \varphi \leq \pi \quad . \\ \Gamma_- &: \quad \bar{r}(\varphi,-\tfrac{L}{2}) \end{aligned} \tag{3.5.7:B}$$

The pore wall must fit to the cylindrical meniscus S. The pore is (at least in the vicinity of Γ_+ and Γ_-) rotationally symmetric around the z-axis. See figure 3.5.7:I.

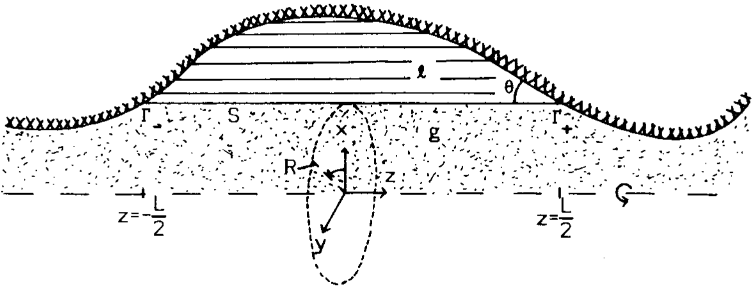


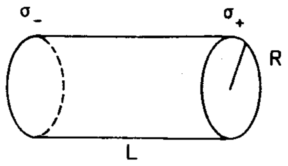
Figure 3.5.7:I The figure shows a cylindrical meniscus in S in a rotationally symmetric pore. The liquid phase ℓ lies between S and the pore wall in an annulus. The height of the cylinder is L. The boundary Γ is composed of the two circles Γ_+ and Γ_- of the cylinder.

The liquid phase lies outside the cylinder between S and the pore wall in an annulus. The angle of contact at Γ_+ and Γ_- is equal to the contact angle θ. The curvature κ_s of the pore wall at Γ_+ and Γ_- in the direction perpendicular to Γ_+ and Γ_- is κ_s^+ respectively κ_s^-. The curvature κ_m of S at Γ in the direction perpendicular to Γ, that is in the z direction, is zero. Thus we have for the boundary function σ from formula 3.5.1:B:

$$\sigma = \frac{\kappa_m \cos(\theta) - \kappa_s}{\sin(\theta)} = \begin{cases} -\dfrac{\kappa_s^+}{\sin(\theta)} = \sigma_+ & \text{on } \Gamma_+ \\ \\ -\dfrac{\kappa_s^-}{\sin(\theta)} = \sigma_- & \text{on } \Gamma_- \end{cases} \qquad (3.5.7{:}C)$$

The constants σ_+ and σ_- may assume any values including $+\infty$.

Schematically we have the following stability problem:



$-\infty < \sigma_+ \leq +\infty$

$-\infty < \sigma_- \leq +\infty$

$R > 0 \quad L > 0$

Figure 3.5.7:II The figure shows schematically the stability problem studied in section 3.5.7. The boundary function σ assumes constant values σ_+ and σ_- on the two boundary circles of the cylindrical meniscus.

Formulas for our special surfaces are given in appendix 1. From formulas A1:W,A' and B' we have:

$$J[\psi] = \iint_S \left\{ \left(\frac{\partial\psi}{\partial z}\right)^2 + \frac{1}{R^2}\left(\frac{\partial\psi}{\partial\varphi}\right)^2 - \frac{1}{R^2}\,\psi^2 \right\} dS + \oint_\Gamma \sigma\,\psi^2\, ds \qquad (3.5.7{:}D)$$

$$L(\psi) = -\left\{ \frac{\partial^2\psi}{\partial z^2} + \frac{1}{R^2}\,\frac{\partial^2\psi}{\partial\varphi^2} + \frac{1}{R^2}\,\psi \right\} \qquad (3.5.7{:}E)$$

$$\begin{aligned} L_{\Gamma_+}(\psi) &= \sigma_+\psi + \frac{\partial\psi}{\partial z} \\ L_{\Gamma_-}(\psi) &= \sigma_-\psi - \frac{\partial\psi}{\partial z} \end{aligned} \qquad (3.5.7{:}F)$$

Let us first note from the discussion in section 3.5.2 that the prospects of stability are diminished when for a given cylinder σ_+ or σ_- is diminished. This is also true for weak or strong stability. Especially we have that instability for the case $\sigma_+ = \sigma_- = +\infty$ implies the instability for all σ_+ and σ_-. We also note that, for the case $\sigma_+ = \sigma_- = +\infty$, the prospects of stability diminish, when the surface S is extended. Thus we diminish the prospects of stability when L is increased for $\sigma_+ = \sigma_- = +\infty$ and for fixed R.

We will first study the conditions on L, R, σ_+ and σ_- for strong stability. We will then first study the eigenvalue problem of formula 3.5.5:H:

$$L(\psi) = \lambda\psi \qquad L_\Gamma(\psi) = 0 \qquad (3.5.7{:}G)$$

or with formulas 3.5.7:E and F:

$$\frac{\partial^2\psi}{\partial z^2} + \frac{1}{R^2}\frac{\partial^2\psi}{\partial\varphi^2} + (\frac{1}{R^2} + \lambda)\psi = 0 \qquad (3.5.7{:}H)$$

$$\sigma_\pm \psi \pm \frac{\partial\psi}{\partial z} = 0 \qquad z = \pm\frac{L}{2} \quad . \qquad (3.5.7{:}I)$$

We will use the technique of separation of variables in order to get solutions of 3.5.7:H. Put

$$\psi(\varphi,z) = Z_m(z)\cdot\cos(m\varphi + \varphi_m) \qquad m=0,1,\ldots \quad . \qquad (3.5.7{:}J)$$

Here φ_m is any constant. Then $Z_m(z)$ must satisfy:

$$\frac{d^2Z_m}{dZ^2} + (\frac{1-m^2}{R^2} + \lambda)Z_m = 0 \quad . \qquad (3.5.7{:}K)$$

When $\lambda = 0$ we get the following solutions of 3.5.7:K:

$$m=0 : \quad \cos(\frac{z}{R}) \qquad \sin(\frac{z}{R}) \tag{3.5.7:L}$$

$$m=1 : \quad \cos(\varphi_1+\varphi_1) \qquad z\cdot\cos(\varphi+\varphi_1') \tag{3.5.7:M}$$

$$m\geq 2 : \quad \cosh(\frac{\sqrt{m^2-1}}{R}z)\cos(m\varphi+\varphi_m) \qquad \sinh(\frac{\sqrt{m^2-1}}{R}z)\cos(m\varphi+\varphi_m') \tag{3.5.7:N}$$

We will try to find a function ϕ which is suitable for criterion 3.5.3:P on strong stability. Let ϕ be a linear combination of the two solutions 3.5.7:L:

$$\phi = \cos(\frac{z}{R} + \varphi_0) \quad . \tag{3.5.7:O}$$

We will use the notations

$$\eta = \frac{L}{2R} \tag{3.5.7:P}$$

and

$$\beta_+ = \operatorname{arctg}(R\sigma_+) \qquad \beta_- = \operatorname{arctg}(R\sigma_-) \tag{3.5.7:Q}$$

Then we have, choosing $\varphi_0 = \frac{\beta_+-\beta_-}{2}$:

$$L(\phi) = 0$$

$$L_{\Gamma_+}(\phi) = \frac{\sin(\beta_+-\eta-\varphi_0)}{R\cos(\beta_+)} = \frac{\sin(\frac{\beta_++\beta_-}{2}-\eta)}{R\cos(\beta_+)} \tag{3.5.7:R}$$

$$L_{\Gamma_-}(\phi) = \frac{\sin(\beta_--\eta+\varphi_0)}{R\cos(\beta_-)} = \frac{\sin(\frac{\beta_++\beta_-}{2}-\eta)}{R\cos(\beta_-)}$$

Suppose now that

$$\frac{\beta_++\beta_-}{} > \eta \quad . \tag{3.5.7:S}$$

Then it is easy to verify that

$$0 < \frac{\beta_+ + \beta_-}{2} - \eta < \pi \qquad -\frac{\pi}{2} < \frac{z}{R} + \varphi_0 < \frac{\pi}{2} \qquad (3.5.7:T)$$

Thus ϕ is positive on S, and $L_\Gamma(\phi) > 0$. The function ψ fulfils criterion 3.5.3:P and we have strong stability. When we have equality in 3.5.7:S, then $L_\Gamma(\phi)$ is zero. Thus from formula 3.5.3:H $J[\phi]$ will be zero, and we do not have strong stability. The equation $\frac{\beta_+ + \beta_-}{2} = \eta$ must give the boundary between strong stability and weak stability.

In conclusion we have strong stability precisely when

$$\frac{\operatorname{arctg}(R\sigma_+) + \operatorname{arctg}(R\sigma_-)}{2} > \frac{L}{2R} \quad . \qquad (3.5.7:U)$$

This region of strong stability is shown in figures 3.5.7:IV,V,VI for different values of σ_+ and σ_-.

We now turn to the problem of finding the region of weak stability. We first note that the eigenfunction $\psi = \sin(\frac{z}{R})$ from formula 3.5.7:L gives a condition for weak stability for $\sigma_+ = \sigma_- = +\infty$. When $\eta = \frac{L}{2R} = \pi$, we have for this ψ:

$$\begin{array}{ll} L(\psi) = 0 & S_\psi = 0 \\ \psi|_\Gamma = 0 & (\Gamma_\psi = 0) \end{array} \qquad (3.5.7:V)$$

Then $J[\psi]$ is zero and we do not have weak stability. When the surface is extended, that is when $\eta = \frac{L}{2R} > \pi$, we must get strong instability. We have strong instability for $\eta > \pi$, when $\sigma_+ = \sigma_- = +\infty$, and thus for all σ_+ and σ_-.

For the investigation of weak stability we need meniscus solutions. The functions $\phi = \cos(\frac{z}{R})$ and $\phi = \sin(\frac{z}{R})$ from formula 3.5.7:L and the constant $\phi = 1$ satisfy $L(\phi) = C$, where C is a constant.

From these functions we get the following fundamental meniscus solutions:

$$\phi_V = \frac{1}{4\pi R^2} \; \frac{\cos(\frac{z}{R}) - \cos(\eta)}{\sin(\eta) - \eta\cos(\eta)} \tag{3.5.7:W}$$

$$\phi_A = \frac{1}{4\pi R} \; \{\frac{\sin(\eta) - \eta\cos(\frac{z}{R})}{\sin(\eta) - \eta\cos(\eta)} - \frac{R\sigma_+ - R\sigma_-}{2\cos(\eta) + (R\sigma_+ + R\sigma_-)\sin(\eta)} \sin(\frac{z}{R})\}$$

(3.5.7:A')

The fundamental meniscus solutions are defined except when $tg(\eta) = \eta$ or $2\cot(\eta) + R\sigma_+ + R\sigma_- = 0$. The equation $tg(\eta) = \eta$ has not any solutions for $0 < \eta \leq \pi$.

The fundamental meniscus solutions satisfy 3.5.6:M and N:

$$\begin{array}{llll} L(\phi_V) = D_{VV} & S_{\phi_V} = 1 & L(\phi_A) = D_{VA} & S_{\phi_A} = 0 \\ L_\Gamma(\phi_V) = D_{VA} & \Gamma_{\phi_V} = 0 & L_\Gamma(\phi_A) = D_{AA} & \Gamma_{\phi_A} = 1 \end{array} \tag{3.5.7:B'}$$

The constants D_{VV}, D_{VA}, and D_{AA} are given by:

$$D_{VV} = \frac{1}{4\pi R^4} \cdot \frac{1}{tg(\eta) - \eta} \qquad D_{VA} = \frac{-1}{4\pi R^3} \; \frac{tg\,\eta}{tg(\eta) - \eta}$$

(3.5.7:C')

$$D_{AA} = \{\frac{(R\sigma_+ + R\sigma_-)\cot(\eta) + 2R\sigma_+ \cdot R\sigma_-}{2\cot(\eta) + R\sigma_+ + R\sigma_-} + \frac{\eta\, tg(\eta)}{tg(\eta) - \eta}\} \frac{1}{4\pi R^2}$$

The function $\psi = \sin(\frac{z}{R})$ from formula 3.5.7:L satisfies $L(\psi) = 0$,

$S_\psi = 0$, and $\Gamma_\psi = 0$. In the special case when $2\cot(\eta) + R\sigma_+ + R\sigma_- = 0$, we get that $L_{\Gamma_+}(\psi) = L_{\Gamma_-}(\psi)$. Then from formula 3.5.3:I we get that $J[\psi] = 0$. We do not have weak stability. Thus we have strong instability in the region

$$R\sigma_+ + R\sigma_- < 2\cot(\eta) \qquad 0<\eta<\pi \quad . \qquad (3.5.7:D')$$

In the region $0<\eta\leq\pi$, $R\sigma_+ + R\sigma_- \geq -2\cot(\eta)$ there is a boundary surface between strong instability and weak stability. The boundary surface may in part coincide with the boundaries $\eta=\pi$ and $R\sigma_+ + R\sigma_- = -2\cot(\eta)$ of the considered region and in part lie in the interior of the region. In the interior ϕ_V and ϕ_A are defined everywhere. Then from theorem of formulas 3.5.6:J,K we have for values of η , $R\sigma_+$ and $R\sigma_-$ on the boundary surface in the interior of the considered region that there exists a non-zero solution to the following problem:

$$\begin{aligned} &L(\psi) = 0 \qquad && S_\psi = 0 \\ &L_\Gamma(\psi) = 0 \qquad && \Gamma_\psi = 0 \end{aligned} \qquad (3.5.7:E')$$

The general solution of $L(\psi) = 0$ is a linear combination of the functions 3.5.7:L-N. The conditions $S_\psi = 0$ and $\Gamma_\psi = 0$ are fulfilled, if $\cos(\frac{z}{R})$ is omitted in the linear combination. The boundary condition $L_\Gamma(\psi) = 0$ remains to be satisfied.

