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The Influence of the Surface on Phase Transitions in Two-component Systems

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The results of theoretical and experimental studies on phase transitions in semi-infinite two-component systems (immiscible liquids and polymer systems) are examined. The conditions for the formation on the substrate surface of a wetting layer of one of the equilibrium phases are discussed in detail within the framework of the average field theory taking into account the small-radius interactions between the substrate and the mixture components. The theoretical conclusions are compared with experimental data. The role of the long-range forces in the wetting transitions and the appearance of anomalously large fluctuations in the wetting films are considered in relation to the simplest models. The results of the study of critical adsorption are briefly described.
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I. INTRODUCTION

The idea, formulated in the 1960's, that fluctuations play a decisive role in the universal behaviour of various systems near the critical point (CP) has been the basis of modern theories of critical phenomena. The scaling theory and the renormalised group method[1-3] have provided a new stimulus to the study of phase transitions (PT).[4-6] Systems whose components are high-molecular compounds (solutions and mixtures of polymers) were added to the traditional objects of study (magnetic substances, alloys, liquids, two-component liquids, etc.).[7-11] The improvement of the experimental technique and the development of novel methods have made it possible to find more accurately the critical parameters characterising the variation of properties in the vicinity of the CP and to conclude that polymer systems belong to the same class, in terms of their universality, as liquids and binary mixtures of liquids.

Together with the continuation of studies on PT in the bulk phase,[12,13] the study of PT in bounded systems is of great interest. Initially the question of the influence of the surface of the substrate on the PT was considered within the framework of Landau's theory[14] applied to the magnetisation of ferromagnetic substances[15,16] and the superfluidity of helium.[17] The transition from limited to complete wettability of the surface near the CP for two-component and pure liquids has been analysed.[18,19] The characteristic features

of the PT in semi-infinite systems discovered in the above studies have attracted the attention of many investigators to this problem and at the present time various questions concerning wetting transitions are being actively elucidated.[20,21] This field of knowledge is going through a period of rapid development, associated with the appearance of an increasing number of new facts. The present review is devoted to the analysis of the behaviour of liquids with limited miscibility and polymer systems in the vicinity of the surface of the substrate. The questions discussed here, concerning the conditions governing the appearance of a wetting layer of one of the equilibrium phases, the order of the transition from complete wetting to limited wetting, and the phenomenon of critical adsorption, are analysed within the framework of the average field (AF) theory.

II. PHENOMENOLOGICAL THEORY OF PHASE TRANSITIONS IN SEMI-INFINITE SYSTEMS

The modifying effect of the substate on PT has been analysed in detail within the framework of the phenomenological theory, whose universal procedures make it possible to consider different phenomena such as surface magnetisation.[15,16,20,22] the superfluidity of helium near the λ-point,[17] and wetting transitions in immiscible liquids.[23]

The fundamental postulates of the phenomenological theory reduce to the following: (1) by analogy with the theory of PT of the second kind,[14,17] it is assumed that in the vicinity of the transition point the free energy density $f(\psi)$ can be expanded in series in terms of the order parameter ψ:

$$f(\psi) = C\psi^2 + D\psi^4 - h\psi, \tag{1}$$

where $C = C_0 t$ and C_0 and D are positive constants. Here and henceforth $t = (T - T_c)/T_c$, T is the temperature, and T_c is the critical temperature. For a two-component system, the deviation of the concentration φ from the critical value φ_c is chosen as ψ, whereupon h characterises the deviation of the difference between the chemical potentials of the components $\Delta\mu$ from the corresponding difference on the coexistence curve $\Delta\mu_c$; $h = (\Delta\mu - \Delta\mu_c)/k_B T$. (2) The wall infringes the spatial invariance of the system and in the boundary layer of the specimen the order parameter is different from its bulk-phase value. The increase in the free energy of the system as a result of the spatial inhomogeneity which has arisen at the boundary is taken into account by introducing a term proportional to the square of the gradient of the order parameter. (3) It is assumed that the forces acting from the sides of the substrate on the system involve only the first layer of molecules, which makes it possible to take into account the contribution to the free energy of the system by the interactions of the substrate with the molecules in the nearest layer with the aid of the term F_s.

Then, neglecting fluctuations and assuming that $\psi(z)$ is the average value of the order parameter in a plane parallel to the surface of the substrate and separated from it by a distance z, the free energy functional of the semi-infinite system can be written in the following form:[20]

$$F[\psi] = F_s + \int_0^\infty dz \left[f(\psi) + \frac{1}{2} k (\nabla\psi)^2 \right], \tag{2}$$

where $k > 0$ is assumed to be constant. The difference between the properties in the surface layer and in the bulk phase promotes the formation of the order parameter profile ensuring a minimum in the free energy of the system. The spatial distribution of $\psi(z)$ is obtained by solving Euler's equation:

$$k \frac{d^2\psi}{dz^2} = \frac{\partial f(\psi)}{\partial \psi} \tag{3}$$

with the following boundary conditions on the surface ($z = 0$) and in the bulk phase:

$$k \frac{d\psi}{dz}\bigg|_{z=0} = \frac{\partial F_s}{\partial \psi}\bigg|_{\psi_s = \psi(z=0)}, \tag{4}$$

$$\lim_{z\to\infty} \psi(z) = \psi_b, \tag{5}$$

where ψ_b and ψ_s are the values of the order parameter in the bulk phase and on the surface respectively.

