Examples of wetting transition: the effect of long and short range interaction

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Keywords : experimental method, ellipsometry, interfacial tension, wetting, short and long range interaction

Abstract

The thickness profiles of microdroplets spreading spontaneously on solid surfaces have been studied using spatially resolved ellipsometry. Information on interaction and rheology can be extracted. We present experimental findings illustrating how long or short range interaction may induce a wetting transition in an isotropic liquid.

The parameters modified to approach the transition are the silica thickness of a silicon substrate and the atmospheric relative humidity. The first one induces a change in long range interaction and the second one a change of conformation in liquid molecules in contact with the solid.

Introduction

Thin liquid films properties are of theoretical interest and of practical importance. Isotropic liquids play an important role in industrial processes dealing with coating and adhesion. The performance of coating or adhesion is controlled at the microscopic scale. However, microscopic mechanisms are still largely unknown and a complete

characterization of the thin structure should help to understand wetting behaviors. We present an experimental study of the evolution of non volatile liquids droplets deposited on solid surfaces. The wetting condition may be very sensitive in changes of parameters as surface energy, atmospheric relative humidity or temperature. If the wetting condition is achieved, at least at the molecular scale, the thickness profile of the spreading film is recorded by a spatially resolved ellipsometer. The qualitative study of the drop' profile and the quantitative analysis of the dynamics lead to information on short and long range interaction. We present experimental finding illustrating how these interactions may induce a wetting transition in an isotropic liquid. In the first part, the wetting condition is achieved on a wafer bearing a 20 Å layer of silica while on a thicker layer (≥ 100 Å) the macroscopic contact angle is non zero. Therefore a wetting transition is induced by the change in long range interaction when the silica thickness is varied. In the second part, the wetting transition is crossed by changing the atmospheric relative humidity and then the quantity of water adsorbed on the surface. To optimize the interaction with the substrate across the water layer, the liquid molecules in the first layer change conformation leading to an autophobic effect for the upper layers. In this case, short range interaction is involved.

Experimental set-up

Technical details of our home made ellipsometer are available in literature [1]. Let us remind the lateral and thickness resolution respectively of 30 × 120 μm and 0.2 Å. These good resolutions allow us to look at the very thin details in the thickness profile of the drop. The solid substrates are silicon wafers bearing a natural oxide layer of around 20 Å which thickness can be increased by heating under controlled atmosphere. They are cleaned by U.V. ozone exposure [2] leading to a hydrophilic high energy surface. The wetting fluid is tetrakis(2-ethylhexoxy)silane (**TK**, M_w = 545 g/mol, ν = 6.8 cstk) an isotropic liquid composed in bulk of star shaped molecules with four alkane arms and a silicon center.

Examples of wetting transitions in isotropic liquids

The effect of silica thickness

Figure 1 presents a typical ellipsometric thickness profile of a drop of TK spreading on an oxidized silicon wafer. The silica thickness is 70 Å. Close to the substrate, a step-like profile develops while the profile is smooth for larger thickness ($z \gtrsim 20$ Å). This difference of behavior is controlled by molecular interactions. "Short range" interaction acts on molecular distances and the formation of layers with a thickness equal to the size of a molecule is induced by steric interaction [3]. "Long range" interaction ($z \gtrsim 20$ Å) is mainly due for a non ionic liquid like TK, to van der Waals interaction [4]. The thickness profile of figure 1 is a thin, quasi flat film ($\frac{\partial z}{\partial x} << 1$) obtained at long time and may be analyzed in term of disjoining pressure [5]. The disjoining pressure π in a thin liquid film of thickness z on a solid is a consequence of the difference of its chemical potential μ_z from the one in a thick film μ_b [6]:

$$\pi(z) = \frac{\mu_b - \mu_z}{v_m} \tag{1}$$

where v_m is the volume of the molecule. $\pi(z)$ may be positive or negative, respectively promoting or opposing the wetting. The disjoining pressure isotherm is then generally non monotonous and is a combination of short and long range interaction with a predominance of one at a given thickness. The wetting condition is achieved at the macroscopic scale when the integral of the disjoining pressure over the thickness is positive i.e. when the initial spreading coefficient S is positive.

$$S = \int_0^\infty \pi(z)dz = \gamma_{sa} - \gamma_{sl} - \gamma_{la} \tag{2}$$

The γ_{ij} refer to the interfacial tensions solid/air, solid/liquid and liquid/air.