We have already discussed the solution $\psi = \sin(\frac{z}{R})$. We got the condition $R\sigma_+ + R\sigma_- = -2\cot(\eta)$. Let us then try a combination $\psi = (A+B\cdot z)\cos(\varphi + \varphi_1)$ from formula 3.5.7:M. Then we get the conditions:

$$\begin{aligned} L_{\Gamma_+}(\psi) &= [A\,\sigma_+ + B(\frac{\sigma_+ L}{2} + 1)] \quad \cos(\varphi + \varphi_1) = 0 \\ L_{\Gamma_-}(\psi) &= [A\,\sigma_- - B(\frac{\sigma_- L}{2} + 1)] \quad \cos(\varphi + \varphi_1) = 0 \end{aligned} \qquad (3.5.7:F')$$

There is a non-zero solution when:

$$\sigma_+\sigma_- L + \sigma_+ + \sigma_- = 0$$

or

$$(\sigma_+ L + 1)(\sigma_- L + 1) = 1 \qquad (3.5.7:G')$$

or

$$2\eta + \frac{1}{\sigma_+ R} + \frac{1}{\sigma_- R} = 0$$

The graph of 3.5.7:G' is a hyperbola:

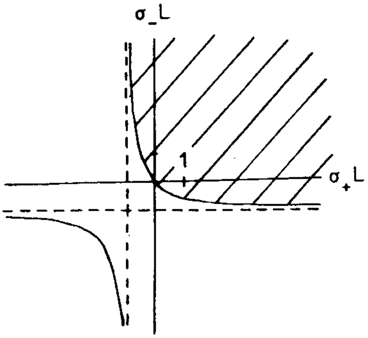


Figure 3.5.7:III The graph illustrates condition 3.5.7:H' for weak stability. The stability condition is satisfied in the shaded region.

On the upper branch $J[\psi]$ is zero due to 3.5.7:E'. We do not have weak stability. Thus we certainly have strong instability below and to the left of the upper branch. We have the following necessary condition for weak stability:

$$\begin{aligned} &\sigma_+ L + 1 > 0 \\ &(\sigma_+ L + 1)(\sigma_- L + 1) > 1 \end{aligned} \qquad (3.5.7:H')$$

This is the shaded area in the figure 3.5.7:III above.

We must also study the other possible solutions given by 3.5.7:N. For each $m \geq 2$ we get a condition for non-zero solutions. It is shown below that all these conditions are weaker than 3.5.7:H'. Thus 3.5.7:D' and 3.5.7:H' give the region of weak stability (and of course the region of strong stability).

A direct verification of the fact that the solutions 3.5.7:N give weaker conditions than 3.5.7:M is rather laborious. But we may instead use the theorem of formula 3.5.3:R to show this. A suitable ϕ is a certain linear combination from 3.5.7:M:

$$\phi = (\frac{\sigma_+ L + \sigma_- L}{2} + 2 - (\sigma_+ - \sigma_-)z) \cos(\varphi + \varphi_1) \quad . \quad (3.5.7{:}I')$$

This ϕ satisfies:

$$L(\phi) = 0 \qquad \phi \, L_\Gamma(\phi) = (\sigma_+ \sigma_- L + \sigma_+ + \sigma_-) \cos^2(\varphi + \varphi_1) \quad (3.5.7{:}J')$$

Thus $\phi \, L_\Gamma(\phi) \geq 0$, when 3.5.7:H' holds. Then we also have that the linear expression in z in 3.5.7:I' is positive, so that ϕ is zero, only when $\cos(\varphi + \varphi_1)$ is zero. Let now ψ be any function from 3.5.7:N for a certain m . This ψ is zero, when ϕ is zero, if we choose an appropriate value for φ_1 . The quotient $\frac{\psi}{\phi}$ is well-behaved, and we get from 3.5.3:R and formula 3.5.3:Q that $J[\psi] > 0$. The function ψ cannot be a solution to 3.5.7:E', since this implies that $J[\psi] = 0$. Thus when 3.5.7:H' holds, there are no solutions of 3.5.7:E' for the functions 3.5.7:N.

We may also use the conclusions of section 3.5.2 to show that the functions of 3.5.7:N cannot give the boundary between weak stability and strong instability. Suppose as an example that the following function from 3.5.7:N gives the boundary:

$$\psi = \cosh(\frac{\sqrt{3}}{R^2} \cdot z + z_0) \cdot \sin(2\varphi) \qquad (3.5.7{:}K')$$

$$J[\psi] = 0$$

Consider now a new stability problem for one half of the cylinder. On the two new boundaries $\varphi = 0$ and $\varphi = \pi$ $(-\frac{L}{2} \leq z \leq \frac{L}{2})$ we prescribe that $\sigma = +\infty$. On the other two parts of the boundary we keep the old values σ_+ and σ_-. This new case has better stability than the old one. Because of the factor $\sin(2\varphi)$, ψ is zero on the two new boundaries $\varphi = 0$ and $\varphi = \pi$. We also have that

$$S_{\Gamma}^{0.5} = 0 \qquad \Gamma_{\psi}^{0.5} = 0 \quad . \qquad (3.5.7{:}L')$$

Here $S_{\psi}^{0.5}$ is the integral of ψ over the new half of the cylinder. Let $J^{0.5}$ denote the J-functional for the new problem. The weak stability is better for the new problem. Then we must have that $J^{0.5}[\psi] > 0$. But from 3.5.7:K' we have $J^{0.5}[\psi] = \frac{1}{2} J[\psi] = 0$. Thus ψ cannot give the boundary between weak stability and strong instability.

In conclusion we have weak stability precisely when the following conditions are fulfilled:

$$\frac{L}{2R} < \pi$$

$$R\sigma_+ + R\sigma_- > -2\cot(\frac{L}{2R})$$

$$\sigma_+ L + 1 > 0 \qquad (\sigma_+ L + 1)(\sigma_- L + 1) > 1 \qquad (3.5.7{:}M')$$

$$\frac{\operatorname{arctg}(R\sigma_+) + \operatorname{arctg}(R\sigma_-)}{2} < \frac{L}{2R}$$

The last line excludes the region of strong stability.

Figure 3.5.7:IV below summarizes the obtained results in the special case when $\underline{\sigma_+ = \sigma_- = \sigma}$.

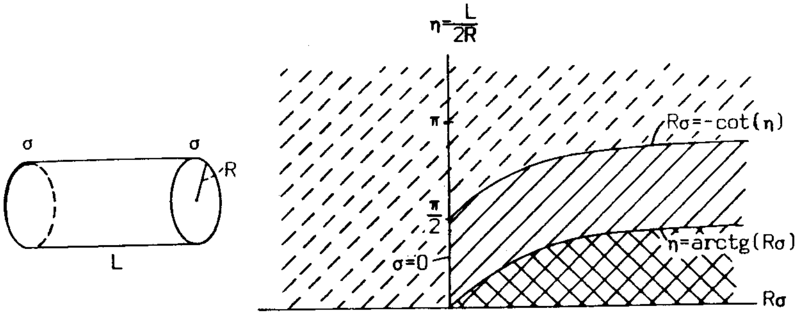


Figure 3.5.7:IV The figure shows the regions of strong stability ⊠⊠⊠, weak stability ////, and strong instability ⁄⁄⁄⁄ for a cylindrical meniscus with constant boundary function ($\sigma_+ = \sigma_- = \sigma$).

The point $L = 2\pi R$, $\sigma = +\infty$ gives the limit between weak stability and strong instability for a cylindrical surface, which is kept fixed at the boundaries. This is a classical result proved by Poincaré 17). This case is also discussed in reference 16).

The case, when the meniscus is kept fixed at Γ_- , is given by $\underline{\sigma_- = +\infty}$. The conditions for weak stability is then from 3.5.7:M':

$$\frac{L}{2R} < \pi \qquad \sigma_+ L + 1 > 1 \qquad \frac{1}{2}\,\mathrm{arctg}(R\sigma_+) + \frac{\pi}{2} < \frac{L}{2R} \quad (3.5.7{:}N')$$

The second inequality above may be written $\eta \cdot (R\sigma_+) > -1$. The obtained results on stability in this case are summarized in figure 3.5.7:V below.

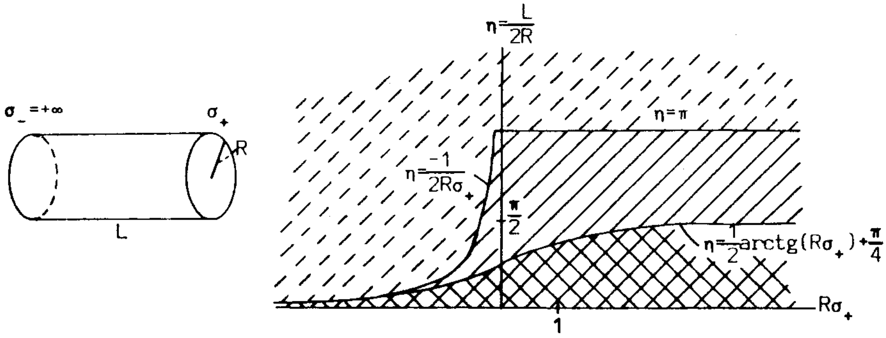
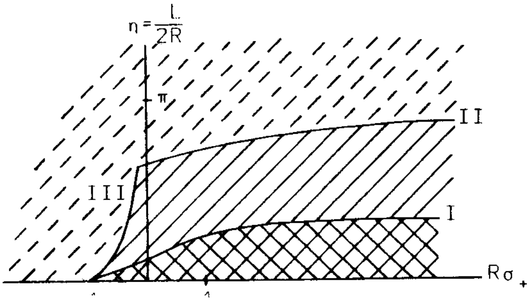


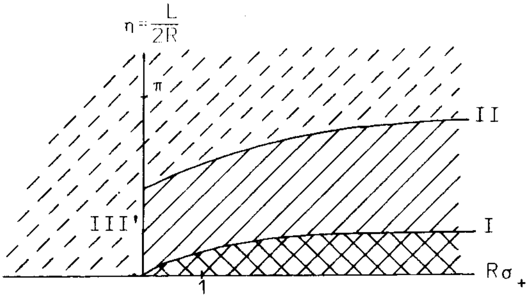
Figure 3.5.7:V The figure shows the regions of strong stability XXXX , weak stability //// , and strong instability /‚/‚/‚/ for a cylindrical meniscus, which is kept fixed at one end ($\sigma_- = +\infty$) , for different constant values σ_+ for the boundary function at the other end.

The figures 3.5.7:VI (A-E) below give the regions of strong stability, weak stability and strong instability for some different values of $R\sigma_-$.