The first integral is

$$\frac{d\psi}{dz} = \pm \{2[f(\psi) - f(\psi_b)]/k\}^{1/2}. \tag{6}$$

The sign of the derivative is determined by the ratio of the values of ψ in the bulk phase and on the boundary: if $\psi > \psi_b$, then $d\psi/dz < 0$ and conversely. It follows from Eqns.(4) and (6) that

$$\frac{\partial F_s}{\partial \psi} = \pm \{2k[f(\psi_s) - f(\psi_b)]\}^{1/2}. \tag{7}$$

Hence one can find the order parameter on the surface ψ_s. If Eqn.(7) has several roots, then each of them leads to a definite spatial distribution of $\psi(z)$. The profile ensuring the minimum surface free energy σ corresponds to the condition for equilibrium:

$$\sigma = F_s + \int_0^\infty dz \left[k \left(\frac{d\psi}{dz} \right)^2 \right]. \tag{8}$$

Having specified a simple expression for F_s, it is possible to obtain a solution to Eqns.(3)–(5) in an analytical form and to analyse the possible situations. In the main, the following form of F_s is investigated:[20,23]

$$F_s = -\frac{1}{2} g \psi_s^2 - h_1 \psi_s. \tag{9}$$

It describes the perturbing influence of the wall on the semi-infinite system as a result of the modification of the chemical potentials of the components (second term) and the changes in the interactions between the molecules at the boundary (first term). The relation between the extrapolation length $\lambda = -k/g$ and the energy of the interaction of the sites in the surface layer J_s has been established with the aid of lattice models. Having characterised the difference between J_s and the energy of the interaction of sites in the bulk phase J by the quantity $\Delta_s = J_s/J - 1$, Mills[24] and Binder and Hohenberg[25] found $\lambda^{-1} = 1 - \Delta_s/\Delta_c$, where Δ_c is the critical value of Δ_s ($\Delta_c = 4$).[26]

We shall now consider the results obtained in the solution of Eqns.(3)–(5) and (9) for the simplest case where $h = h_1 = 0$ (Figs. 1 and 2). For fixed cohesion forces of the molecules in the surface layer Δ_s, it is always possible to differentiate in the phase diagram the temperature range in which the entire specimen is in a non-ordered state: $\psi(z) = 0$ (region V in Fig.1). For $\Delta_s < \Delta_c$ ($\lambda > 0$), this state persists until the attainment of the bulk-phase PT temperature. When non-zero values of the order parameter appear in the bulk phase, the substrate tends to disorder the system (region I), which diminishes $\psi(z)$ in the vicinity of the surface (Fig.2*a*). If the interaction energy of the molecules in the surface layer exceeds the critical value ($\Delta_s > \Delta_c$, $\lambda < 0$), the non-ordered state exists throughout the bulk of the specimen at temperatures $t > t_s > 0$. At t_s, order appears in the boundary layer of molecules (the C^1_{sur} surface transition takes place), but the non-ordered state of the substance persists away from the wall. Region II in the phase diagram (Fig.1) differentiates the states of the system for which the order parameter on the surface differs from the bulk-phase value but approaches

$\psi_b = 0$ on moving away from the boundary (Fig.2*b*). The decrease in temperature to the critical value induces a bulk phase transition (extraordinary C^{∞}_{ext} transition) and the establishment in region III (Fig.1) of the profile illustrated in Fig.2*c*. The boundaries of the ordinary (C^{∞}_{ord}), extraordinary, and surface transitions converge at a single point *Sp*, where $\Delta_s = \Delta_c$ ($\lambda^{-1} = 0$). The condition $\Delta_s = \Delta_c$ means that the presence of the wall does not influence the interaction energy of the molecules, so that, as a result of a special transition (*Sp*), the state of the system changes simultaneously throughout its bulk at the critical temperature. For $t < 0$, the distribution of the order parameter is shown in Fig.2*b*.

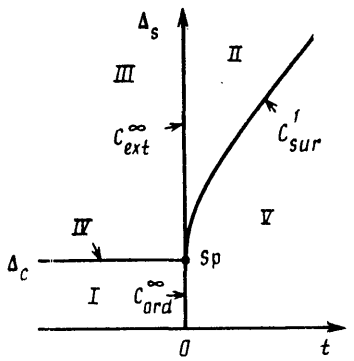


Figure 1. Schematic illustration of the phase transitions occurring in a semi-finite system[22] (for the explanation, see text).

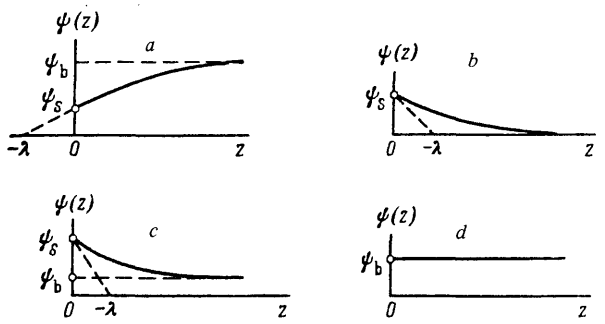


Figure 2. Variation of the order parameter ψ with the distance from the substrate surface for different values of the extrapolation length $\lambda = -k/g$ and temperatures t:[20] (a) $\lambda > 0$, $t < 0$; (b) $\lambda < 0$, $t > 0$; (c) $\lambda < 0$, $t < 0$; (d) $\lambda^{-1} = 0$, $t < 0$ ($h = h_1 = 0$ throughout).

