332. *Sorption Hysteresis. Part II.* The Rôle of the Cylindrical Meniscus Effect.*

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The correct formulation of the equations for the cylindrical meniscus effect is discussed and applied to a critical review of Cohan's theory of the point of hysteresis inception. It is shown that during the early stages of the sorption process the effect assists layer formation and that Cohan's mechanism for pore blocking becomes operative later, only if certain conditions are fulfilled. The potential due to layer adsorption is calculated from Brunauer, Emmett, and Teller's (B.E.T.) theory and compared with that due to capillary condensation in the same pore. The total potential, arising from the combination of layer adsorption with the cylindrical meniscus effect, passes through a minimum at some stage of the sorption process and it is suggested that hysteresis will occur only when the Kelvin potential curve intersects this total potential curve before the minimum is reached. When both the pore radius and the number of adsorbed layers are large, a simplified mathematical treatment leads to the prediction that hysteresis is possible when the product $V\gamma/\boldsymbol{R}T\sigma$ for the adsorbed liquid exceeds unity (where V is the molar volume, γ the surface tension, and σ the molecular diameter).

The open-pore theory of sorption hysteresis (Foster, *Trans. Faraday Soc.*, 1932, **28**, 645) assumes that the equilibrium pressures on the desorption branch of the hysteresis loop are determined by the Kelvin equation, and attributes the higher pressures observed during adsorption to delayed meniscus formation. The adsorptive forces become weaker

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* Part I, *J. Phys. Colloid. Chem.*, 1951, **55**, 638.

as layer formation proceeds and molecules are held at a greater distance from the surface. At the same time, the space remaining empty in the centre of the capillaries becomes smaller and a point is reached at which the cohesive forces should, by capillary condensation, be able to effect a greater lowering of vapour pressure than the adsorptive forces. It is, however, not possible for condensation to occur at this stage unless the pores are already blocked at their narrowest points by the adsorbed layer. If no meniscus is present the liquid must remain on the walls until a higher pressure is reached. In its original form the open-pore theory assumed that layer adsorption persisted until enough liquid was present to block the pores and form a meniscus. It was later pointed out (Foster, *Proc. Roy. Soc.*, 1934, *A*, **147**, 138) that continued layer adsorption would be assisted by a capillary condensation effect, due to the cylindrical meniscus presented by the adsorbed layer, which produces a free-energy decrease approximately one-half of that due to normal condensation at a spherical meniscus in a pore of the same radius. An analysis of the extensive data of Lambert and Clark (*ibid.*, 1929, *A*, **122**, 497) for the sorption of benzene by ferric oxide gel showed that the desorption equilibria were consistent with the capillary theory, whilst the adsorption equilibria were consistent with the Polanyi "potential" theory (*Verhandl. deut. physik. Ges.*, 1916, **18**, 55) of multimolecular adsorption. Later Brunauer, Deming, Deming, and Teller (*J. Amer. Chem. Soc.*, 1940, **62**, 1723) showed that these adsorption data could be interpreted satisfactorily by a modification of the original B.E.T. theory.

In Cohan's version (*J. Amer. Chem. Soc.*, 1944, **66**, 98) of the open-pore theory, multilayer formation is ignored and all sorption effects beyond the monolayer are attributed to capillary condensation. During adsorption, the equilibria are determined by the cylindrical meniscus effect, and during desorption by the normal condensation process in accordance with the Kelvin equation. Both branches of the loop are thus attributed to capillary effects, and the theory leads to a simple quantitative relation between the adsorption and desorption pressures in pores of given radius. It is further predicted that the pressure at which hysteresis begins (point of hysteresis inception) should correspond to a Kelvin radius $r = 2\sigma$, where σ is the diameter of the adsorbed molecule (or, more strictly, the thickness of an adsorbed layer). Emmett and Cines (*J. Phys. Coll. Chem.*, 1947, **51**, 1260) have pointed out that the observed radii generally lie between 2σ and 3σ and have predicted a value of 3σ, a slight modification of Cohan's original argument being used. Some recent observations (Brown and Foster, *J. Phys. Coll. Chem.*, in the press) on the sorption of amines by silica gels also indicate values lying between 2σ and 3σ.