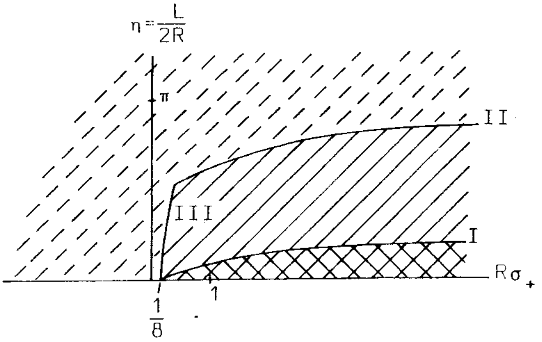
A: $R\sigma_- = +1$



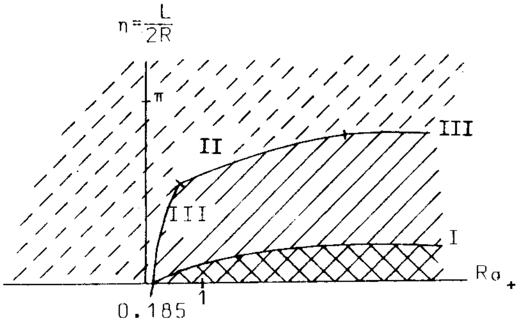
B: $R\sigma_- = 0$



C: $R\sigma_- = -\frac{1}{8}$



D: $R\sigma_- = -0.185$



Boundary curves:

I: $\eta = \frac{1}{2}\,\mathrm{arctg}(R\sigma_+) + \frac{1}{2}\,\mathrm{arctg}(R\sigma_-)$

II: $R\sigma_+ + R\sigma_- = -2\cot(\eta)$

III: $\eta = -\frac{1}{2R\sigma_+} - \frac{1}{2R\sigma_-}$ III': $R\sigma_+ = 0$ $(R\sigma_- = 0)$

E: $R\sigma_- = -0.25$

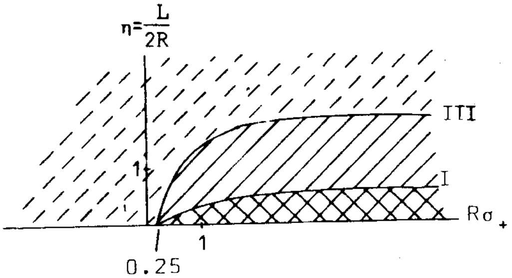


Figure 3.5.7:VI The figures A-E show the regions of strong stability xxx , weak stability /// , and strong instability /‚/‚/ for a cylindrical meniscus for some different values σ_- of the boundary function at one end.

Finally we will investigate the stability of J_t . We have stability when J is strongly stable, and instability when J is strongly unstable. For the remaining region of weak stability there is stability when the quadratic form 3.5.6:P is positive definite or when the inequalities 3.5.6:Q hold. The constants D_{VV} , D_{VA} , and D_{AA} are given by 3.5.7:C'. Thus we get the following conditions for stability:

$$\frac{1}{tg(\eta)-\eta} + 4\pi R^4 \beta_{VV} > 0 \qquad (3.5.7:O')$$

$$\left(\frac{1}{tg(\eta)-\eta} + 4\pi R^4 \beta_{VV}\right) \left(4\pi R^2 D_{AA} + 4\pi R^2 \beta_{AA}\right) > \left(\frac{tg(\eta)}{tg(\eta)-\eta} + 4\pi R^3 \beta_{VA}\right)^2$$

(3.5.7:P')

where D_{AA} is found in formula 3.5.7:C'.

Condition 3.5.7:O' is illustrated in figure 3.5.7:VII below. When $\sigma_+ = \sigma_- = +\infty$, condition 3.5.7:P' becomes the same as 3.5.7:O'. In this case there is strong stability, when $0 < \eta < \frac{\pi}{2}$ and weak stability when $\frac{\pi}{2} < \eta < \pi$. The shaded region in the figure below gives the region of stability for this special case.

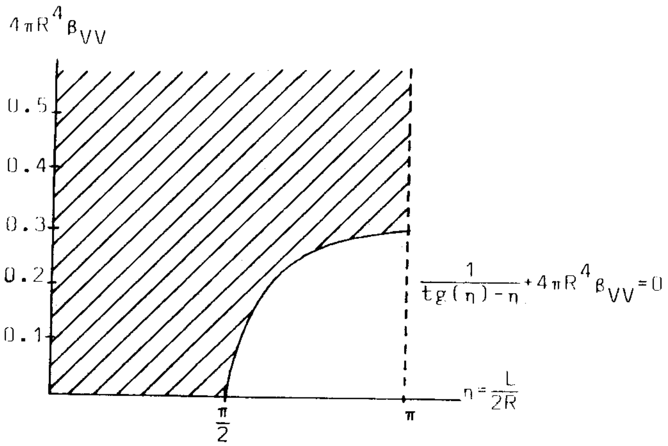


Figure 3.5.7:VII The shaded area gives the domain of stability for a meniscus region, which contains a cylindrical meniscus that is fixed at the boundaries. The constant β_{VV} is a measure of the restoring effects of the surrounding meniscus region in a displacement of the meniscus.

3.5.8 Stability of a spherical cap.

In this section we will study the stability for a meniscus, which has the form of a spherical cap. The surface is in standard spherical coordinates given by:

$$S: \quad \bar{r} = (R\sin(\bar{\theta})\cos(\varphi)\ ,\ R\sin(\bar{\theta})\sin(\varphi)\ ,\ R\cos(\bar{\theta})) \quad (3.5.8:A)$$

$$0 \leq \bar{\theta} \leq \bar{\theta}_0 \quad , \quad 0 \leq \varphi \leq 2\pi$$

We use a bar over θ to denote the azimuthal angle in order to distinguish it from the contact angle θ. The radius of the spherical surface is R. The angle $\bar{\theta}_0$ satisfies $0 < \bar{\theta}_0 < \pi$. The boundary Γ to S is given by 3.5.8:A with $\bar{\theta} = \bar{\theta}_0$.

The pore wall is rotationally symmetric around the z-axis and fits to the boundary Γ of S.

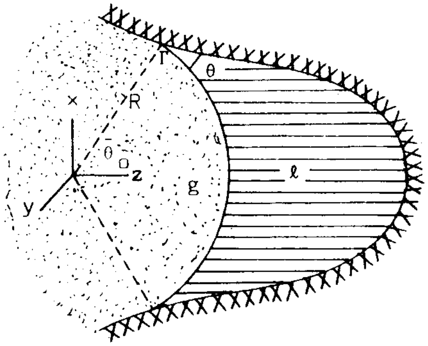
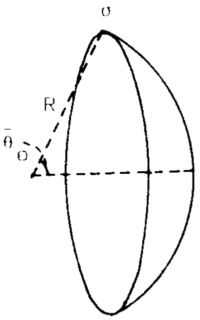


Figure 3.5.8:I The figure shows a spherical meniscus in a rotationally symmetric pore. The meniscus has the form of a spherical cap.

The contact angle is θ . The curvature of the pore wall at Γ in the direction perpendicular to Γ is κ_s . The curvature κ_m of S at Γ in the direction perpendicular to Γ is of course $\frac{1}{R}$. Then the boundary function σ is according to formula 3.5.1:B:

$$\sigma = \frac{\frac{1}{R}\cos(\theta)-\kappa_s}{\sin(\theta)} \quad . \tag{3.5.8:B}$$

Here σ is constant along Γ and may assume any value including $+\infty$.



$0 < \bar{\theta}_0 < \pi$

$-\infty < \sigma \leq +\infty$

$R > 0$

Figure 3.5.8:II The figure shows schematically the stability problem studied in section 3.5.8. The function σ is constant on the boundary circle.

For a surface of spherical form we have from formulas A1:D', E', and F' appendix 1:

$$J[\psi] = \iint_S \{\frac{1}{R^2}(\frac{\partial\psi}{\partial\bar{\theta}})^2 + \frac{1}{R^2\sin^2(\bar{\theta})}(\frac{\partial\psi}{\partial\varphi})^2 - \frac{2}{R^2}\psi\}\, dS + \oint_\Gamma \sigma\,\psi^2\, ds \tag{3.5.8:C}$$

$$L(\psi) = -\{\frac{1}{R^2\sin(\bar{\theta})}\frac{\partial}{\partial\bar{\theta}}(\sin(\bar{\theta})\frac{\partial\psi}{\partial\bar{\theta}}) + \frac{1}{R^2\sin^2(\bar{\theta})}\frac{\partial^2\psi}{\partial\varphi^2} + \frac{2}{R^2}\psi\} \quad . \tag{3.5.8:D}$$

For the boundary $\bar{\theta} = \bar{\theta}_0$ we have:

$$L_\Gamma(\psi) = \sigma\,\psi + \frac{1}{R}\cdot\frac{\partial\psi}{\partial\bar{\theta}} \quad . \tag{3.5.8:E}$$

We will first study the conditions for strong stability. We will again start with a study of the eigenvalue problem 3.5.5.H:

$$L(\psi) = \lambda\psi \qquad\qquad L_\Gamma(\psi) = 0 \tag{3.5.8:F}$$

or with formulas 3.5.8:D and E:

$$\frac{1}{\sin(\bar{\theta})}\cdot\frac{\partial}{\partial\bar{\theta}}(\sin(\bar{\theta})\frac{\partial\psi}{\partial\bar{\theta}}) + \frac{1}{\sin^2(\bar{\theta})}\cdot\frac{\partial^2\psi}{\partial\varphi^2} + (2 + \lambda R^2)\psi = 0 \tag{3.5.8:G}$$

$$R\,\sigma\psi + \frac{\partial\psi}{\partial\bar{\theta}} = 0 \qquad\qquad \bar{\theta} = \bar{\theta}_0 \quad . \tag{3.5.8:H}$$

The solutions to 3.5.8:G involve the associated Legendre functions. Put

$$\psi(\bar{\theta},\varphi) = f_m(\cos(\bar{\theta}))\cdot\cos(m\varphi + \varphi_m) \qquad m=0,1,\ldots \tag{3.5.8:I}$$

Then $f_m(t)$ must satisfy Legendre's differential equation:

$$(1-t^2)\,\frac{d^2f_m}{dt^2} - 2t\,\frac{df_m}{dt} + \{\nu(\nu+1) - \frac{m^2}{1-t^2}\}\,f_m = 0 \qquad (3.5.8:J)$$

$$\cos(\bar{\theta}_0) \leq t \leq 1$$

Here we have put $\nu(\nu+1) = 2 + \lambda R^2$.

The solutions to 3.5.8:J are the associated Legendre functions $P_\nu^{-m}(t)$ and $Q_\nu^{-m}(t)$. See reference 18). Only $P_\nu^{-m}(t)$ is regular in $t = +1$. We have then the following solutions to 3.5.8:G.

$$P_\nu^{-m}(\cos(\bar{\theta}))\cdot\cos(m\varphi + \varphi_m) \qquad m=0,1,\ldots \qquad (3.5.8:K)$$

where φ_m is a constant.

The functions $P_\nu^{-m}(t)$ may according to 18) be expressed in terms of the hypergeometric function $F(a,b;c;x)$:

$$P_\nu^{-m}(t) = \frac{1}{m!}\,\left(\frac{1-t}{1+t}\right)^{\frac{m}{2}} F(-\nu,\nu+1;1+m;\frac{1-t}{2}) \quad . \qquad (3.5.8:L)$$

The power series expansion of F is given in the following sections in formula 3.5.9:H. When $\lambda = 0$ or $\nu = 1$ only the first two terms in the power series 3.5.9:H of the hypergeometric function are non-zero. Then we get for $\lambda = 0$ the following solutions to 3.5.8:G:

$$m=0: \quad \cos(\bar{\theta}) \qquad (3.5.8:M)$$

$$m=1: \quad \sin(\bar{\theta})\,\cos(\varphi + \varphi_1) \qquad (3.5.8:N)$$

$$m\geq 2: \quad \left(\frac{1-\cos(\bar{\theta})}{1+\cos(\bar{\theta})}\right)^{\frac{m}{2}}(\cos(\bar{\theta}) + m)\,\cos(m\varphi + \varphi_m) \ . \qquad (3.5.8:O)$$

The function 3.5.8:M is suitable for criterion 3.5.3:P on strong stability. We have for $\phi = \cos(\bar{\theta})$:

$$L(\phi) = 0$$

$$L_\Gamma(\phi) = \frac{\cos(\bar{\theta}_0)}{R}\{R\sigma - \mathrm{tg}(\bar{\theta}_0)\} \qquad (3.5.8:P)$$

The function ϕ is positive on S, when $\bar{\theta}_0 < \frac{\pi}{2}$. The quantity $L_\Gamma(\phi)$ is then positive, when $R\sigma > \mathrm{tg}(\bar{\theta}_0)$. Thus ϕ fulfils criterion 3.5.3:P, when $R\sigma > \mathrm{tg}(\bar{\theta}_0)$, $0 < \bar{\theta}_0 < \frac{\pi}{2}$, and we have strong stability. The quantity $L_\Gamma(\phi)$ is zero on the curve $R\sigma = \mathrm{tg}(\bar{\theta}_0)$, $0 < \bar{\theta}_0 < \frac{\pi}{2}$. Then $J[\phi]$ is zero, and we do not have strong stability.