Thus, even in the simplest case, the phenomenological theory makes it possible to discover a significant difference between the properties of the specimen in the bulk phase and in the surface layer. The nature of the transitions near the CP is controlled by the interaction energy of the molecules at the wall: an increase in Δ_s (and hence in g) increases the temperature of the surface transition and an order parameter different from the bulk-phase value appears above the critical temperature. The problem has been investigated in greatest detail in studies;[15,16,22,23] limitations on the values of the parameters h and h_1 were removed, non-classical temperature variations of the coefficients in Eqn.(1) were considered etc. More complex cases of semi-infinite systems with two order parameters have also been analysed.[27]

III. CAHN'S THEORY AND EXPERIMENTAL STUDIES ON WETTING TRANSITIONS

Consider a liquid consisting of components A and B with an upper consolute temperature (UCT). Above T_c, the liquid consists of a homogeneous phase with the composition φ_0 (concentration of component B). Below T_c, the mixture decomposes into the phases α and β, whose compositions φ_α and φ_β depend on temperature. We shall assume that phase β contains an excess of component B ($\varphi_\beta > \varphi_0$), whereupon phase α is enriched in component A ($\varphi_\alpha < \varphi_0$). As T_c is approached, the compositions of the phases coexisting at equilibrium approach one another and the interfacial tension at the $\alpha-\beta$ boundary diminishes. In the vicinity of T_c, simple scaling relations apply:[12,13]

$$\varphi_\beta - \varphi_\alpha \propto t^{\beta}, \tag{10}$$

$$\sigma_{\alpha\beta} \propto t^{\mu}, \tag{11}$$

where $\beta = 0.33$ and $\mu = 1.26$ are critical parameters. We now bring the mixture into contact with the wall, which adsorbs preferentially one of the mixture components (for example B). The behaviour of the two-phase system near the wall S is determined by the interfacial energies $\sigma_{\alpha s}$, $\sigma_{\beta s}$, and $\sigma_{\alpha\beta}$ at the S$-\alpha$, S$-\beta$, and $\alpha-\beta$ boundaries respectively. Under conditions where $\sigma_{\alpha s} - \sigma_{\beta s} - \sigma_{\alpha\beta} < 0$, the equilibrium wetting angle θ arises and Young's law holds:[28]

$$\sigma_{\alpha\beta} \cos\theta = \sigma_{\alpha s} - \sigma_{\beta s}. \tag{12}$$

In his analysis of the temperature variation of θ in the two-component system considered, Cahn[18] suggested that the difference between the interfacial energies ($\sigma_{\alpha s} - \sigma_{\beta s}$) in the vicinity of T_c is determined mainly by the compositions of the equilibrium phases and depends on temperature in the same way as $\varphi_\beta - \varphi_\alpha$. Then, taking into account Eqns.(10) and (11), we have from (12)

$$\cos\theta \propto t^{\beta-\mu}, \quad \beta-\mu = 0.93. \tag{13}$$

According to Eqn.(13), the condition for the complete wetting of the substrate surface by phase β ($\theta = 0$) is attained at a certain temperature T_W, which differs from the critical temperature. Then, when $T_c > T > T_W$, we have $\sigma_{\alpha s} - \sigma_{\beta s} - \sigma_{\alpha\beta} > 0$ and, for liquids with limited miscibility, contact with the wall by the component with the higher interfacial energy (A in the present instance) becomes unfavourable, which leads to the formation on the surface S of a layer of the phase in which the concentration of this component is lower.

The structure of the liquid at the substrate surface has been studied within the framework of the average field theory.[18] Here it is assumed that the microstructure produced in the liquid is controlled by the volume properties of the mixture, the concentration gradients, and the forces acting from the side of the wall only on the layer of molecules of the liquid adjoining it. The initial functional of the interfacial free energy has the form[18]

$$\sigma[\varphi] = F_s + \int_0^{\infty} dz \left[\Delta f(\varphi) + k\left(\frac{d\varphi}{dz}\right)^2 \right], \tag{14}$$

$$\Delta f(\varphi) = f(\varphi) - f(\varphi_0) - (\varphi - \varphi_0)\left(\frac{\partial f}{\partial \varphi}\right)\Big|_{\varphi=\varphi_0}, \tag{15}$$

where $f(\varphi)$ is the local density of the free energy of the homogeneous

liquid. The function $\Delta f(\varphi)$ reaches its minimum values for compositions corresponding to phase equilibrium [$\Delta f(\varphi_\alpha) = \Delta f(\Delta_\beta) = 0$] and has a local maximum at $\varphi_\alpha < \varphi < \varphi_\beta$. As the temperature approaches the critical value, $\Delta f(\varphi)$ at the local maximum diminishes and is very low in the vicinity of T_c.

The solution of the variational problem [Eqns.(14) and (15)] yields the spatial distribution of the concentration at the wall in each of the coexisting phases:

$$z(\varphi) = -\int_{\varphi_s}^{\varphi} [k/\Delta f(\varphi)]^{1/2}\, d\varphi. \qquad (16)$$

An elegant graphical analysis carried out by Cahn[18] established that near T_c the surface concentration φ_s is the same in both equilibrium phases and exceeds φ_β (the bulk phase concentration) for the more concentrated phase. Then, the function $\varphi(z)$ in phase α initially diminishes from φ_s *to* φ_β and at $\varphi = \varphi_\beta$ we have $\Delta f(\varphi_\beta) = 0$ and, according to Eqn.(16), $z \to \infty$, i.e. a macroscopic layer arises between the wall and phase α. Thus, a two-step transition is observed at the S$-\alpha$ interface: initially S$-\beta$ and then $\beta-\alpha$. When the temperature is appreciably below T_c, the adsorption of component B from phase α is slight and the condition $\varphi_s < \varphi_\beta$ holds. Since φ_s determines the lower integration limit in Eqn.(16), the profile of the variation of the concentration between the coexisting bulk phases β and α,[29] cut off at $\varphi = \varphi_s$, can be used to obtain the concentration profile $\varphi(z)$ at the S$-\alpha$ boundary. The transition from limited to complete wetting takes place at a definite temperature T_w and is a transition of the first kind.