Cohan used an approximate equation for the cylindrical meniscus effect which is not accurate for small radii, and the original object of this paper was to repeat his calculations, using the correct equation. This led to the view that a value 3σ for the radius at the point of hysteresis inception could be predicted by assuming more extensive layer formation during adsorption than during desorption—a view which, although quite plausible, is untenable in a theory which postulates that layer adsorption does not extend beyond the monolayer. In attempting to develop a more consistent theory, the basic ideas of the author's original version have been combined with Cohan's idea that the cylindrical meniscus effect provides a mechanism for pore filling. The following discussion thus falls into three parts: (*a*) a correct formulation of the equations for the cylindrical meniscus effect, (*b*) a critical review of Cohan's theory of the point of hysteresis inception, and (*c*) an attempt to combine the basic ideas of the two versions of the "open-pore" theory.

Theory of the Cylindrical Meniscus Effect.—According to the Kelvin equation the vapour pressure of a liquid of surface tension γ and molar volume V contained in a cylinder of radius r is given by

$$p = p_0 \exp(-2V\gamma/r\boldsymbol{R}T) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where p_0 is the saturation vapour pressure over a plane surface at the same temperature T. Since there must be an adsorbed layer present on the walls of the pore before condensation can occur, r is not the true pore radius r_0 but is lower by an amount D which represents the thickness of this layer. It is generally assumed that the vapour pressure over a cylindrical meniscus is given by

$$p = p_0 \exp(-V\gamma/r\boldsymbol{R}T) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

since the Gauss curvature of the cylindrical surface is half that of the corresponding spherical surface. However, this is no longer quite true when r is of the same order as the molecular diameter σ. The correct relation (Foster, *loc. cit.*, 1934) is

$$p = p_0 \exp\{-V\gamma/(r - \sigma/2)\boldsymbol{R}T\} \quad . \; . \; . \; . \; . \; . \; . \quad (3)$$

which reduces to (2) when $r \gg \sigma$. An alternative form of this equation, which will be used later, is

$$p = p_0 \exp\{-V\gamma/(r + \sigma/2)\boldsymbol{R}T\} \quad . \; . \; . \; . \; . \; . \; . \quad (3a)$$

where r is taken as the *final* radius, the *initial* radius being $r + \sigma$.

Point of Hysteresis Inception.—The essential feature of Cohan's theory is that when the pressure, during adsorption, reaches a value p_a given by equation (2), the capillary fills completely, whereas during desorption the same pore will not empty until the pressure has been reduced to the lower value p_d given by equation (1). The reason for complete filling at p_a is that, although initially the pressure must by raised to this value in order that one more layer may condense on the walls, yet once this layer has formed, a second can then form at the still lower pressure corresponding to $r - \sigma$, and so on until the pore is completely filled. Cohan assumes that the mechanism of adsorption on a porous solid consists in the formation of a unimolecular layer followed by capillary condensation, but in applying the Kelvin equation he takes the radius as r_0 and not $r_0 - \sigma$. However, in considering the application of equation (2), the effective radius is taken as $r_0 - \sigma$, and the point of hysteresis inception is calculated in the following manner. The desorption pressure p_d is given by

$$p_d = p_0 \exp(-2V\gamma/r_0\boldsymbol{R}T) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

whereas the adsorption pressure p_a is given by

$$p_a = p_0 \exp\{-V\gamma/(r_0 - \sigma)\mathrm{R}T\} \quad . \; . \; . \; . \; . \; . \; . \quad (5)$$