No general expression of the disjoining pressure for short range interaction is available but the dependence with thickness should be of the form [7]

$$\pi_s \quad e^{-\frac{z}{d}} \tag{3}$$

where d is a molecular thickness. The expression of the van der Waals long range part of the disjoining pressure is usually given for a film of medium 3 between media 1 and 2, as

$$\pi_l(z) = -\frac{A_{132}}{6\pi z^3} \tag{4}$$

where A_{132} is the Hamaker constant.

The study of drop' profiles leads to information on the schematic shape of the disjoining pressure. The dynamic of growth of the drop can be quantified by a "thickness dependent diffusion coefficient" D(z) linking the change $\Delta R(z,t)$ in the radius at thickness z to the square root of the time $\Delta R(z,t) = \sqrt{D(z)t}$. In relatively thick films, the flow in the film is a Poiseuille flow [8] and

$$D_l(z) = -\frac{z^3}{3\eta}\frac{d\pi}{dz} = -\frac{A_{132}}{6\pi\eta z} \tag{5}$$

where η is the bulk liquid viscosity. For thinner films, D(z) is still proportional to the disjoining pressure gradient but the no-slip condition is changed in a pure slip condition on the solid wall and the diffusion coefficient becomes [9]:

$$D_s(z) = -\frac{zv_m}{\alpha}\frac{d\pi}{dz} \tag{6}$$

where α is a molecule-surface friction coefficient. If short range interaction (3) is dominant, one has :

$$D_s = \frac{zv_m}{\alpha d} e^{-\frac{z}{d}} = Be^{-\frac{z}{d}} \tag{7}$$

Let us try to analyze the experimental results in terms of this simple model. Figure 2 presents the diffusion coefficient versus the thickness for two drops of TK spreading on a silicon wafer bearing (a) a 20 Å thick layer of silica (b) a 70 Å layer of silica. We have also observed that a droplet deposited on a 100 Å thick layer of silica does not wet anymore the substrate, suggesting a negative contribution of the silica in the long range part of the disjoining pressure. To analyze this long range part, the expression (5) has to be modified in order to take into account the oxide layer. We now deal with a four layer system: 1, air; 3, TK; 4, oxide layer (thickness δ); 2, silicon. $\pi(z)$ can be expressed as a function of the Hamaker constants [10] of the three layer systems air-TK-silicon A_{231}, oxide-TK-air A_{431}, and the various thicknesses:

$$\Pi(z) = -\frac{A_{231} - A_{431}}{6\pi(\delta + z)^3} - \frac{A_{431}}{6\pi z^3} = -\frac{A(\delta,z)}{6\pi z^3} \qquad (8)$$

here, $A(\delta,z)$ is the effective Hamaker constant dependent of the oxide thickness. The expression of the diffusion coefficient becomes :

$$D_l(z) = -\frac{1}{6\pi\eta z}\left[\frac{(A_{231} - A_{431})z^4}{(\delta + z)^4} + A_{431}\right] \qquad (9)$$

Experimentally, values of D(z) for (a) and (b) cases coincide for thickness below 20Å (short range) and then for thickness over 100 Å (long range). For intermediate thickness $20 < z < 100$ Å, the curve (b) decreases faster than (a). On figure 2 are also presented the expected behaviors of diffusion coefficient (c) due to short range interaction and (d) to long range interaction according to expressions (7) and (5). The full line indicates the predominance of one in the corresponding range of thickness. The numerical values of $D_s = Be^{-\frac{z}{d}}$ have been chosen to fit the curve: d = 15 Å is coherent with the range of short range interaction while $B = 6\ 10^{-10}\ m^2/s$ is phenomenological, as we do not know the value of the friction coefficient. For (d), we used $A = 5\ 10^{-21}$ J.