The formation of a surface layer in which the concentration is close to φ_β is possible even in a homogeneous system for $\varphi_0 < \varphi_\alpha$ (under the conditions of the instability of the bulk phase having the composition φ_β). The difference from the two-phase system consists in the fact that the thickness of this layer is in this case finite, since $\Delta f(\varphi_\beta) \neq 0$.

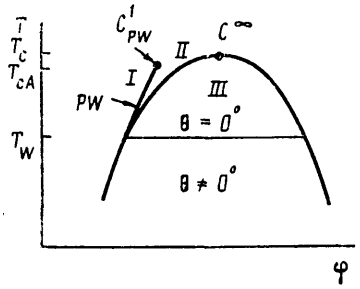


Figure 3. Phase diagram for a two-component semi-infinite system[18] (for explanation, see text).

The influence of the substrate on the two-component system is illustrated in the phase diagram in Fig.3. In the single-phase region I, the degree of adsorption of component B is low ($\varphi_s < \alpha_\beta$) and the composition of the surface layer never reaches φ_β even for $\varphi_0 = \varphi_\alpha$. Region II is one where the surface concentration exceeds the bulk phase concentration of component B in phase β. The appearance of a layer having a finite thickness with composition close to φ_β is characteristic of it. The *PW* line, separating these adsorption regions describes the concentrations of the homogeneous solution at which two profiles with different surface concentrations φ_s correspond to a single minimum in the functional (14). With increase in temperature the difference between these profiles diminishes and vanishes completely at the temperature T_{cA} at the critical point for the C^1_{PW} surface transitions (Fig.3).

Overall thermodynamic analysis[30] and the results of calculations based on different models[31–34] show that the *PW* line has a common tangent with the binodal curve at the point corresponding to the temperature T_W and the transition from the low adsorption region to the high adsorption region for systems having a UCT takes place on cooling. The deviation of T_{cA} from T_W varies from several to tens of degrees according to different estimates.[33–35] In region III (the region corresponding to complete wetting of the substrate), phase α is displaced from the surface of the wall by a macroscopic layer of phase β.

The strategy of the experimental studies of wetting transitions is determined mainly by the results of the theoretical analysis of the problem. The possibility of the appearance of wetting layers has been demonstrated already in the first study[36] of the influence of the substrate on the cyclohexane–methanol two-phase system (with a small amount of added water). The boundary with the non-critical phase (vapour) also played the role of a wall in the experiments.

Subsequent experimental studies of systems with a UCT [35,37–42] and systems with a lower consolute temperature (LCT),[43,44] carried out by various methods (visual observation,[37] capillary rise,[43] ellipsometry,[38–41] and light scattering[44] and reflection[42]), demonstrated convincingly that the formation of wetting layers is a general phenomenon associated with the influence of the surface of the wall. (The pattern arising under these conditions is illustrated schematically in Fig.4). The temperature of the transition from complete to limited wetting (T_W) differs significantly from the critical temperature. For systems with a UCT, it lies below T_c (for example, in the isopropyl alcohol–perfluoromethylcyclohexane system, $T_W = 38.0 \pm 0.1$ °C, while $T_c = 90.5° \pm 0.5$ °C [40]) and, for systems with a LCT, it lies above T_c (in the 2,6-lutidine–water system, $T_W \simeq 48$ °C, while $T_c = 34$ °C [43,44]).

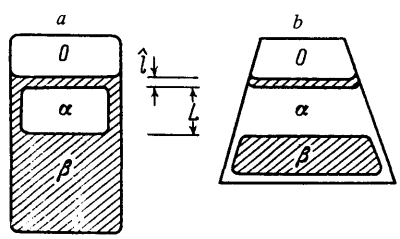


Figure 4. Experimentally observed wetting phenomena:[38] (a) methanol–cyclohexane system with added water in a glass bulb. The denser methanol phase β wets the glass surface and is distributed at the interface with the vapour 0; (b) the perfluoromethylcyclohexane–methylcyclohexane system in a quartz bulb. The lighter phase α with an increased methylcyclohexane contact wets quartz; the layer of phase β (enriched in C_7F_{14}) is distributed at the interface with the vapour.

Before considering experimental data referring to the measurement of the thickness of the wetting layers, we may note that Cahn's theory[18] was constructed without taking into account external fields.

Consequently, in the absence of the gravitational field, the wetting layer might be very thick and might occupy a considerable proportion of the volume of the system. In the gravitational field, the increased potential energy of the layer of the denser phase β at the interface with the vapour (Fig.4*a*) [or of the lighter phase α at the lower wall (Fig.4*b*)] tends to make it thinner. As a result of the balance between the gravitaional and surface forces, the equilibrium thickness of the layer $\hat{l}$ is attained. It follows from the analysis of the surface forces[45] that

$$\Pi(\hat{l}) = \Delta\rho g L, \tag{17}$$

for $\pi(\hat{l})$ represents the forces acting per unit of each of the phases separated by a film; $\Delta\rho = \rho_\beta - \rho_\alpha$, ρ_α and ρ_β are the densities of phases α and β respectively, g is the acceleration in the free fall, and L is the thickness of the layer of phase α separating the wetting film and the bulk phase β (Fig.4).