In conclusion we have strong stability precisely when

$$R\sigma > \mathrm{tg}(\bar{\theta}_0) \quad , \; 0 < \bar{\theta}_0 < \frac{\pi}{2} \quad . \qquad (3.5.8:Q)$$

This region of strong stability is shown in figure 3.5.8:III.

We now turn to the problem of finding the region of weak stability. We need meniscus solutions. The function $\phi = \cos(\bar{\theta})$ from 3.5.8:M and the constant $\phi = 1$ satisfy $L(\phi) = C$, where C is a constant.

From these two functions we get the following fundamental meniscus solutions:

$$\phi_V = \frac{1}{\pi R^2}\cdot\frac{\cos(\bar{\theta})-\cos(\bar{\theta}_0)}{(1-\cos(\bar{\theta}_0))^2} \qquad (3.5.8:R)$$

$$\phi_A = \frac{1}{2\pi R}\cdot\frac{1+\cos(\bar{\theta}_0)-2\cos(\bar{\theta})}{\sin(\bar{\theta}_0)(1-\cos(\bar{\theta}_0))} \quad . \qquad (3.5.8:S)$$

The solutions are always defined, since $0 < \bar{\theta}_0 < \pi$.

The fundamental meniscus solutions satisfy 3.5.6:M and N with the constants:

$$D_{VV} = \frac{1}{\pi R^4} \cdot \frac{2\cos(\bar{\theta}_0)}{(1-\cos(\bar{\theta}_0))^2} \qquad D_{VA} = \frac{-1}{\pi R^3} \cdot \frac{\sin(\bar{\theta}_0)}{(1-\cos(\bar{\theta}_0))^2}$$

$$D_{AA} = \frac{1}{2\pi R^2 \sin(\bar{\theta}_0)} \{\sigma R + 2\cot(\frac{\bar{\theta}_0}{2})\} \qquad (3.5.8:T)$$

Outside the region 3.5.8:Q of strong stability there is a boundary line between weak stability and strong instability. From the theorem of formula 3.5.6:K we have that on this boundary there is a non-zero solution to the problem:

$$L(\psi) = 0 \qquad S_\psi = 0$$
$$L_\Gamma(\psi) = 0 \qquad \Gamma_\psi = 0 \qquad (3.5.8:U)$$

The general solution to $L(\psi) = 0$ is a linear combination of the functions 3.5.8:M-O. The conditions $S_\psi = 0$ and $\Gamma_\psi = 0$ are fulfilled when the solution $\cos(\bar{\theta})$ is omitted. It remains to fulfil the boundary condition $L_\Gamma(\psi) = 0$.

The second function 3.5.8:N gives the condition:

$$L_\Gamma(\psi) = \frac{\sin(\bar{\theta}_0)\cdot\cos(\varphi+\varphi_1)}{R}\{R\sigma + \cos(\bar{\theta}_0)\} = 0 \quad . \qquad (3.5.8:V)$$

We get the boundary line $R\sigma + \cos(\bar{\theta}_0) = 0$, $0 < \bar{\theta}_0 < \pi$. On the boundary line we have $J[\psi] = 0$, $S_\psi = 0$, and $\Gamma_\psi = 0$. There is not weak stability on this line. Then there is strong instability when $R\sigma + \cot(\bar{\theta}_0) < 0$.

The other functions from formula 3.5.8:O have more nodal lines and will give weaker conditions for weak stability. This may be shown in the same way as in the previous section, when we studied the weak stability of a cylinder.

In conclusion we have weak stability outside the domain 3.5.8:Q of strong stability when:

$$R\sigma > -\cot(\bar{\theta}_0) \quad . \tag{3.5.8:W}$$

The obtained results on the stability of a spherical cap are shown graphically in the figure below.

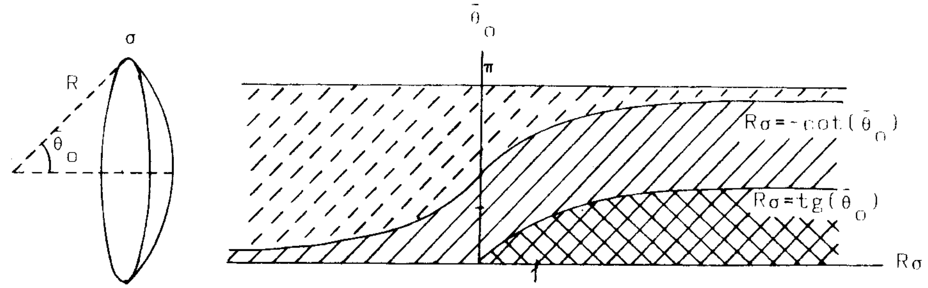


Figure 3.5.8:III The figure shows the regions of strong stability XXXX , weak stability //// , and strong instability /'/'/' for a meniscus that has the form of a spherical cap.

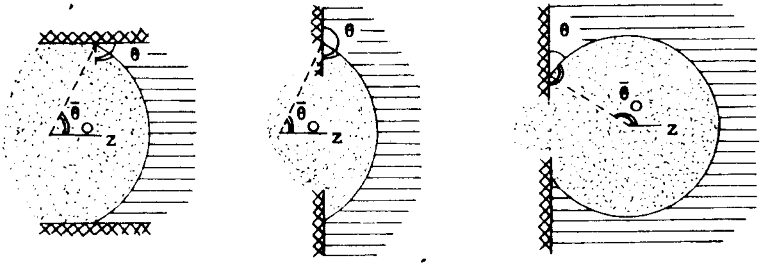
The boundary curves between the different stability regions have a simple interpretation, when κ_s is zero, that is when the pore wall is not curved in the z-direction. Then we have from 3.5.8:B:

$$R\sigma - \mathrm{tg}(\bar{\theta}_0) = \frac{\cos(\theta+\bar{\theta}_0)}{\sin(\theta)\cos(\bar{\theta}_0)} \qquad R\sigma + \cot(\bar{\theta}_0) = \frac{\sin(\theta+\bar{\theta}_0)}{\sin(\theta)\sin(\bar{\theta}_0)} \tag{3.5.8:A'}$$

The region of strong stability is then given by the condition $\theta + \bar{\theta}_o < \frac{\pi}{2}$. The region of weak stability is given by

$$\frac{\pi}{2} < \theta + \bar{\theta}_o < \pi \quad . \qquad (3.5.8:B')$$

Figure 3.5.8:IV A below illustrates the transitional situation between strong and weak stability. The other two figures B and C illustrate the transitional case between weak stability and strong instability for $\bar{\theta}_o < \frac{\pi}{2}$ and $\bar{\theta}_o > \frac{\pi}{2}$ respectively.



A B C

Figure 3.5.8:IV Figure A shows the transitional case between strong and weak stability, when the curvature κ_s of the pore wall in the direction perpendicular to the boundary is zero. Figures B and C show the transitional case between weak stability and strong instability for $\bar{\theta}_o < \frac{\pi}{2}$ respectively $\bar{\theta}_o > \frac{\pi}{2}$ for a pore wall with $\kappa_s = 0$.

The limit between strong and weak stability is given by the case, when the pore wall is parallel to the z-axis. The limit between weak stability and strong instability occurs when the pore wall is perpendicular to the z-axis.

There is also an elucidative interpretation of the limit between weak stability and strong instability in the general case

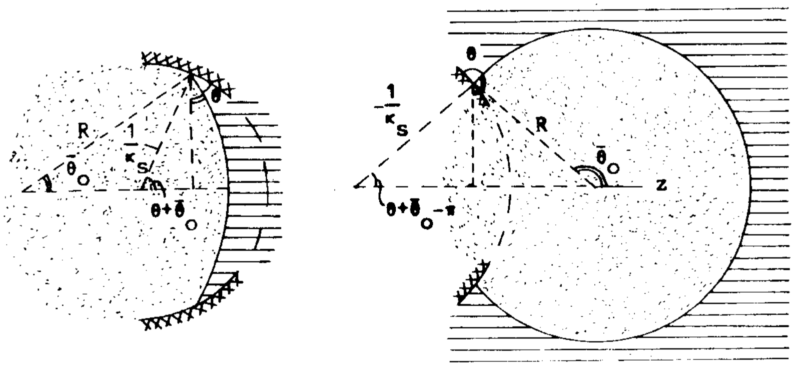
$(\kappa_s \neq 0)$. From 3.5.8:B we have on the boundary line:

$$R\sigma + \cot(\bar{\theta}_0) = \frac{\sin(\theta+\bar{\theta}_0)}{\sin(\theta)\sin(\bar{\theta}_0)} - \frac{R\,\kappa_s}{\sin(\theta)} = 0$$

(3.5.8:C')

$$\frac{1}{\kappa_s}\sin(\theta + \bar{\theta}_0) = R\sin(\bar{\theta}_0) \quad .$$

Here $\frac{1}{\kappa_s}$ is the radius of curvature of the pore wall in the z-direction. Equation 3.5.8:C' implies that the corresponding centre of curvature lies on the z-axis. See figure 3.5.8:V below. Then the pore wall along the boundary Γ is part of a sphere with its centre on the z-axis and with the radius $\frac{1}{|\kappa_s|}$. The situation is illustrated in figure 3.5.8:V for positive and negative κ_s .



A

B

Figure 3.5.8:V The figures show the transitional case between weak stability and strong instability. The pore wall follows in the vicinity of the boundary circle Γ a sphere with the centre on the z-axis. The curvature κ_s is positive in fig. A and negative in fig. B . The meniscus may slide rigidly on the spherical pore wall.

The meniscus may slide rigidly on the spherical pore wall. In such a displacement there is not any changes in areas or volumes, and J is zero.

The conditions for stability on J_t are from 3.5.6:I and 3.5.8:T (for the region of weak stability):

$$\frac{2\cos(\bar\theta_o)}{(1-\cos(\bar\theta_o))^2} + \pi R^4 \beta_{VV} > 0 \qquad (3.5.8{:}D')$$

$$\left(\frac{2\cos(\bar\theta_o)}{(1-\cos(\bar\theta_o))^2} + \pi R^4 \beta_{VV}\right)\left(\frac{\sigma R + 2\cdot\cot(\frac{\bar\theta_o}{2})}{2\sin(\bar\theta_o)} + \pi R^2 \beta_{AA}\right) >$$

$$> \left(-\frac{\sin(\bar\theta_o)}{(1-\cos(\bar\theta_o))^2} + \pi R^3 \beta_{VA}\right)^2 \qquad (3.5.8{:}E')$$

The first condition 3.5.8:D' is illustrated in figure 3.5.8:VI

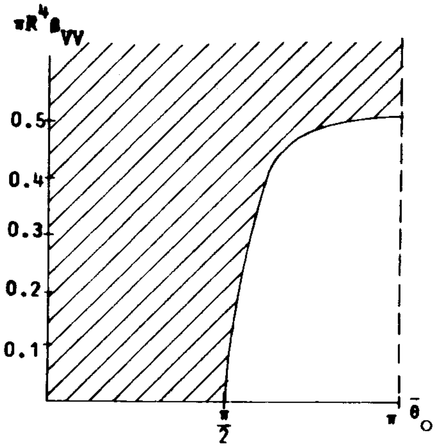


Figure 3.5.8:VI
The shaded area is the domain of stability for a meniscus region, which contains a meniscus, when the meniscus has the form of a spherical cap. The meniscus is fixed at the boundary circle. The constant β_{VV} is a measure of the restoring effects of the surrounding meniscus region in a displacement of the meniscus.

The second condition 3.5.8:E' becomes identical with the first condition 3.5.8:D' when $\sigma = +\infty$. This is the case when the meniscus is kept fixed at the boundary. In this case there is strong stability for $0 < \bar{\theta}_0 < \frac{\pi}{2}$ and weak stability for $\frac{\pi}{2} < \bar{\theta}_0 < \pi$. There is never strong instability. The shaded region in figure 3.5.8:VI above then gives the region of stability, when $\sigma = +\infty$.