For large thickness, $z >> \delta$, the effective Hamaker constant tends to the one of the air-TK-silicon system. For z ~ 300 Å, we still observe a decrease of the diffusion coefficient below the -1 straight line (log-log plot). This result suggests a non negligible contribution of the short range interaction and a value of the Hamaker constant A_{231} (usually in the range 10^{-20}-10^{-21} J) much lower than $A = 5\ 10^{-21}$ J .

For small thickness, z < 20Å, the spreading occurs at the same velocity on wafer (a) and (b): the short range contribution to the disjoining pressure is positive in both cases and due to the silica surface.

For intermediate thickness, as we do not expect a change of the short range contribution, the lower value of the diffusion coefficient on wafer (b) is due to a decrease of the effective Hamaker constant. $A(z,\delta)$ being a combination of A_{231} and A_{431}, we conclude that the long range part contribution to the disjoining pressure of the silica layer is

negative and tends to oppose wetting. This is confirmed on a 100 Å thick layer of silica where no wetting is observed.

In summary, interaction are dominated by the short range contribution ($\pi_s > 0$) coming from the silica surface. The van der Walls contribution depends on the silica thickness δ and is a combination of a positive and a negative Hamaker constant (figure 3). An increasing negative contribution to the disjoining pressure ($\delta \gtrsim$ 100Å) leads to a negative value of the spreading coefficient S associated to a non wetting situation.

The effect of humidity

Silicon substrates cleaned by UV-ozone procedure are high energy and hydrophilic surfaces and so, very sensitive to impurities and water. We performed spreading experiments with TK changing the relative atmospheric humidity (RH). Figure 4 shows the ellipsometric profiles for increasing RH. Up to RH = 80 %, complete wetting is observed: a step-like profile develops. The thickness of the first layer is around 8 Å while the upper ones have a thickness close to 12 Å. Between 80 and 85 % a wetting transition builds up, the second step changes from monolayer to multilayer and its thickness ultimately diverges when the liquid becomes macroscopically nonwetting (RH > 85 %). This effect is analyzed in term of a progressive autophobic effect due to the change of conformation of molecules lying on the solid surface in the first layer.

According to the relative freedom of the aliphatic arms around the hydrophilic center, the TK molecule will adapt its conformation to the molecular environment. In contact with an hydrophilic wall, the molecule is compact (α); the center ($Si(-O)_4$) turns to the wall while the four aliphatic arms point away. The size of the molecule in this conformation is around 8 Å [11]. In the other way, a single molecule in space adopts an isotropic configuration (β) which diameter is around 12-14 Å. This conformation is also expected in bulk and layers excepted in the first one in contact with the silica.

Silicon oxide is chemically non homogeneous: on surface, hydrophobic siloxane bridges and hydrophilic silanol groups are coexisting. As the humidity increases, water molecules

adsorb in islands on silanol groups and percolate for RH ~ 80 % [12, 13]. We know that surface inhomogeneities act on the steepness of the first monolayer: strong inhomogeneities lead to smooth profiles. This effect, observed for a well developed first layer, is seen on the curve (f) of the figure 4. TK spreading at RH = 90 % has a steep profile suggesting a homogeneous surface due to a quasi compact monolayer of water on the solid surface.

Let us try to explain why a wetting transition takes place. For weak humidity, water molecules condense in packs around silanols groups. Water free surface is available on which the TK prefers a conformation close to the (β) one (~ 10Å, observed in dry atmosphere and on bare silicon wafer without UV ozone cleaning). When water molecules percolate, the number of TK molecules in the (α) conformation increases. The first monolayer becomes compact and presents to the upper liquid a dense package of hydrophobic groups $-CH_2$ and $-CH_3$ i.e. a surface with a lower critical surface tension. The effect is then the same as the one already observed with light polymer on grafted surfaces [14]: the wetting transition is the result of a competition between a long range positive contribution and a short range negative one. The external parameter to approach this transition, by varying the short range interaction, is the atmospheric humidity. Water adsorbed on the silica surface induces a modification of the TK conformation in the first monolayer increasing the negative short range contribution to the disjoining pressure. The evolution of the disjoining pressure with humidity is presented on figure 5.