If the attenuation of the wetting layer under the influence of the gravitational field is coupled with the rearrangement of the structure of the liquid owing to the overlap of the concentration profiles formed at the boundary of the film with the vapour and phase α, then $\pi(\hat{l})$ is determined by structural repulsion forces $\pi_c(\hat{l})$. Using the expression proposed by Widom,[46]

$$\Pi_c(\hat{l}) = \sigma' \exp(-\hat{l}/\xi), \tag{18}$$

where ξ is the correlation radius of fluctuations in the bulk phase, we find that the thickness of the wetting film at the boundary with the vapour depends only slightly on the thickness of the layer of phase α but is extremely sensitive to temperature near T_c (by virtue of the temperature dependence of the correlation radius):

$$\hat{l} = \xi \ln\left|\frac{\sigma'}{\Delta\rho g L}\right|. \tag{19}$$

Under conditions remote from T_c, where structural forces do not exert a decisive influence, the layer may be stabilised by long-range van der Waals forces:[47]

$$\Pi_м(\hat{l}) = W\hat{l}^{-q}, \tag{20}$$

$$\hat{l} = \left(\frac{W}{\Delta\rho g L}\right)^{1/q}, \tag{21}$$

where W is a coefficient which depends on the polarisabilities of phases α and β.[45] The exponent q reflects the presence or absence of a lag in the molecular forces: $q = 3$ for non-lagging forces and $q = 4$ for lagging forces.[45] Since the parameter W is proportional to the difference between the polarisabilities of the equilibrium phases, which depends on temperature in the same way as $\Delta\rho$,[47] the thickness of the wetting layers stabilised by molecular forces varies only slightly with temperature. The derivation of Eqn.(21) was based on a model in which the layer is assumed to be homogeneous up to its boundaries. The model inevitably breaks down and the thickness of the zone corresponding to the transition from the layer to the bulk phase is comparable to $\hat{l}$, which may occur when L is large and the thickness of the layer $\hat{l}$ is equal to several molecular diameters or if the width of the transition region, proportional to the correlation radius of the bulk phase fluctuations, increases as the temperature approaches T_c. In such cases there is a possibility of a transition from one stabilisation regime to another.[48] When $W < 0$ (attraction between the phases separated by a layer), only structural forces prevent the attenuation of the film. The final result depends on the balance between molecular, structural, and gravitational forces.

The thickness of wetting layers at the boundary with the vapour in systems having different chemical compositions (see Table) has been investigated by the ellipsometric method.[38–41] The results show that, below the wetting temperature, the thickness of the layer does not exceed 2 nm (in the *iso*-$C_3H_7OH - C_7F_{14}$ system[40,41]). Above T_W, the thickness of the layer reaches several tens of nm.

Studies over a wide temperature range indicate clearly the existence of two different mechanisms of the stabilisation of wetting layers. The role of molecular forces in the formation of wetting layers is manifested under conditions remote from T_c, where $\hat{l} \propto L^{-1/3}$ according to experimental data and small variations in thickness with temperature are observed. However, for large values of L, structural forces are apparently involved in stabilisation, which in fact leads to a weak dependence of the thickness on L (see Table, system 2). Near the critical temperature, where the zones corresponding to the transition from the film to the phases bounding it (the gas phase and phase α in Fig. 4*a*) begin to overlap, this is found

The thicknesses of the wetting layers at the interface with the vapour (experimental data).

No. of system	Layer	Second phase	T_c, °C	T, °C	L, mm	$\hat{l}$, mm	$-1/q$	Refs.
1*	C_7F_{14}	C_7H_{14}	46.0±0.2	23 45.27	6—22 3—10	7—40 70	1/3 0	[38]
2*	CH_3OH**	C_6H_{12}	50.8	room	8—200 >200	7—15 7	1/3 0	[38]
3*	CH_3OH***	C_6H_{12}	56.18	49—53	10	10—30	—	[39]
4	C_7F_{14}	iso-C_3H_7OH	90.5±0.5	38—50	2—20	35—45	0.06	[40 41]
5****	CH_3NO_2	CS_2	63.264	<60 60.264—63.064 63.064—63.114 63.114—63.263	8.2 8.2 8.2 8.2	400 400—600 600—200 200—800	— — — —	[42]

*The wetting transition temperature is below the freezing point of the mixture.
**The water content in the system is 0.4%.
***The water content in the system is 0.333%.
****At the interface with glass.

to be the decisive factor which regulates the temperature variation of the thickness of the [wetting?] layer[39,42] and ensures the absence of a dependence on the thickness of the layer of phase α. The formation of thick wetting layers of the polar nitromethane from a nitromethane–carbon disulphide mixture on a horizontal glass surface can hardly be accounted for by the stabilising action of dispersion forces. On the other hand, calculations of the Hamaker constant performed[49,50] for this system on the basis of the Dzyaloshinskii–Lifshits–Pitaevskii theory[51] have shown that dispersion forces tend to destabilise the layer of nitromethane on the glass surface. The existence under equilibrium conditions of layers hundreds of nm thick requires the presence of forces acting over long distances. It has been suggested[49,50] that, in the presence of a polar component (nitromethane), having a high dielectric constant, the hydroxy-groups dissociate on the glass surface and the resulting electrostatic forces are involved in the stabilisation of the layer. How correct this model is will be shown by studies with careful monitoring of the surface charge.