The condition for $p_d = p_a$ is that $2/r_0 = 1/(r_0 - \sigma)$ or $r_0 = 2\sigma$. This is the radius at the point of hysteresis inception, at which both equations (1) and (2) give the same value for p. It is clear that, unless the effective radii during adsorption and desorption are assumed to be different (*e.g.*, in this case, r_0 and $r_0 - \sigma$), it is impossible to derive any relation between r and σ, thus if the radius is taken as r_0 in both cases, then p_a is *always* $> p_d$. The assumption that $r = r_0$ during desorption but $r = r_0 - \sigma$ during adsorption, though quite inconsistent with the postulate of an initial monolayer, is essential to Cohan's theory in order to predict the value $r_0 = 2\sigma$ which he maintains is in agreement with experiment. Emmett and Cines (*loc. cit.*) have also commented on this inconsistency and have sought to resolve it by assuming that *two* adsorbed layers are present on the walls during adsorption but that only *one* remains during desorption. This makes $r = r_0 - 2\sigma$ for adsorption and $r = r_0 - \sigma$ for desorption, and substitution of these values in (1) and (2) makes $p_a = p_d$ when $2/(r_0 - \sigma) = 1/(r_0 - 2\sigma)$ or $r_0 = 3\sigma$. It is necessary to distinguish carefully between r_0, the true pore radius, and r, the value obtained by the usual method of calculation based on the Kelvin equation. Thus, Cohan's result $r_0 = 2\sigma$ and that of Emmett and Cines ($r_0 = 3\sigma$) correspond to identical *Kelvin* radii, since Cohan puts $r = r_0$ whilst Emmett and Cines put $r = r_0 - \sigma$, hence if $r_0 = 3\sigma$, r must be 2σ.

It is now necessary to see how these arguments are modified by the use of equation (3) instead of (2). Cohan's relation becomes $2/r_0 = 1/(r_0 - \frac{1}{2}\sigma - \sigma)$ or $r_0 = 3\sigma$, whilst the method of Emmett and Cines gives $r = 3\sigma$ or $r_0 = 4\sigma$. If, on the other hand, one assumes that the thickness of the adsorbed layer remains the same during adsorption, then $2/r = 1/(r - \frac{1}{2}\sigma)$ or $r = \sigma$ and $r_0 = 2\sigma$ for one adsorbed layer. This result is clearly not in agreement with experiment since the observed values of r lie between 2σ and 3σ. It therefore seems to be necessary to revert to the less simple view that the number of adsorbed layers does not remain constant and to consider whether this concept has any theoretical basis.

Equilibrium between Adsorbed and Condensed Liquid.—The equilibrium pressure due to capillary condensation in a pore of radius r_0 can only be calculated by means of the Kelvin equation if the number of adsorbed layers (n) is known, since the Kelvin radius $r = r_0 - n\sigma$.

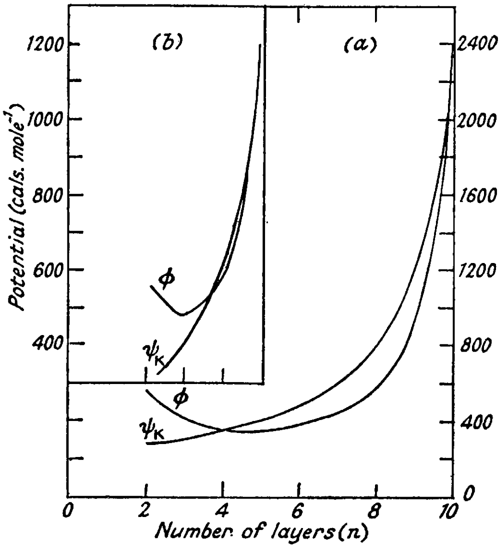
In general, there is no definite and unambiguous method of determining n, although in many systems hysteresis begins when the total amount adsorbed corresponds to roughly twice the amount required to form a complete monolayer. If it be assumed that layer adsorption is followed by capillary condensation as the amount adsorbed increases, then conversely, during desorption the initial stages represent an emptying of pores filled by capillary condensation and a film of liquid several molecules thick will remain behind on the walls during the later stages. The thickness of this layer will depend on the relative magnitudes of the forces causing layer adsorption and those causing condensation. The thicker the adsorbed layer, the larger will be the value of n and hence the smaller the value of r, so that a thick adsorbed layer would at first sight appear to favour a low condensation pressure. This is, of course, true, but the higher the value of n, the greater is the pressure over the multilayer, and presumably a balance between the cohesive and adsorptive forces occurs when the equilibrium pressures due to the two mechanisms are equal. It should therefore be possible to obtain an approximate solution by equating the pressure given by the Kelvin equation to that given by the B.E.T. multilayer adsorption theory for the same value of n. For the purpose of a rough calculation, one of the simple limiting cases of the general B.E.T. equation may be employed. Thus, when the heat of adsorption in the first layer is very much greater than that in the subsequent layers, the amount adsorbed a, expressed as a multiple of the monolayer capacity, is given by