Conclusion

This work shows that the spreading at the microscopic scale is a sensitive process, where a weak change of the surface properties may induce a wetting transition. Macroscopically the wetting condition is achieved for the spreading coefficient superior or equal to zero. S being the integral of the disjoining pressure, an increasing negative contribution to π leads to a non wetting situation. The modification of short or long range interaction can induce this transition. Close to the wetting threshold, the droplet shape

greatly changes: the thickness of the second step which is a monolayer far from transition, increases and ultimately diverges when negative short range interaction just balances the long range positive one. If the long range interaction is modified then the thick part of the drop does not spread anymore.

List of symbols

α : friction coefficient

δ : thickness of the silica layer

γ : interfacial tension

η : dynamic viscosity

μ : chemical potential

ν : cinematik viscosity (1 cstk = 10^{-6} m^2/s)

π : disjoining pressure

A : Hamaker constant

$B = \frac{z v_m}{\alpha d}$: a constant

d : a molecular thickness

M_w : molar mass

S : spreading coefficient

v_m : molecular volume

z : thickness of the liquid film

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Figures captions

Figure 1 : Ellipsometric thickness profiles of a tetrakis (2-ethylhexoxy)-silane drop spreading on a silicon wafer. The thickness measured far from the drop is non-zero because of the 70 Å-thick surface layer of silicon oxide. This base line thickness corresponds to the bare solid on which the liquid spreads. The times t after droplet deposition are t = 5h30 (dotted), t = 6h30 (thick, full) and t = 22 h (thin, full).

Figure 2 : Measured values of the "diffusion coefficient" D(z) versus the film thickness z for TK microdroplets spreading spontaneously on a silicon wafer bearing (a) a 20 Å thick layer of silica (b) a 70 Å layer of silica. (c) and (d) are respectively the expected behaviors of the diffusion coefficient due to short and long range interaction.

Figure 3 : Schematic behavior of the disjoining pressure $\pi(z)$ for TK on a silicon wafer bearing (a) a 20 Å thick layer of silica, (b) a 70 Å thick layer of silica. A thicker layer of silica leads to an increasing negative contribution to the disjoining pressure.

Figure 4 : Thickness profiles of three different microdroplets of TK on a hydrophilic wafer bearing a 20 Å thick layer of silica. (e) RH = 20 %, t = 1h30; (f) RH = 82 %, t = 6h30; (g) RH = 90 %, t = 4h30.

Figure 5 : Schematic behavior of the disjoining pressure $\pi(z)$ for TK on a silicon wafer bearing a 20 Å thick layer of silica. (e) RH = 20 %, a dampted oscillation, accounting for steric interaction, is superimposed to a positive, monotonic decay. Unstable parts are not observed and give rise to thickness transitions determined by the Maxwell rule. (f) RH = 82 %, a negative, short range contribution is superimposed to a monotonic positive decay. Unstable parts in $\pi(z)$ are again associated with horizontal transitions between films. The extension of the second plateau increases with the negative short range contribution and ultimately diverges for RH = 90% (g).