The special case when the meniscus has the form of a plane circular disc with the radius R_0, is also of interest. We get this case in the limit:

$$R \to +\infty \qquad \bar{\theta}_0 = \arcsin(\frac{R_0}{R}) \to 0 \quad . \qquad (3.5.8:F')$$

From 3.5.8:B we get $\sigma = -\kappa_s/\sin(\theta)$. When σ is positive, that is when κ_s is negative, we get according to figure 3.5.8:III strong stability. When κ_s is positive, we must study the limit of $R\sigma + \cot(\bar{\theta}_0)$. We get weak stability precisely when:

$$-1 < R_0\sigma < 0 \quad . \qquad (3.5.8:G')$$

From 3.5.8:T we get the values of D_{VV}, D_{VA}, D_{AA} in the limit 3.5.8:F'. From 3.5.6:Q we then have stability (in the region 3.5.8:G' of weak stability) when

$$(\frac{8}{\pi R_0^4} + \beta_{VV})(\frac{1}{2\pi R_0^2}(\sigma R_0 + 4) + \beta_{AA}) > (-\frac{4}{\pi R_0^3} + \beta_{VA})^2 \qquad (3.5.8:H')$$

3.5.9 Stability for a symmetric spherical zone.

In this section we will study the stability for a meniscus, which has the form of a symmetric spherical zone. The surface is in standard spherical coordinates given by:

$$S: \quad \bar{r} = (R \sin(\theta) \cos(\varphi) \ , \ R \sin(\bar{\theta}) \sin(\varphi) \ , \ R \cos(\bar{\theta})) \quad (3.5.9{:}A)$$

$$\frac{\pi}{2} - \bar{\theta}_1 \leq \bar{\theta} \leq \frac{\pi}{2} + \bar{\theta}_1 \qquad 0 \leq \varphi \leq 2\pi$$

Here $\bar{\theta}$ is the azimuthal angle, and R is the radius. The angle $\bar{\theta}_1$ lies in the interval $0 < \bar{\theta}_1 < \frac{\pi}{2}$. The boundary Γ consists of two circles Γ_+ and Γ_- given by 3.5.9:A for $\bar{\theta} = \frac{\pi}{2} - \bar{\theta}_1$ respectively $\bar{\theta} = \frac{\pi}{2} + \bar{\theta}_1$.

The pore wall is rotationally symmetric around the z-axis and fits to the boundaries Γ_- and Γ_+ :

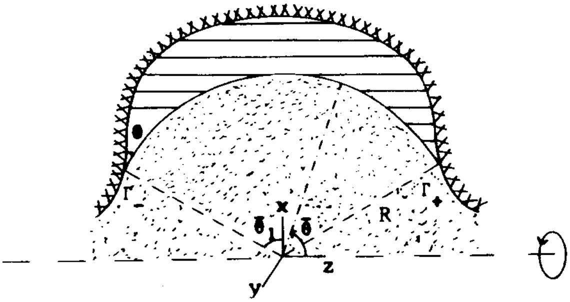


Figure 3.5.9:I The figure shows a meniscus which has the form of a symmetric spherical zone, in a rotationally symmetric pore. The liquid phase lies in an annulus between the pore wall and the meniscus.

The boundary function σ is given by 3.5.8:B. We assume that σ has the same value on Γ_- and Γ_+. The constant σ may assume any value including $+\infty$.

Schematically we have the following stability problem:

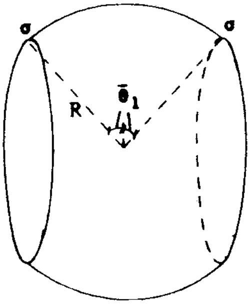


Figure 3.5.9:II The figure shows schematically the stability problem studied in present section 3.5.9.

The quantities $J[\psi]$ and $L(\psi)$ are given by 3.5.8:C and 3.5.8:D. For the boundaries Γ_+ and Γ_- we have:

$$L_{\Gamma_+}(\psi) = \sigma\psi - \frac{1}{R}\frac{\partial\psi}{\partial\bar{\theta}} \qquad \bar{\theta} = \frac{\pi}{2} - \bar{\theta}_1$$

$$L_{\Gamma_-}(\psi) = \sigma\psi + \frac{1}{R}\frac{\partial\psi}{\partial\bar{\theta}} \qquad \bar{\theta} = \frac{\pi}{2} + \bar{\theta}_1 \qquad (3.5.9:B)$$

We will first study the conditions for strong stability. From 3.5.5:H we shall study the eigenvalue problem:

$$L(\psi) = \lambda\psi \qquad L_\Gamma(\psi) = 0 \qquad (3.5.9:C)$$

or from 3.5.8:G:

$$\frac{1}{\sin(\bar{\theta})}\frac{\partial}{\partial\bar{\theta}}\left(\sin(\bar{\theta})\frac{\partial\psi}{\partial\bar{\theta}}\right) + \frac{1}{\sin^2(\bar{\theta})}\cdot\frac{\partial^2\psi}{\partial\varphi^2} + (2 + \lambda R^2)\psi = 0 \qquad (3.5.9:D)$$

$$\sigma R\cdot\psi - \frac{\partial\psi}{\partial\bar{\theta}} = 0 \qquad \bar{\theta} = \frac{\pi}{2} - \bar{\theta}_1$$

$$\sigma R\cdot\psi + \frac{\partial\psi}{\partial\bar{\theta}} = 0 \qquad \bar{\theta} = \frac{\pi}{2} + \bar{\theta}_1 \qquad (3.5.9:E)$$

The solutions to 3.5.9:D have been studied in the previous section. With ψ given by 3.5.8:I we arrived at Legendre's differential equation 3.5.8:J. In our new case $t = \cos(\bar{\theta})$ shall vary between $-\sin(\bar{\theta}_1)$ and $\sin(\bar{\theta}_1)$. We get both solutions $P_\nu^{-m}(t)$ and $Q_\nu^{-m}(t)$, since the critical point $t=-1$ is excluded. Because of the symmetry of the problem we will instead use even and odd solutions to Legendre's differentical equation. From reference 18) we may get an even solution to 3.5.8:J, which we denote p_ν^m:

$$p_\nu^m(t) = (1-t^2)^{\frac{m}{2}} \; F(\frac{m+\nu+1}{2} , \frac{m-\nu}{2} ; \frac{1}{2} ; t^2) \qquad (3.5.9:F)$$

and an odd solution denoted q_ν^m:

$$q_\nu^m(t) = t(1-t^2)^{\frac{m}{2}} \; F(\frac{m+\nu+2}{2} , \frac{m-\nu+1}{2} ; \frac{3}{2} ; t^2) . \qquad (3.5.9:G)$$

Here $F(a,b;c;x)$ is the hypergeometric function defined by the infinite power series:

$$F(a,b;c;x) = 1 + \frac{a \cdot b}{c} x + \frac{a(a+1) \cdot b(b+1)}{c(c+1)} \frac{x^2}{2!} + \dots \qquad (3.5.9:H)$$

We now have the following solutions to 3.5.9:D (with $\nu(\nu+1) = 2 + R^2\lambda$):

$$p_\nu^m(\cos(\bar{\theta})) \cdot \cos(m\varphi+\varphi_m) \qquad q_\nu^m(\cos(\bar{\theta})) \cdot \cos(m\varphi+\varphi_m') \qquad (3.5.9:I)$$

$$m=0,1,2,\dots$$

For $\lambda=0$ or $\nu=1$ we have immediately from 3.5.9:F-H:

$$q_1^0(t) = t \qquad p_1^1(t) = \sqrt{1-t^2} \quad . \qquad (3.5.9:J)$$

The function $p_1^0(t)$ is a bit more complicated. From formulas in reference 18) we get:

$$p_1^0(t) = - Q_1^0(t) = 1 - \frac{t}{2} \ln(\frac{1+t}{1-t}) \quad . \qquad (3.5.9:K)$$

Then we have the following solutions to 3.5.9:D for $\lambda=0$:

$$m=0: \quad 1 - \frac{\cos(\bar{\theta})}{2} \ln \frac{1+\cos(\bar{\theta})}{1-\cos(\bar{\theta})} \qquad \cos(\bar{\theta}) \qquad (3.5.9:L)$$

$$m=1: \quad \sin(\bar{\theta})\cdot\cos(\varphi+\varphi_1) \qquad q_1^1(\cos(\bar{\theta}))\cdot\cos(\varphi+\varphi_1') \qquad (3.5.9:M)$$

$$m\geq 2: \quad p_1^m(\cos(\bar{\theta}))\cdot\cos(m\varphi+\varphi_m) \qquad q_1^m(\cos(\bar{\theta}))\cdot\cos(m\varphi+\varphi_m') \qquad (3.5.9:N$$

The solutions $\cos(\bar{\theta})$ and $\sin(\bar{\theta})\ \cos(\varphi+\varphi_1)$ are regular in $\bar{\theta} = \frac{\pi}{2}$. They appear in the previous section. The first solution on each line above is even in $\bar{\theta} - \frac{\pi}{2}$ and the second is odd.

The even solution of 3.5.9:L is suitable for criterion 3.5.3:P on strong stability. Put

$$\phi = 1 - \frac{\cos(\bar{\theta})}{2} \ln \frac{1+\cos(\bar{\theta})}{1-\cos(\bar{\theta})} \quad . \qquad (3.5.9:O)$$

Then we have

$$\begin{aligned} &L(\phi) = 0 \\ &L_{\Gamma_\pm}(\phi) = \phi\Big|_\Gamma \frac{1}{R}\{\sigma R - h(\bar{\theta}_1)\} \quad , \end{aligned} \qquad (3.5.9:P)$$

where

$$h(\bar{\theta}_1) = \frac{\dfrac{\cos(\bar{\theta}_1)}{2} \ln \dfrac{1+\sin(\bar{\theta}_1)}{1-\sin(\bar{\theta}_1)} + \operatorname{tg}(\bar{\theta}_1)}{1 - \dfrac{\sin(\bar{\theta}_1)}{2} \ln \dfrac{1+\sin(\bar{\theta}_1)}{1-\sin(\bar{\theta}_1)}} \qquad (3.5.9:Q)$$

Figure 3.5.9:III below shows the function $\phi(\bar{\theta})$ from formula 3.5.9:O.

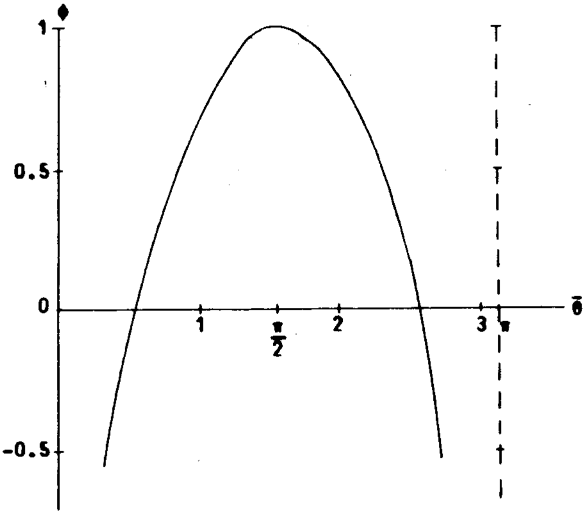


Figure 3.5.9:III The graph shows the test function ϕ for strong stability. The function ϕ is given by formula 3.5.9:O.

The function $\phi(\bar{\theta})$ is zero for $\bar{\theta} = \frac{\pi}{2} \pm 0.9855$. Put

$$\bar{\theta}_g = 0.9855 \ldots \qquad (56.5^o) \quad . \qquad (3.5.9:R)$$

The function ϕ satisfies condition 3.5.2:L when $\bar{\theta}_1 = \bar{\theta}_g$. Thus for $\bar{\theta}_1 > \bar{\theta}_g$ there is not strong stability independently of the value of σ . Figure 3.5.9:IV below shows $h(\bar{\theta}_1)$ which is defined by formula 3.5.9:Q.

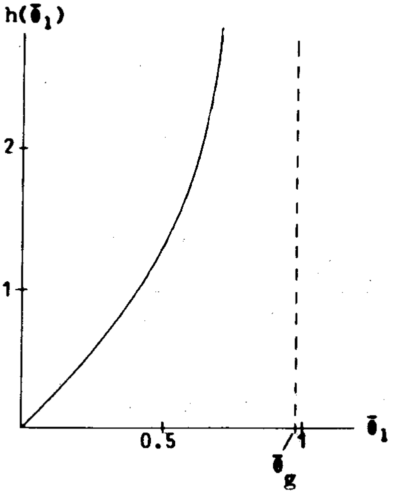


Figure 3.5.9:IV The figure shows the function $h(\bar{\theta}_1)$ defined by formula 3.5.9:Q for $0<\bar{\theta}_1<\bar{\theta}_g = 0.9855 \ldots$. This function gives the limit between strong and weak stability.