$$a = 1/(1 - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where x is the relative pressure (Foster, *J.*, 1945, 770). The Kelvin equation may be applied by assuming for the product $V\gamma$ a rough average value of 1200, which is quite close to the actual values for water and alcohol. However, the quantity a (which is identical with V/V_m in the original B.E.T. notation) does not necessarily represent the actual number of adsorbed layers but merely the ratio of the amount adsorbed to that which would be required to cover the surface completely with a monolayer. According to the B.E.T. theory, a should not be identified with any particular value of n, but Halsey (*J. Chem. Phys.*, 1948, **16**, 931) maintains that, until a given layer is almost complete, further adsorption in the next layer is negligible, and a similar picture has also been suggested by Tompkins (*Trans. Faraday Soc.*, 1950, **46**, 569) and by Barrer and Robins (*ibid.*, 1951, **47**, 785). It therefore appears reasonable to regard a and n as identical and to argue that the transition between layer adsorption and capillary condensation occurs when equations (1) and (2) give the same value for x. However, once the existence of multimolecular adsorption is admitted, the free-energy decrease during the filling of a pore can no longer be attributed solely to capillary forces, but must be regarded as consisting of *two* parts, one due to the layer adsorption forces and the other due to capillary forces. The original version of the open-pore theory recognised this fact but failed to formulate it quantitatively; Cohan's version, with less justification, since it appeared some years after the B.E.T. theory, ignores it and endeavours to explain hysteresis in terms of equations (4) and (5) alone.

Calculation of Potential Curves for Adsorption and Capillary Condensation.—The logical basis for a quantitative treatment is to find a simple expression for the layer "adsorption potential" (or free-energy decrease) ψ_e, and to combine this with the potential ψ_c due to the cylindrical meniscus effect in order to obtain the *total* free-energy decrease accompanying the formation of a given adsorbed layer. Since ψ_e is initially *high* and falls off as layer formation proceeds, whilst ψ_c is initally *low* and increases as adsorption proceeds (because the radius of the free space remaining in the centre of the pore is decreasing), the *total* potential ϕ $(= \psi_e + \psi_c)$ must pass through a *minimum*. *Before* this minimum is reached, the nth layer is *more* stable than the $(n + 1)$th layer and will be nearly completed before the latter forms appreciably. *Beyond* this minimum, the nth layer becomes *less* stable than the $(n + 1)$th and the pores then fill completely at the pressure corresponding to this potential. Thus, the effect of taking layer adsorption into account is to show that the cylindrical meniscus effect assists layer formation initially and operates as a pore-blocking mechanism only after a number of adsorbed layers have been formed. If true capillary condensation is to be stable, the potential ψ_K given by the Kelvin equation ($\psi_K = \boldsymbol{R}T \log p_0/p = 2V\gamma/r$) cannot be less than the total potential ϕ. ψ_K, like ψ_c, is initially small, and for the same reasons increases as more layers are formed. When the curve showing the variation of ψ_{K} with the number of adsorbed layers a, intersects the ϕ–a curve, the pressure over the spherical meniscus of the condensed liquid will be equal to that over the cylindrical meniscus of the adsorbed liquid and no further layer adsorption will occur, since any liquid so held would have a higher pressure, corresponding to the lower potential of the ϕ–a curve (which then lies below the ψ_{K}–a curve), so that the pore would fill by capillary condensation at this pressure provided that the spherical meniscus were already present. If the pore is open at both ends and has a uniform diameter, or if it is tapering and is not yet blocked at its narrowest part, there will be no meniscus present and further layer adsorption will occur until the minimum of the ϕ–a curve is reached and the pores block completely.