The pronounced discrepancies between the thicknesses of the wetting layer measured experimentally and calculated using the theory of dispersion interactions[51] for certain systems[52] require the estimation of the time intervals necessary for the attainment of equilibrium. Such an estimate has been made[52] for two mechanisms of the variation of the thickness of the layer—diffusion of the mixture components to the interface and the leakage of the liquid from the layer via channels formed by the wetting layers on the surface of the vessel walls. If the growth of the layer is regulated by the diffusion of the components, then under conditions remote from T_c, the formation of the equilibrium wetting layer from liquids with limited miscibility on the surface of the substrate takes days and even months. As T_c is approached, the time required for the attainment of equilibrium increases. In a stirred system, this time is shortened but the thickness of the layer increases with increasing rate of stirring, which indicates a quasi-equilibrium state of the layer. If the equilibration mechanism in the attenuating layer is determined by the flow of liquid, then the equilibration time depends on the width of the channel and may amount to years.

A number of facts which cannot be explained within the framework of the above theoretical considerations have been discovered experimentally: a weak dependence of $\hat{l}$ on the thickness of the upper phase in the isopropyl alcohol–perfluoromethylcyclohexane (PFMCH) system (Table, system 4) and the decrease in the thickness of the wetting layer near T_c.[39,42] The results of a study of the phenol–water system are fairly unexpected from the theoretical point of view.[53] Expecting to observe a thick layer of phenol in the two-phase region at the boundary with the vapour, the authors[53] observed instead the appearance of hundreds of tiny drops which exist near the boundary for a long time.

Furthermore, studies on the wetting transitions in different systems have shown that the attainment of the critical temperature is not always accompanied by the formation of wetting layers. There are no layers at the boundary with the vapour in the cyclohexane–methanol two-component system[39] (only the addition of small amounts of water initiates transitions at the suface). This is clearly manifested in experiments on the wetting of solid substrates. Thus the temperature of the wetting transition on the glass surface in the 2,6-lutidine–water system diminishes, approaching T_c, with increase in the concentration of potassium chloride.[54] At the salt concentrations in excess of 0.072 M, the transition is suppressed and there is only limited wetting of the glass by the phase enriched in lutidine.

Glass capillaries whose surface has been methylated to different extents have been used[55,56] to investigate the wetting transitions in the nitromethane–carbon disulphide system. On a weakly methylated surface, the approach to the critical temperature is accompanied by wetting transitions of the first kind. However, when the polarity of the substrate diminishes so much that the preferential adsorption of carbon disulphide begins, the wetting transition vanishes over the entire temperature range below T_c and limited wetting of the capillary surface by the carbon disulphide phase takes place. Measurements of the wetting angle θ on glass in the systems cyclohexane–methanol with small amounts of added water, cyclohexane–aniline, and ethyl salicylate–diethylene glycol[57] have shown that in the vicinity of T_c the angle θ reaches 90°. The experimental data presented show that Cahn's theory[18] does not exhaust the entire wide variety of situations arising in real systems. The restriction of the zone where the substrate exerts an influence to direct wall–liquid contacts is an extremely controversial postulate of the theory.

The question of the existence on the phase diagram of a line separating the regions corresponding to strong and weak adsorption of one of the components also requires careful experimental confirmation (Fig.3). An attempt has been made[35] to observe a jump in the adsorption of PFMCH from an isopropyl alcohol–PFMCH mixture at the boundary with the vapour. When the homogeneous mixture was cooled slowly, the ellipticity coefficient of the light reflected from the liquid–vapour surface increased sharply. It was coupled with the appearance of a PFMCH film. Thick films are formed and persist indefinitely at a temperature higher by 0.18 K than the phase transition temperature in the bulk phase. However, when the cooling of the system was interrupted by vigorous shaking and subsequent standing until equilibration, this effect was absent. Consequently, in this instance there is no abrupt change in the degree of adsorption. The size of monodisperse spherical quartz pellets in the lutidine–water single-phase system has been measured[44] by the light scattering method as a function of the mixture composition and temperature. Having observed an increase in the intensity of the scattered light as the lutidine concentration approaches the value corresponding to the coexistence curve, the authors[44] postulated that this is due to the increase in the thickness of the adsorption layer of lutidine on the surface of the particles of the dispersion phase. It was also established that a decrease in the lutidine concentration in the mixture entails the aggregation of the particles. The curve corresponding to the aggregation of the particles on the phase diagram for this system was identified with the PW line.

IV. GENERALISED PHASE DIAGRAMS AND SURFACE SPINODAL CURVES

The place occupied by the phenomena involving wetting and the formation of a layer with a finite thickness in the overall pattern of the influence of the surface on PT is clearly defined by the phenomenological theory.[23] The inclusion of the $h\psi$ and $h_1\psi_s$ terms in Eqns.(1) and (9) for the free energy density and the direct contact energy made it possible to construct diagrams for the transitions in the space of the variables $\{t, h, h_1, g\}$.[23] Fig.5 presents the results obtained for the three previously differentiated regions based on different values of the parameter g. It follows from the functional (2) and Eqns.(1) and (9) that, when the signs of the parameters h and h_1 are changed, the quantities F, $f(\varphi)$, and F_s retain their values when ψ is replaced by $-\psi$. This means that, in the vicinity of the critical temperature, all the effects associated with the influence of