The function ϕ is positive when $\bar{\theta}_1 < \bar{\theta}_g$. Thus ϕ satisfies criterion 3.5.3:P, when $R\sigma > h(\bar{\theta}_1)$, $0 < \bar{\theta}_1 < \bar{\theta}_g$, and we have strong stability. On the curve $R\sigma = h(\bar{\theta}_1)$ $J[\phi]$ is zero due to formula 3.5.9:P. The curve gives the boundary between strong stability and weak stability.

In conclusion we have strong stability precisely when:

$$R\sigma > h(\bar{\theta}_1) \qquad 0<\bar{\theta}_1<\bar{\theta}_g(=0.9855\ldots) , \qquad (3.5.9:S)$$

where $h(\bar{\theta}_1)$ is given by 3.5.9:Q. The region of strong stability is shown in figure 3.5.9:V.

We now turn to the problem of finding the region of weak stability. We need meniscus solutions. From the function 3.5.9:O and the constant $\phi=1$ we get the following fundamental meniscus solutions:

$$\phi_V = \frac{1}{4\pi R^2} \frac{X - \sin(\bar\theta_1)\ Y}{Z} \tag{3.5.9:T}$$

$$\phi_A = \frac{1}{4\pi R\ \cos(\bar\theta_1)} \frac{\sin(\bar\theta_1) - \frac{\cos^2(\bar\theta_1)}{2}\ Y - \sin(\bar\theta_1)X}{Z} \tag{3.5.9:U}$$

$$X = \cos(\bar\theta)\ \ln \frac{1+\cos(\bar\theta)}{1-\cos(\bar\theta)} \qquad Y = \ln \frac{1+\sin(\bar\theta_1)}{1-\sin(\bar\theta_1)}$$

$$Z = \sin(\bar\theta_1) - \frac{1+\sin^2(\bar\theta_1)}{2}\ Y \quad .$$

The denominators are never zero for $0<\bar\theta_1<\frac{\pi}{2}$. The fundamental meniscus solutions satisfy 3.5.6:J and K with the constants:

$$D_{VV} = \frac{-1}{\pi R^4} \frac{1-\frac{\sin(\bar\theta_1)}{2}\ Y}{Z}$$

$$D_{VA} = \frac{1}{4\pi R^3} \frac{2\ \mathrm{tg}(\bar\theta_1) + \cos(\bar\theta_1)\ Y}{Z} \tag{3.5.9:V}$$

$$D_{AA} = \frac{1}{4\pi R^3\cos(\bar\theta_1)} \{ R\,\sigma - \frac{\sin(\bar\theta_1)[\cos(\bar\theta_1)Y + 2\mathrm{tg}(\bar\theta_1)]}{Z} \}$$

Outside the region 3.5.9:S of strong stability there is a boundary line between weak stability and strong instability. From the theorem of formula 3.5.6:K we have that on this boundary there is a non-zero solution to the problem:

$$\begin{aligned} L(\psi) &= 0 \qquad & S_\psi &= 0 \\ L_\Gamma(\psi) &= 0 \qquad & \Gamma_\psi &= 0 \end{aligned} \tag{3.5.9:W}$$

The general solution to $L(\psi) = 0$ is a linear combination of the functions 3.5.9:L-N. The conditions $S_\psi = 0$ and $\Gamma_\psi = 0$ are fulfilled, when the first even function of 3.5.9:L is omitted. It remains to fulfil the boundary condition $L_\Gamma(\psi) = 0$.

Each one of the odd and even functions satisfies the boundary condition for certain values on $\bar{\theta}_1$ and $R\sigma$. For $\psi = \cos(\bar{\theta})$ we get:

$$L_\Gamma(\psi) = \frac{\pm\sin(\bar{\theta}_1)}{R}\,(R\sigma + \cot(\bar{\theta}_1)) = 0 \quad . \qquad (3.5.9{:}A')$$

For $\psi = \sin(\bar{\theta})\cos(\varphi+\varphi_1)$ we get:

$$L_\Gamma(\psi) = \frac{\cos(\bar{\theta}_1)\ \cos(\varphi+\varphi_1)}{R}\{\sigma R - \mathrm{tg}(\bar{\theta}_1)\} = 0 \quad . \qquad (3.5.9{:}B')$$

Equation 3.5.9:B' gives a stronger condition than 3.5.9:A'. On the boundary line $\sigma R = \mathrm{tg}(\bar{\theta}_1)$ we have $J[\psi] = 0$, $S_\psi = 0$ and $\Gamma_\psi = 0$. There is not weak stability. Then there is strong instability, when $R\sigma < \mathrm{tg}(\bar{\theta}_1)$.

The remaining functions of 3.5.9:M and N have more nodal lines and will give weaker conditions for weak stability. This may be shown in the same way as in section 3.5.7, when we studied the weak stability of a cylinder.

In conclusion we have weak stability outside the region 3.5.9:S of strong stability precisely when:

$$R\sigma > \mathrm{tg}(\bar{\theta}_1) \quad . \qquad (3.5.9{:}C')$$

The obtained results on the stability of a spherical symmetric zone are shown graphically in figure 3.5.9:V below.

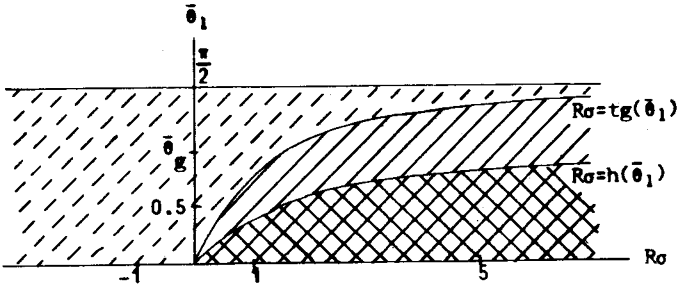


Figure 3.5.9:V Regions for strong stability XXX , weak stability /// , and strong instability /,/,/ for a symmetric spherical zone.

The boundary curve $R\sigma = tg(\bar{\theta}_1)$ has a simple geometrical interpretation. The equation for the boundary curve may with formula 3.5.8:B be written:

$$\frac{1}{\kappa_s} \cos(\theta + \bar{\theta}_1) = R \cos(\bar{\theta}_1) \quad . \qquad (3.5.9{:}D')$$

The quantity $\frac{1}{\kappa_s}$ is the radius of curvature of the pore wall in the z-direction. Equation 3.5.9:D' implies that the corresponding center of curvature lies on the z-axis. See figure 3.5.9:VI below. Then the pore wall along the right boundary Γ_+ is part of a sphere with its centre on the z-axis and with the radius $\frac{1}{\kappa_s}$. The pore wall along the left boundary Γ_- is part of a symmetrically placed second sphere.

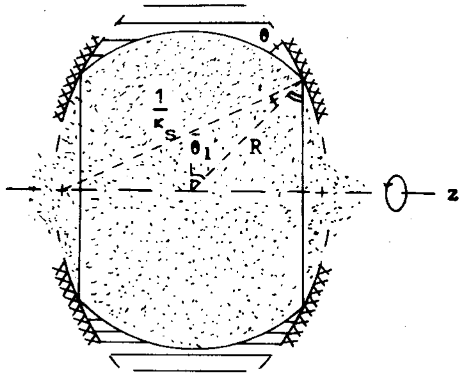


Figure 3.5.9:VI The figure shows the transitional case between weak stability and strong instability. The pore wall has in this case the form of spheres in the vicinity of the boundary circles Γ_+ and Γ_-. The meniscus may slide rigidly on these spheres.

The meniscus may slide rigidly on the two spheres of the pore wall. In such a displacement there are no changes in areas or volumes, and J is zero.

The conditions for stability for J_t are from 3.5.6:Q:

$$D_{VV} + \beta_{VV} > 0 \quad , \qquad (3.5.9:E')$$

$$(D_{VV} + \beta_{VV})(D_{AA} + \beta_{AA}) > (D_{VA} + \beta_{VA})^2 \quad , \qquad (3.5.9:F')$$

where D_{VV} , D_{VA} and D_{AA} are given by 3.5.9:V.

The first condition 3.5.9:E' is given in fig. 3.5.9:VII below. The second condition 3.5.9:F' becomes identical with the first condition 3.5.9:E' when $\sigma = +\infty$. The shaded region in figure 3.5.9.VII below will then give the region of stability.

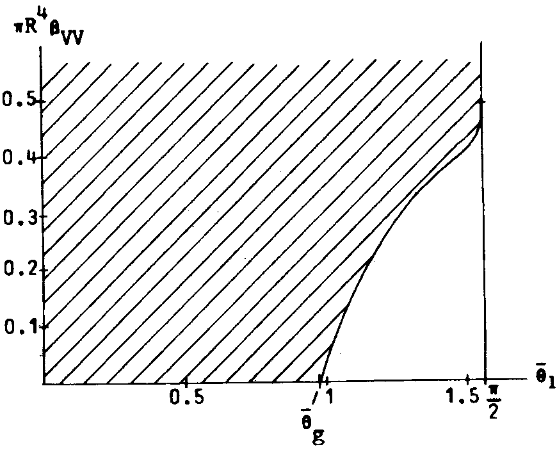


Figure 3.5.9:VII Region of stability when $\sigma = +\infty$. The constant β_{VV} is a measure of the restoring forces from the phases of the meniscus region in a displacement.

3.5.10 Stability of a rectangular cylindrical meniscus fixed at the boundaries.

In this section we will study the stability for a meniscus which has the form of a rectangular part of a cylindrical surface. The surface S is in standard cylindrical coordinates given by:

$$S: \quad \bar{r}(\varphi,z) = (R\cos(\varphi)\,,\, R\sin(\varphi), z) \qquad \begin{matrix} -\frac{L}{2} \le z \le \frac{L}{2} \\ \\ -\frac{\varphi_0}{2} \le \varphi \le \frac{\varphi_0}{2} \end{matrix} \quad . \qquad (3.5.10:A)$$

Here R is the radius of the cylinder. The length of the cylindrical rectangle is L, while its breadth is $R\,\varphi_0$.

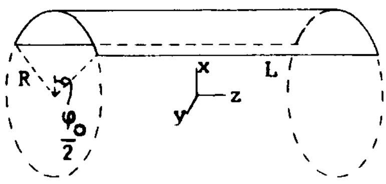
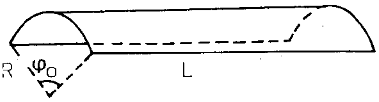


Figure 3.5.10:I The figure shows the rectangular cylindrical meniscus studied in section 3.5.10.

The boundary Γ consists of four parts: $z = \pm \frac{L}{2}$, $-\frac{\varphi_0}{2} < \varphi < \frac{\varphi_0}{2}$ and $\varphi = \pm \frac{\varphi_0}{2}$, $-\frac{L}{2} < z < \frac{L}{2}$.

We will only study the case, when the meniscus is kept fixed at the boundaries Γ, that is when $\sigma = +\infty$. Schematically we have the following stability problem:

$\sigma = +\infty$



$0 < \varphi_0 \leq 2\pi$

$R > 0$, $L > 0$

Figure 3.5.10:II The stability problem studied in section 3.5.10.

The expression $L(\psi)$ is from formula 3.5.7:E given by:

$$L(\psi) = -\left\{\frac{\partial^2\psi}{\partial z^2} + \frac{1}{R^2}\frac{\partial^2\psi}{\partial\varphi^2} + \frac{1}{R^2}\psi\right\} \quad . \tag{3.5.10:B}$$

The function ψ is zero at the boundary Γ:

$$\psi\big|_\Gamma = 0 \quad . \tag{3.5.10:C}$$

The line integral of $J[\psi]$ vanishes because of 3.5.10:C. Then from 3.5.7:D $J[\psi]$ is given by:

$$J[\psi] = \iint_S \left\{\left(\frac{\partial\psi}{\partial z}\right)^2 + \frac{1}{R^2}\frac{\partial^2\psi}{\partial\varphi^2} - \frac{1}{R^2}\psi^2\right\} dS \quad . \tag{3.5.10:D}$$

In order to get the conditions for strong stability we must study the eigenvalue problem 3.5.5:H:

$$L(\psi) = \lambda\psi \qquad \psi\big|_\Gamma = 0 \quad . \tag{3.5.10:E}$$

This is an elementary problem in mathematical physics. The eigenfunctions and corresponding eigenvalues are:

$$\psi_{m,n} = \sin\left(\frac{m\pi(z+\frac{L}{2})}{L}\right)\sin\left(\frac{n\pi(\varphi+\frac{\varphi_0}{2})}{\varphi_0}\right) \qquad \begin{array}{l} m=1,2,\ldots \\ n=1,2,\ldots \end{array} \tag{3.5.10:F}$$

$$\lambda_{m,n} = \frac{m^2\pi^2}{L^2} + \frac{n^2\pi^2}{R^2\varphi_0^2} - \frac{1}{R^2}$$

There is strong stability, when the smallest eigenvalue is positive. Thus we have strong stability precisely when:

$$\frac{\pi^2}{L^2} + \frac{\pi^2}{R^2\varphi_0^2} - \frac{1}{R^2} > 0 \quad , \qquad (3.5.10:G)$$

or, with the notation $\eta = \frac{L}{2R}$ from section 3.5.7:

$$\frac{1}{\eta^2} > \frac{4}{\pi^2}\left(1 - \frac{\pi^2}{\varphi_0^2}\right) \quad . \qquad (3.5.10:H)$$

When $0<\varphi_0<\pi$, there is strong stability for all η. The region of strong stability is shown in figure 3.5.10:III.