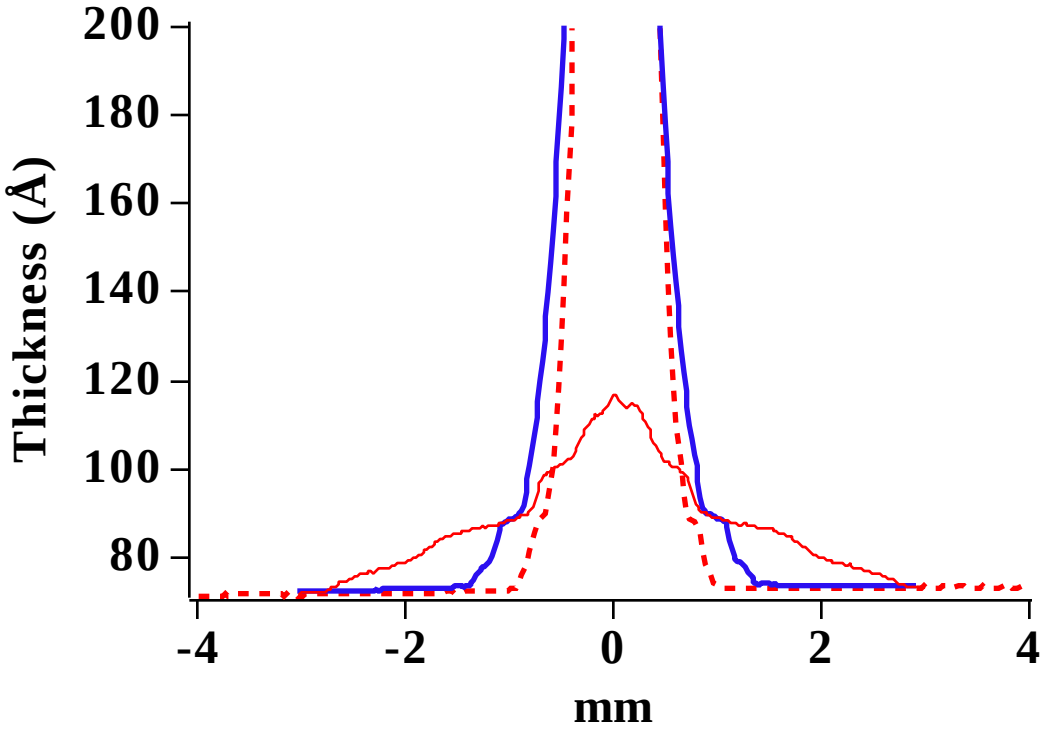

Figure 1

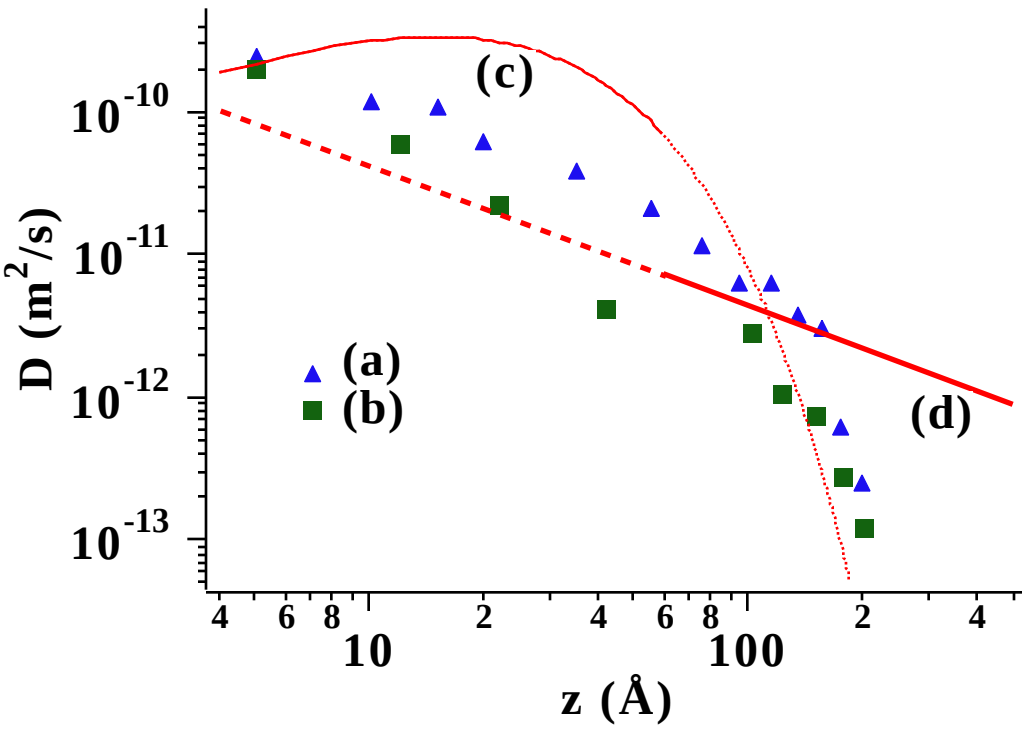