From the typical potential curves plotted in the figure, the derivation of which is described later, it is seen that the point of intersection may lie on either side of the minimum. The basic idea of the new theory is that hysteresis will be observed only when the ψ_{K}–a and the ϕ–a curve intersect *before* the latter reaches its minimum value. True capillary condensation becomes *thermodynamically stable* before the necessary meniscus can be formed, so that during adsorption the pores fill at the pressure corresponding to the minimum of the ϕ–a curve, whereas during desorption, when a meniscus has been formed, the same pores do not empty until the pressure corresponding to the point of intersection is reached; this point must necessarily lie at a higher potential than the minimum, and hence correspond to a lower pressure.



During desorption the states represented by that part of the ϕ–a curve lying to the *right* of the minimum are all *unstable* relative to the ψ_{K}–a curve, and the point of intersection represents the effective minimum potential at which a stable system can exist during pore emptying. The regions where $\mathrm{d}\phi/\mathrm{d}a$ is positive correspond to unstable states (pressure falling with increasing adsorption), which cannot be realised in practice. When the intersection occurs after the minimum is reached, there is in theory a transition point between layer adsorption and capillary condensation but, since this lies in the experimentally unrealisable region, the pores will both empty and fill at the pressure corresponding to the minimum.

Conditions for Occurrence of Hysteresis.—The accurate determination of these potential curves would make it possible to predict whether or not hysteresis would occur in a given system. The simplest, though not necessarily the most exact, basis for quantitative treatment is to use the B.E.T. limiting equation (6) to obtain the variation of ψ_e with the distance from the surface (which is assumed to be proportional to the number of adsorbed layers). Thus, since $x = 1 - 1/a$, this potential is given by

$$\psi_e = -\mathbf{R}T \log x = -\mathbf{R}T \log (1 - 1/a) \quad . \quad . \quad . \quad . \quad (7)$$

The cylindrical meniscus potential is given by (3*a*) as

$$\psi_c = \mathbf{R}T \log p_0/p = V\gamma/(r + \sigma/2)$$

where r is the radius of the space remaining *after* the formation of the ath layer. If r is expressed as a multiple $n\sigma$ this becomes

$$\psi_c = 2V\gamma/(2n + 1)\sigma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and the total potential for the formation of the ath layer in a cylinder of total radius $n_0\sigma$ will be

$$\phi = \psi_e + \psi_c = -\mathbf{R}T \log (1 - 1/a) + 2V\gamma/(2n + 1)\sigma \quad . \quad . \quad . \quad (9)$$

where $a + n = n_0$. The Kelvin potential, ψ_K, which determines the pressure at which capillary condensation occurs in the *same* capillary when a adsorbed layers are present, is given by equation (1) with the appropriate value of $r = n\sigma$. Hence $\psi_K = 2V\gamma/n\sigma$ and both the potential curves can be calculated for any given pore radius if the constants V, γ, and σ are known. The figure shows two such sets of curves: (*a*) for pore radius 50 Å (10σ) and $V\gamma = 2520$, and (*b*) for pore radius 25 Å (5σ) and $V\gamma = 1260$. In the former, the intersection occurs before the minimum is reached, but in the latter, where the capillary forces are smaller, layer adsorption predominates and the intersection does not occur until after the minimum. The graphical solution of these equations becomes laborious for large values of n_0, but fortunately a simple mathematical solution is possible for the limiting case where both a and n are large, since the logarithmic term in equation (9) can then be expanded and the $(2n + 1)$ factor in the second term replaced by $2n$, giving

$$\phi = (\mathbf{R}T/a) + [b/2\sigma(n_0 - a)] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where b is the value of $2V\gamma$ expressed in calories per mole. ϕ clearly has a minimum when

$$\mathbf{R}T/a^2 = b/2\sigma(n_0 - a)^2$$

or

$$n_0/a = 1 + K^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where $K = b/2\mathbf{R}T\sigma$. The point of intersection occurs when $\psi_K = \psi_e + \psi_c$ or

$$b/n\sigma = \mathbf{R}T/a + b/2n\sigma$$

whence

$$\mathbf{R}T/a = b/2n\sigma \text{ or } n_0/a = 1 + K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Thus in large pores, the ϕ–a curve has a minimum at $a = n_0/(1 + K^{\frac{1}{2}})$ and intersects the ψ_K–a curve at $a = n_0/(1 + K)$. When $K = 1$ the two points coincide and the condition for the intersection to occur before the minimum is reached, and hence for hysteresis to appear, is that the constant K shall be greater than unity.