We now turn to the problem of finding the region of weak stability. First we note that the functions ψ_{mn} from 3.5.10:E satisfy $S_\psi = 0$ and $\Gamma_\psi = 0$, when m or n is even. We get the strongest condition for weak stability from λ_{21} :

$$\frac{4\pi^2}{L^2} + \frac{\pi^2}{R^2\varphi_0^2} - \frac{1}{R^2} > 0$$

or (3.5.10:I)

$$\frac{1}{\eta^2} > \frac{1}{\pi^2}\left(1 - \frac{\pi^2}{\varphi_0^2}\right)$$

From 3.5.1:H and I we get the following conditions for weak stability:

$$\frac{\pi}{2\cdot\sqrt{1-\frac{\pi^2}{\varphi_0^2}}} < \eta < \frac{\pi}{\sqrt{1-\frac{\pi^2}{\varphi_0^2}}} \qquad \pi<\varphi_0\leq 2\pi \qquad (3.5.10:K)$$

We now need the fundamental meniscus solution ϕ_V which shall satisfy 3.5.6:R. In this case we cannot get meniscus solutions as easily as in the previous cases. We have to use the method outlined at the end of section 3.5.6. We need the normalized eigenfunctions in 3.5.10:E. These are:

$$\psi'_{mn} = \sqrt{\frac{2}{L}}\cdot\sqrt{\frac{2}{R\varphi_o}}\cdot\psi_{mn} \qquad \begin{matrix} m=1,2,\dots \\ n=1,2,\dots \end{matrix} \qquad (3.5.10:L)$$

The functions ψ'_{mn} are a complete orthonormal set of functions on S .

The fundamental meniscus function ϕ_V is from formula 3.5.6:I':

$$\phi_V = \frac{1}{\sum\limits_{m=1}^{\infty}\sum\limits_{n=1}^{\infty}\frac{1}{\lambda_{mn}}(S_{\psi'_{mn}})^2}\sum_{m=1}^{\infty}\sum_{n=1}^{\infty}\frac{1}{\lambda_{mn}}S_{\psi'_{mn}}\,\psi'_{mn}\,. \qquad (3.5.10:M)$$

The eigenvalues λ_{mn} are all different from zero in the region 3.5.10:K. We will show below that the double sum in the denominator is different from zero in the region 3.5.10:K. Then from the theorem of formula 3.5.6:S we have that 3.5.10:K must give precisely the region of weak stability.

Figure 3.5.10:III below summarizes the obtained results.

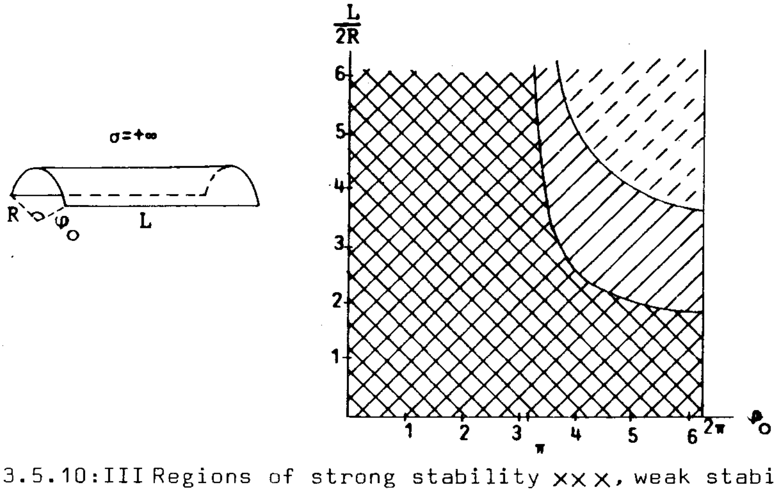


Fig. 3.5.10:III Regions of strong stability xxx, weak stability // and strong instability ⁄,⁄ for a rectangular cylindrical meniscus held fixed at the boundary. The curves between the different regions are given by 3.5.10:K

Formula 3.5.10:M gives the fundamental meniscus solution ϕ_V , which satisfies 3.5.6:R. The constant D_{VV} is from 3.5.6:J', 3.5.10:F, L , and M:

$$\frac{1}{D_{VV}} = \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{1}{\lambda_{mn}} (S_{\psi'_{mn}})^2 =$$

$$= R^4 \frac{8}{\pi^4} \eta\varphi_o \sum_{m'=o}^{\infty} \sum_{n'=o}^{\infty} \frac{1}{(m'+\frac{1}{2})^2} \cdot \frac{1}{(n'+\frac{1}{2})^2} \cdot \frac{1}{\frac{\pi^2}{\eta^2}(m'+\frac{1}{2})^2 + \frac{4\pi^2}{\varphi_o^2}(n'+\frac{1}{2})^2 - 1}$$

(3.5.10:N)

We will use the notation

$$f(\varphi_o,\eta) = - R^4 \quad D_{VV} \quad . \qquad (3.5.10:O)$$

From reference 20) we have the formulas:

$$\sum_{m'=o}^{\infty} \frac{1}{(m'+\frac{1}{2})^2+x^2} = \frac{\pi}{2x} \operatorname{th}(\pi x) \qquad \sum_{m'=o}^{\infty} \frac{1}{(m'+\frac{1}{2})^2-x^2} = \frac{\pi}{2x} \operatorname{tg}(\pi x)$$

(3.5.10:P)

With these formulas we can perform one summation in the double sum 3.5.10:N. Then we get:

$$\frac{1}{f(\varphi_o,\eta)} = \eta\varphi_o \frac{4}{\pi^2} \{ \frac{\pi^2}{2} (1 - \frac{\operatorname{tg}(\frac{\varphi_o}{2})}{\frac{\varphi_o}{2}}) - \frac{4}{1 - \frac{\pi^2}{\varphi_o^2}} \frac{\operatorname{tg}(\eta r_1)}{\eta r_1} +$$

$$+ \sum_{n'=1} \frac{1}{(n'+\frac{1}{2})^2} \frac{1}{\frac{4\pi^2}{\varphi_o^2}(n'+\frac{1}{2})^2 - 1} \frac{\operatorname{th}(\eta r_2)}{\eta r_2} \} \qquad (3.5.10:Q)$$

where

$$r_1 = \sqrt{1 - \frac{\pi^2}{\varphi_o^2}} \qquad r_2 = \sqrt{\frac{4\pi^2}{\varphi_o^2}(n' + \frac{1}{2})^2 - 1} \quad .$$

All terms of 3.5.10:Q are positive in the region 3.5.10:K. Thus ϕ_V is defined throughout this region.

From 3.5.6:B we have strong stability when

$$D_{VV} + \beta_{VV} > 0$$

$$R^4 \beta_{VV} > f(\varphi_o,\eta) \quad . \qquad (3.5.10:R)$$

The function $f(\varphi_o,\eta)$ is given graphically in figure 3.5.10:IV below for the region of weak stability.

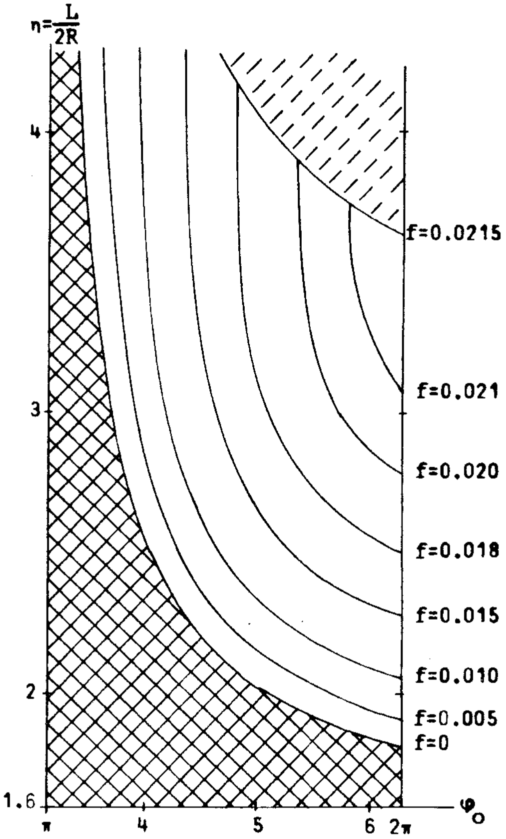


Figure 3.5.10:IV The function $f(\varphi_o,\eta)$ in the region of weak stability.

3.6 Summary of stability conditions.

We will here summarize the conditions for stability for a water meniscus in a pore together with a certain surrounding region. See figure 3.4:I on page 48. Stability requires that the second-order variation $\delta^2 U$ of the energy of the region is positive for any internal variation of constant entropy. The water meniscus is displaced to new positions in these variations. Effects of gravity and salts are not considered. The solid pore walls are assumed to be rigid.

The analysis leads to two functionals:

$$J[\psi] = \iint_S [\nabla\psi \cdot \nabla\psi - (\kappa_1^2 + \kappa_2^2)\psi^2] dS + \oint_\Gamma \sigma\psi^2 \, ds \qquad (3.6:A)$$

$$I[\psi] = \beta_{VV}(S_\psi)^2 + 2\beta_{VA} S_\psi \Gamma_\psi + \beta_{AA}(\Gamma_\psi)^2$$

$$S_\psi = \iint_S \psi \, dS \qquad \Gamma_\psi = \oint_\Gamma \psi \, ds \qquad (3.6:B)$$

The function ψ is defined over the water meniscus S and its boundary Γ. The gradient on the surface S is denoted $\nabla\psi$. The principal curvatures of S are κ_1 and κ_2.

The function σ, defined along the boundary Γ, is given by:

$$\sigma = \frac{\kappa_m \cos(\theta) - \kappa_s}{\sin(\theta)} \qquad (3.6:C)$$

Here κ_m and κ_s are the normal curvatures in the direction perpendicular to the boundary Γ for the water meniscus S respectively for the pore wall.

The second-order variation of the energy in a displacement $d\bar{r}$ of the water meniscus is given by:

$$\delta^2 U = \frac{\gamma_{\ell g}}{2} \{J[\delta n] + I[\delta n]\}$$

$$\delta n = d\bar{r} \cdot \bar{n} \qquad (3.6:D)$$

Here δn is the normal component of the displacement.

The variation $\delta^2 U$ of the energy is divided into two parts. For the first part we have:

$$\frac{1}{2} J[\delta n] = \delta^2 T = \delta^2 A_{\ell g} + \cos(\theta)\ \delta^2 A_{sg} + 2\kappa\ \delta^2 V_{\ell} \quad . \qquad (3.6:E)$$

Here $\delta^2 A_{\ell g}$ denotes the second-order variation of the meniscus area in the displacement. The contact angle is θ , and the mean curvature of the meniscus is κ . The second-order variations in solid-gas area and liquid volume are $\delta^2 A_{sg}$ and $\delta^2 V_{\ell}$ respectively.

The quantity $\frac{1}{2} \gamma_{\ell g}$ $J[\delta n]$ gives the energy required to perform the displacement of the meniscus against the forces of the initial equilibrium state. But pressures, surface tension and so on will change during the displacement. The energy required to overcome these induced additional forces is given by $\frac{1}{2} \gamma_{\ell g}$ $I[\delta n]$. We have that I is never negative. The coefficients β_{VV} , β_{VA} , and β_{AA} depend in a complicated way on the thermodynamical characteristics of the different phases in the considered region around the meniscus.