Figure 2

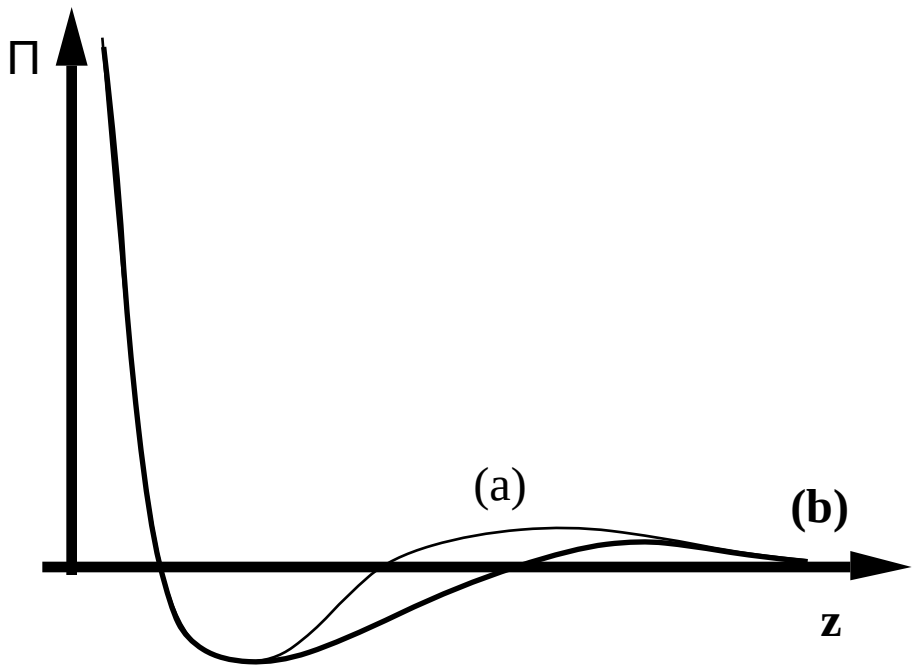

Figure 3