This surprisingly simple result has been derived by considering a highly idealised but by no means unrealisable system, but even if the majority of systems encountered in practice are more complex, their behaviour must still be partly determined by the same parameter K, which is proportional to $V\gamma/\sigma$.

If V is regarded as $\propto \sigma^3$, then $K \propto \sigma^2\gamma$ and it is evident that the molecular diameter is the chief factor determining the magnitude of K, since γ does not show very wide variations for most organic liquids. The table, which records the results of some rough calculations, shows that K for typical liquids lies between 1·0 and 2·0. It seems that values significantly less than unity will not occur frequently, so that, in large pores, hysteresis should actually be observed with most liquids. This agrees with the work of Broad and Foster, (*J.*, 1946

446) and Brown and Foster (*J.*, 1952, 1139) on ferric oxide gel (pore radius ~30 Å) in which large hysteresis loops were observed with all the liquids examined. However, even in pores of radius 100 Å, the extent of the observed hysteresis areas suggests that only two or three adsorbed layers are present. For such a system, with $r = 20\sigma$ and $K = 1$, equations (11) and (12) predict the formation of ten adsorbed layers, hence the quantitative agreement between simple theory and experiment is poor. To remedy this defect it is necessary to have either higher ψ_K or lower ψ_e values, and since the Kelvin equation is unlikely to be seriously in error for large radii, the more probable source of error seems to be in the use of the B.E.T. model for layer adsorption. The limiting B.E.T. equation, which was deliberately chosen for its simplicity, is derived for a plane surface, and its use for adsorption in pores of small radius is not justified. The expansion of the logarithmic term of equation (9) to give $\boldsymbol{R}T/a$ implies that, for large a values, the B.E.T. assumptions are equivalent to a potential which falls off inversely as the distance and corresponds to the existence of long-range adsorption forces.

Substance	σ (Å)	V	γ	$V\gamma$	K
Water	3·5	18	72	1296	1·4
Methyl alcohol	4·6	40	22	880	0·8
Ethyl alcohol	5·2	58	22	1280	1·0
Ethylenediamine	5·4	67	41	2780	2·0
Benzene	5·9	88	29	2552	1·7
Carbon tetrachloride	6·1	98	26	2550	1·6
Toluene	6·3	107	28	3000	1·8
n-Heptylamine	7·2	151	26	3940	2·1

The simple B.E.T. theory thus overestimates the layer adsorption forces at large distances, and in order to develop a more exact treatment it is necessary to adopt a more realistic model for the adsorption potential. It was suggested by Polanyi (*Trans. Faraday Soc.*, 1932, **28**, 321) that the potential was due to the London dispersion force, which varies inversely as the seventh power of the distance. When integrated over the whole surface, this leads to an inverse-cube law for the potential, and it is noteworthy that this model has recently been adopted by Barrer and Robins (*loc. cit.*) in their attempt to develop an alternative to the B.E.T. theory. It is then necessary to assign, somewhat arbitrarily, a definite value (ψ_0) to the potential in the first layer, which introduces an additional variable into the above equations and it is no longer possible to obtain a simple solution for the limiting case because equation (10) will contain a term in $1/a^3$ and will give a biquadratic equation on differentiation. However, the equations are still easily solved by graphical methods when definite values are assigned to ψ_0, r, and σ, but the operations are laborious. It is hoped to discuss these curves in detail in the next paper of this series. For the present it can be said that when $\psi_0 = 4000$—1000 cals./mole, the ϕ–a curves fall more steeply than those in the figure and intersect the ψ_K curves at smaller values of a corresponding to 2—4 adsorbed layers, thus showing better agreement with experiment.

The graphical solutions so far obtained show that, for both models, in average systems the ψ_K–a curve cuts the ϕ–a curve at or before its minimum when n_0 is large, but that as n_0 decreases (σ being constant) the point of intersection moves forward and has usually passed beyond the minimum by the time n_0 has been reduced to a value of 4—5σ. For two adsorbed layers, this corresponds to a Kelvin radius of 2—3σ and is therefore in agreement with the experimental observations on the point of hysteresis inception.

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