The meniscus is strongly stable, if $J[\psi]$ is positive definite. It is weakly stable, if $J[\psi]$ assumes negative values and if $J[\psi]$ is positive, when $S_{\psi} = 0$ and $\Gamma_{\psi} = 0$. Finally, it is strongly unstable, if there is a ψ such that $J[\psi] < 0$, $S_{\psi} = 0$ and $\Gamma_{\psi} = 0$.

Strong stability implies stability for the meniscus together with a surrounding region, while strong instability implies instability for the meniscus together with any surrounding region. The intermediate case of weak stability requires a study of the sum $J+I$ in order to decide on stability

The conditions in the special case, when $\theta=0$ or $\theta=\pi$, are given on page 101. The modifications, when the contact angle θ varies over the pore walls, are given on pages 102-103. The complications, when the pore wall has corners and edges, are discussed on pages 89-90.

Appendix 1. Elements of differential geometry.

This survey of differential geometry is based on references 11) and 12). The latter work deals thoroughly with the gradient operator on a surface.

Let a surface S be given in parametric form by

$$\bar{r} = \bar{r}(u,v) \qquad (u,v) \in \Omega \quad . \tag{A1:A}$$

The parameters u and v vary over a given region Ω of the (u,v)-plane.

The derivates of $\bar{r}(u,v)$ are designated $\bar{r}_u$, $\bar{r}_v$, $\bar{r}_{uu}$ and so on. We will use the following notations:

$$E = \bar{r}_u \cdot \bar{r}_u \qquad F = \bar{r}_u \cdot \bar{r}_v \qquad G = \bar{r}_v \cdot \bar{r}_v \quad . \tag{A1:B}$$

The unit normal to the surface is

$$\bar{n} = \pm \frac{1}{|\bar{r}_u \times \bar{r}_v|} \bar{r}_u \times \bar{r}_v = \pm \frac{1}{\sqrt{EG-F^2}} \bar{r}_u \times \bar{r}_v \quad . \tag{A1:C}$$

The area of a surface element of S is given by:

$$dS = |\bar{r}_u du \times \bar{r}_v dv| = \sqrt{EG - F^2}\, du\, dv \quad . \tag{A1:D}$$

<u>The gradient operator ∇.</u> Let $\psi = \psi(u,v)$ be a function defined on S . Consider two points $\bar{r}(u,v)$ and $\bar{r}(u+du,v+dv)$ on S . Then we have

$$d\bar{r} = \bar{r}(u+du,v+dv) - \bar{r}(u,v) = \bar{r}_u du + \bar{r}_v dv \quad . \tag{A1:E}$$

This gives:

$$\begin{aligned} d\bar{r} \cdot \bar{r}_u &= E\,du + F\,dv \\ d\bar{r} \cdot \bar{r}_v &= F\,du + G\,dv \end{aligned} \tag{A1:F}$$

or

$$du = d\bar{r} \cdot \frac{G\ \bar{r}_u - F\ \bar{r}_v}{EG-F^2} \qquad dv = d\bar{r} \cdot \frac{E\ \bar{r}_v - F\ \bar{r}_u}{EG-F^2} \quad . \qquad \text{(A1:G)}$$

Let $d\psi$ denote the difference in ψ between these two points:

$$d\psi = \psi(u+du, v+dv) - \psi(u,v) = \psi_u\ du + \psi_v\ dv \quad . \qquad \text{(A1:H)}$$

The gradient $\nabla\psi$ on the surface S is defined by:

$$\nabla\psi = \frac{1}{EG-F^2} \{\bar{r}_u(G \frac{\partial}{\partial u} - F \frac{\partial}{\partial v}) + \bar{r}_v(E \frac{\partial}{\partial v} - F \frac{\partial}{\partial u})\}\psi \qquad \text{(A1:I)}$$

Then from A1:G-I we have:

$$d\psi = d\bar{r} \cdot \nabla\psi \quad . \qquad \text{(A1:J)}$$

The vector $\nabla\psi$ lies in the tangent plane of S at the considered point. From A1:J we immediately have that the vector $\nabla\psi$ points in the direction of maximum increase of ψ on the surface. The magnitude $|\nabla\psi|$ gives the rate of increase of ψ in this direction.

We have

$$\nabla(\phi\psi) = \phi\nabla\psi + \psi\nabla\phi \quad . \qquad \text{(A1:K)}$$

It is easy to verify that

$$\nabla\psi \cdot \nabla\psi = \frac{1}{EG-F^2} \{G\ \psi_u^2 - 2F\ \psi_u\psi_v + E\ \psi_v^2\} \quad . \qquad \text{(A1:L)}$$

The divergence of a vector $\bar{w} = \bar{w}(u,v)$, defined for each point on S, is given by:

$$\nabla \cdot \bar{w} = \frac{1}{EG-F^2} \{\bar{r}_u \cdot (G\ \bar{w}_u - F\ \bar{w}_v) + \bar{r}_v \cdot (E\ \bar{w}_v - F\ \bar{w}_u)\} \quad . \qquad \text{(A1:M)}$$

We have the formula

$$\nabla \cdot (\phi \bar{w}) = \nabla\phi \cdot \bar{w} + \phi \nabla \cdot \bar{w} \quad . \qquad \text{(A1:N)}$$

From reference 12) we have the following formula:

$$\nabla \cdot \nabla\psi = \frac{1}{\sqrt{EG-F^2}} \{ \frac{\partial}{\partial u} (\frac{G\ \psi_u - F\ \psi_v}{\sqrt{EG-F^2}}) + \frac{\partial}{\partial v} (\frac{E\ \psi_v - F\ \psi_u}{\sqrt{EG-F^2}}) \} \qquad \text{(A1:O)}$$

Normal curvatures. Let P be a point on S , and let $\bar{t}$ be a unit vector, which gives a direction in the tangent plane of S at P . Consider those circles, which have their centre on the straight line passing through P in the normal direction to S , and which are tangent to the surface at P with tangent direction $\bar{t}$. There is a certain circle among these that fits best to the surface near the tangent point P . The inverted value of the radius of this best-fitting circle is the normal curvature of the surface S at P for the direction $\bar{t}$. The radius is counted positive, if the centre of the circle lies on the side into which the normal $\bar{n}$ is pointing, and it is negative if the centre lies on the other side.

The normal curvature in a direction given by a unit vector $\bar{t}$ is:

$$\kappa_t = - \bar{t} \cdot [(\bar{t} \cdot \nabla)\bar{n}] \quad . \qquad \text{(A1:P)}$$

The normal curvature depends on the direction $\bar{t}$. The normal curvature at the point P attains its maximum in a certain direction and its minimum in another direction. These two directions are orthogonal. The normal curvatures in these two directions are called principal curvatures. We will denote these principal curvatures κ_1 and κ_2 .

The mean curvature κ is given by:

$$\kappa = \frac{\kappa_1 + \kappa_2}{2} \quad . \tag{A1:Q}$$

The Gaussian curvature K is given by:

$$K = \kappa_1 \kappa_2 \quad . \tag{A1:R}$$

The divergence theorem. From reference 12) we have the following important theorem:

$$\iint_S \nabla \cdot \bar{w} \, dS = \oint_\Gamma \bar{w} \cdot \bar{m} \, ds - \iint_S 2\kappa \, \bar{w} \cdot \bar{n} \, dS \quad . \tag{A1:S}$$

Here $\bar{w}$ is a vector defined on the surface S with unit normal $\bar{n}$, mean curvature κ , and boundary Γ . The unit vector $\bar{m}$ denotes the outward tangent to S at the boundary Γ .

We may deduce the following important formula, if we put $\bar{w}$ equal to a constant:

$$\oint_\Gamma \bar{m} \, ds = \iint_S 2\kappa \, \bar{n} \, dS \quad . \tag{A1:T}$$

We obtain another important formula, if we put $\bar{w} = \phi \nabla \psi$:

$$\iint_S \nabla\phi \cdot \nabla\psi \, dS = \oint_\Gamma \phi \bar{m} \cdot \nabla\psi \, ds - \iint_S \phi \nabla \cdot \nabla\psi \, dS \quad . \tag{A1:U}$$

Here we have used formula A1:N and the fact that $\nabla\psi \cdot \bar{n} = 0$.

Formulas for special surfaces.

A cylindrical surface. If the surface S is any part of a cylinder, then a parametric representation of S is:

$$S: \quad \bar{r} = (R\cos\varphi,\ R\sin\varphi, z) \quad . \qquad \text{(A1:V)}$$

The axis of the cylinder is given by the z-axis, and the radius is R . See figure 3.5.7:I.

We have:

$$\bar{r}_z = (0,0,1) \qquad \bar{r}_\varphi = R(-\sin\varphi,\ \cos\varphi, 0)$$

$$E = \bar{r}_z \cdot \bar{r}_z = 1 \qquad F = \bar{r}_z \cdot \bar{r}_\varphi = 0 \qquad G = \bar{r}_\varphi \cdot \bar{r}_\varphi = R^2 \qquad \text{(A1:W)}$$

$$\nabla = \bar{r}_z \frac{\partial}{\partial z} + \frac{1}{R^2}\, \bar{r}_\varphi \frac{\partial}{\partial \varphi} \quad .$$

For a function $\psi = \psi(z,\varphi)$ we get:

$$\nabla\psi \cdot \nabla\psi = \left(\frac{\partial\psi}{\partial z}\right)^2 + \frac{1}{R^2}\left(\frac{\partial\psi}{\partial\varphi}\right)^2$$

$$\text{(A1:A')}$$

$$\nabla \cdot \nabla\psi = \frac{\partial^2\psi}{\partial z^2} + \frac{1}{R^2}\frac{\partial^2\psi}{\partial\varphi^2}$$

The curvatures in the z and φ directions are:

$$\kappa_1 = \kappa_z = 0 \qquad \kappa_2 = \kappa_\varphi = \frac{1}{R}$$

$$\text{(A1:B')}$$

$$\kappa = \frac{1}{2R}$$

The normal to the cylindrical surface is pointing inwards, since R and hence κ_φ are positive.

A spherical surface. When the surface S is a part of a sphere of radius R , a standard parametric representation is:

$$S: \quad \bar{r} = R(\sin(\bar{\theta})\cos(\varphi),\ \sin(\bar{\theta})\sin(\varphi),\ \cos(\bar{\theta})) \qquad \text{(A1:C')}$$

The whole sphere is covered, when $0\leq\bar{\theta}\leq\pi$ and $0\leq\varphi\leq 2\pi$. See figure 3.5.8:I. We have

$$\bar{r}_{\bar{\theta}} = R(\cos(\bar{\theta})\cos(\varphi),\cos(\bar{\theta})\sin(\varphi),-\sin(\bar{\theta}))$$

$$\bar{r}_{\varphi} = R\ \sin(\bar{\theta})(-\sin(\varphi),\cos(\varphi),0) \tag{A1:D'}$$

$$E = \bar{r}_{\bar{\theta}}\cdot\bar{r}_{\bar{\theta}}=R^2 \quad F=\bar{r}_{\bar{\theta}}\cdot\bar{r}_{\varphi}=0 \quad G=\bar{r}_{\varphi}\cdot\bar{r}_{\varphi}=R^2\ \sin^2(\bar{\theta})$$

$$\nabla = \frac{1}{R^2}\ \bar{r}_{\bar{\theta}}\ \frac{\partial}{\partial\bar{\theta}} + \frac{1}{R^2\sin^2(\bar{\theta})}\ \bar{r}_{\varphi}\ \frac{\partial}{\partial\varphi}$$

For a function $\psi = \psi(\bar{\theta},\varphi)$ we get:

$$\nabla\psi\cdot\nabla\psi = \frac{1}{R^2}\ (\frac{\partial\psi}{\partial\bar{\theta}})^2 + \frac{1}{R^2\sin^2(\bar{\theta})}\ (\frac{\partial\psi}{\partial\varphi})^2 \tag{A1:E'}$$

$$\nabla\cdot\nabla\psi = \frac{1}{R^2\sin(\bar{\theta})}\ \frac{\partial}{\partial\bar{\theta}}\ (\sin(\bar{\theta})\frac{\partial\psi}{\partial\bar{\theta}}) + \frac{1}{R^2\sin^2(\bar{\theta})}\ \frac{\partial^2\psi}{\partial\varphi^2}$$

The normal to the sphere is pointing inwards. Then we have (for a positive R):

$$\kappa_1 = \kappa_2 = \frac{1}{R} \quad . \tag{A1:F'}$$

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