the wall and described previously for one of the equilibrium phases ($h = 0$) should be reproduced also for the other phase when the sign of the parameter h_1 changes, i.e. the wetting of the wall by one of the phases should always be observed in the vicinity of T_c. The principal characteristics of the phase diagrams for semi-infinite systems are illustrated in Fig.5: the wetting transitions for phase β (and correspondingly for phase α) at $h = 0$ are represented by the $W(D)$ lines, the set of points corresponding to the sharp change in the thickness of the adsorption layer in the single-phase system forms the $PW(PD)$ surface bounded by the loci of the critical points $C^1_{PW}(C^1_{PD})$. The character of the variation of the wetting lines for small deviations of the temperature from the critical value is described by the power relation $|t| \propto |h_1|^{1/\Delta_1}$, where $\Delta_1 = 1/2$, 1, and 3/2 [23] for $g < 0$, $g = 0$, and $g > 0$ respectively. For $g > 0$, the C^1_{PW} and C^1_{PD} lines extend to $t > 0$, meeting at the surface transition point C^1_{sur} (Fig.5*c*). The positions of the ordinary (C^∞_{ord}), special (Sp), and extraordinary (C^∞_{ext}) transitions (Fig.1) are illustrated in Fig.5 by multicritical points at which the lines of different PT intersect.

The jump in the thickness of the layer adjoining the substrate (to which the PW line in Fig.3 corresponds) may be regarded as a surface transition of the first kind. Since the existence of metastable and unstable states is associated with such transitions, then, by analogy with the PT in the bulk phase, in describing the sharp change in the thickness of the layer one may introduce the concept of the "surface" spinodal curve. The position of the surface instability curve relative to the PW line and the coexistence curve for the bulk phases has been analysed in detail.[32] It has been shown that the branches of the spinodal curve originate from the critical point C^1_{PW} and their positions on the phase diagram depend significantly on the ratio of the interaction energies of the components in the bulk phase of the system and on the surface of the substrate (Fig.6). For example, for $g < 0$, both branches of the spinodal curve terminate at the coexistence curve, the left branch being located under these conditions very close to the PW line (Fig.6*a*). It has been suggested[32,58] that the line, which is a continuation of the spinodal curve into the two-phase region of the bulk of the system, characterises the boundary of the wetting instability. According to this hypothesis, the substrate is wetted in the metastable region after the intersection of the surface spinodal curve, provided that the system was initially in the weak adsorption region and that the transition from one region in the phase diagram to the other was rapid. (If the initial state corresponds to the region with strong adsorption, wetting is observed under the conditions corresponding to the coexistence curve.) On this basis, the hypothesis was put forward that the surface of the substrate may be wetted in the two-phase region below T_W when the system passes rapidly to the region of surface instability.[32] Thus one should expect in the two-phase region a qualitatively different behaviour of the system in the vicinity of the surface of the substrate depending on the initial state and the rate of cooling. The processes occurring at the wall can compete with the initiation of the new phase in the bulk of the system. This occurs when the state of the system in the bulk phase is metastable, being stable with respect to infinitesimal changes in composition, while near the substrate surface it is unstable, i.e. unstable in relation to infinitesimal fluctuations. One can then observe the segregation of a phase from the metastable state via a barrier-free mechanism.

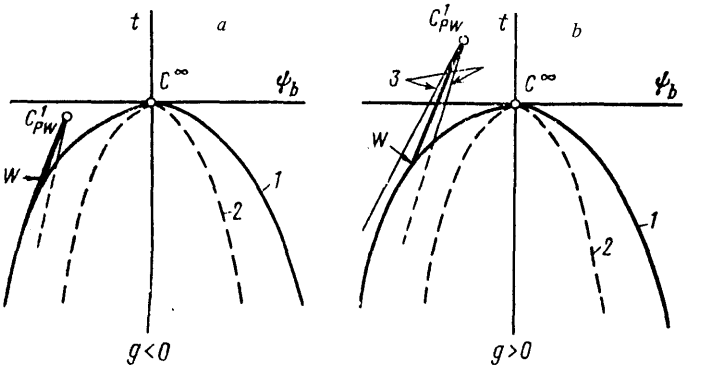


Figure 6. Phase diagram for a semi-infinite system in terms of the coordinates volume order parameter (ψ_b) – temperature (t);[32] 1) coexistence curve; 2) spinodal curve; 3) surface spinodal lines. For the significance of other notation, see the caption to Fig.5.

We shall consider next a generalised phase diagram corresponding to the case where the energy of the interaction between the molecules in the surface layer is smaller than in the bulk phase (Fig.5*a*). Calculations have shown[23] that, for certain values of the parameters h_1 and g, the transition from limited to complete wetting on moving along the coexistence curve may take place continuously and not as a result of an abrupt change in the thickness of the surface layer.