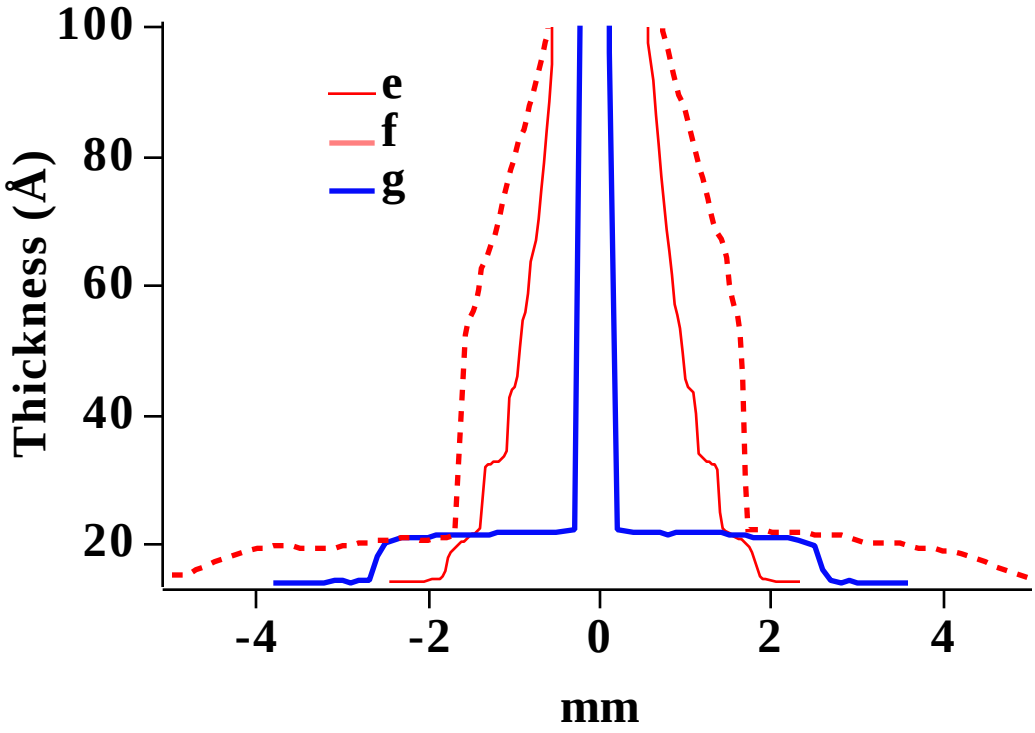

Figure 4

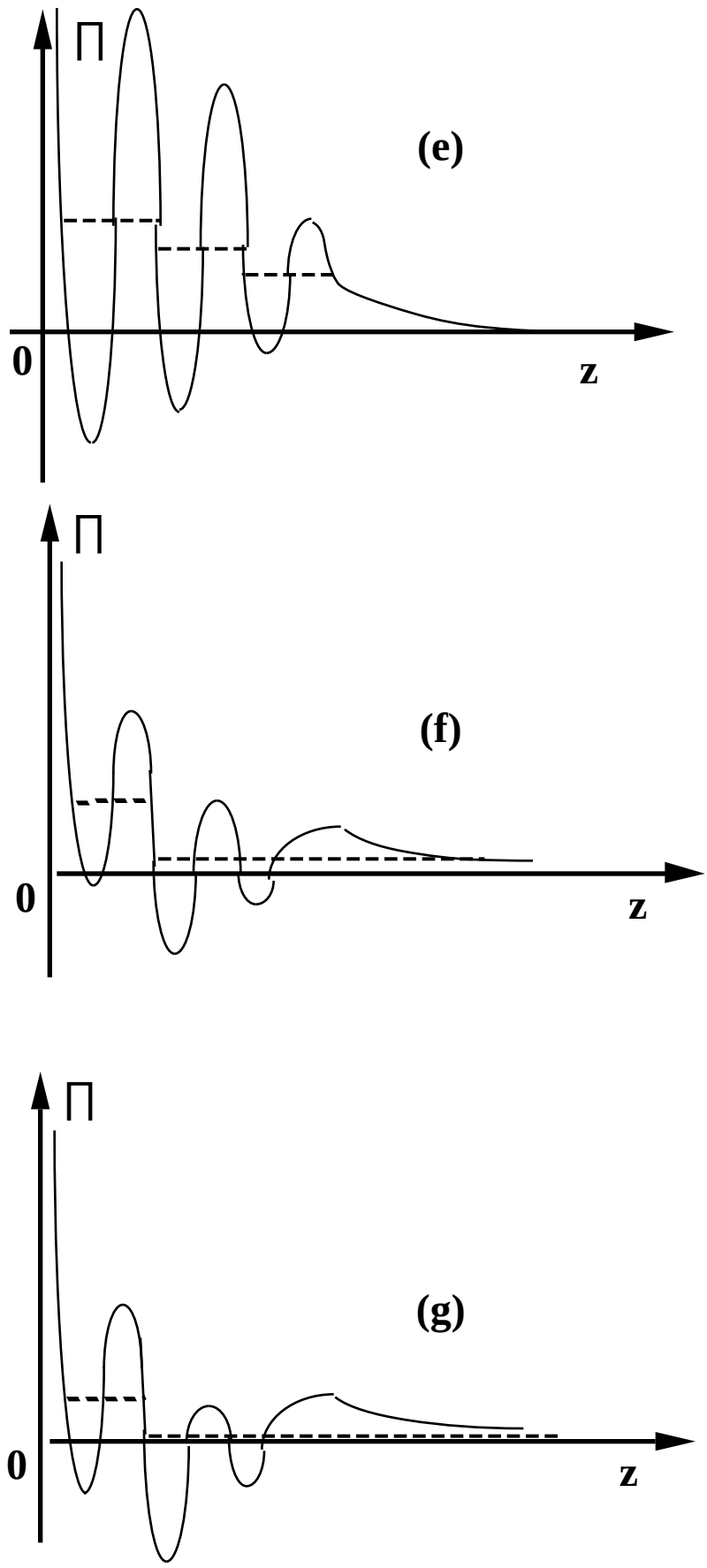

Figure 5