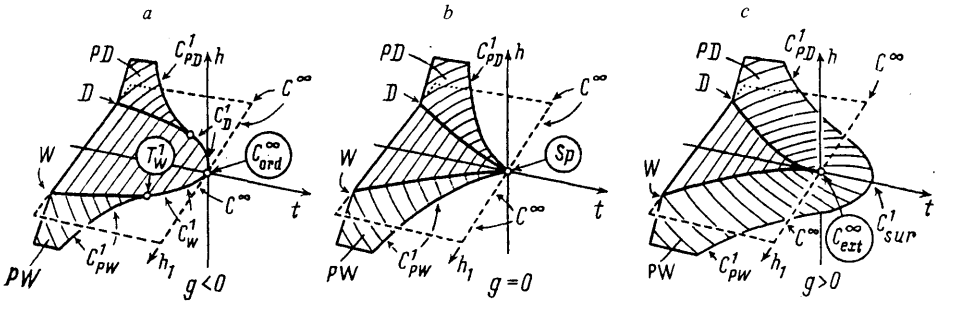


Figure 5. Phase diagram for a semi-infinite system for different values of the parameter g;[23] W, D—wetting lines; C^1_W, C^1_D—critical wetting lines; PW, PD—surfaces separating the regions with weak and strong adsorption; C^1_{PW}, C^1_{PD}—the critical point loci bounding the region; C^1_{sur}—surface transition point; C^∞—line corresponding to the transition in the bulk phase; multicritical effects are indicated within circles.

Such a transition is called a critical wetting transition (the C_W^1 and C_D^1 lines correspond to this transition in Fig.5*a*). The tricritical wetting point T_W^1 separates the W and C_W^1 transitions. The locus of the critical points C_{PW}^1 of the transition associated with the abrupt change in adsorption in single-phase systems (in systems where critical wetting takes place, PW transitions are not observed) terminates at the point T_W^1. Fig. 5*a* shows that the critical wetting occurs when $|h_1| < |h_{1,T_W^1}|$ (with increase in g, $|h_{1,T_W^1}| \to 0$). Consequently, this transition can be observed only in systems with low values of the parameter h_1.

The possibility of the continuous growth of the thickness of the wetting layer under the conditions of coexistence of the bulk phases was first pointed out in studies[59,60] where the wetting transitions were analysed using one-component liquid models. It was shown[59] that, in the critical wetting transitions, the following relation should hold for the interfacial energies:

$$\sigma_{\alpha s} - \sigma_{\beta s} - \sigma_{\alpha\beta} = -C\left(1 - \frac{T}{T_{cW}}\right)^2,$$

which leads to a temperature dependence of the wetting angle differing from the scaling relation (13):

$$\cos\theta = 1 - \frac{C(1 - T/T_{cW})^2}{D(1 - T/T_c)^{1.26}},$$

where C and D are constants and T_{cW} is the critical wetting transition temperature.

The experimental data[35,36,40,41,43,44,54–56] leave no doubt that the first order wetting transition does indeed exist. On moving along the coexistence curve, the degree of adsorption changes abruptly at some instant, becoming (in the absence of external fields) infinite. The possibility of a continuous transition is less evident. Theoretical analysis of specific systems may be of great help in selecting systems in which one should seek critical wetting transitions. As an example, we may refer to a study[61] where wetting transitions were investigated taking into account the orientation of the molecules on the substrate surface. The authors[61] observed an alternation of wetting transitions on moving along the binodal curve towards T_c. Polymer systems must also be included among specific systems: for virtual constancy of the segment–segment and segment–substrate interaction energies in such systems, it is possible to alter significantly the concentration and temperature ranges where wetting transitions may occur by varying the chain length within wide limits.

V. PHASE TRANSITIONS IN SEMI-INFINITE POLYMER SYSTEMS

Numerous theoretical and experimental studies have been devoted to questions of the adsorption of polymers.[62–66] We shall concentrate attention on the investigation of the concentration profile of polymer segments in a poor solvent, following Cahn's ideas[18] and on the basis of the results of a number of studies.[32,67–70] We shall assume that the polymer concentration on the surface is low ($\varphi_s = \lim_{z\to 0}\varphi(z)$, $\varphi_s \ll 1$), which makes it possible to neglect the interaction between the segments of the macromolecules in the first layer and to represent F_s in the form

$$F_s = \sigma_0 + \sigma_1\varphi_s, \qquad (22)$$

where σ_0 is the surface energy at the substrate–solvent interface; $\sigma_1 > 0$ corresponds to an increase in energy with increasing concentration and indicates that the interaction of the macromolecule with the substrate is unfavourable. If the adsorption of the macromolecule reduces the free energy of the system ($\sigma_1 < 0$), then the condition $\varphi_s \ll 1$ holds only for weakly binding substrates: $|\sigma_1| < k_BTa^{-2}$.[69,70]

Under ideal equilibrium conditions, the concentration profile $\varphi(z)$ is determined from the minimum in the functional

$$\sigma - \sigma_0 = -|\sigma_1|\varphi_s + \int_0^\infty dz\left[f(\varphi) - \mu\varphi + \pi + \frac{k_BT}{24a\varphi}\left(\frac{d\varphi}{dz}\right)^2\right], \qquad (23)$$

where

$$f(\varphi) = k_BTa^{-3}(\varphi N^{-1}\ln\varphi - v\varphi^2/2 + w\varphi^3/6)$$

is the local free energy density (in terms of a virial expansion) of the polymer solution,[8] a the size of the site in the Flory lattice,[7] N the number of units in the polymer chain, and v and w are parameters describing the pair and three-particle interactions between segments respectively. For v greater than the critical value v_c, it is possible to differentiate on the phase diagram a concentration range in which the formation of two phases with different polymer concentrations ensures a minimum in the free energy of the system. The functional (23) has been analysed in detail[67,68] in relation to a range of low polymer concentrations in a poor solvent. In this case, the osmotic pressure π of the macromolecules in solution is very low and one can assume that $\pi \simeq 0$ and that the chemical potential is large: $\mu \simeq k_BTa^{-3}N^{-1}\ln\varphi_0$. The introduction of the variables $\gamma = 6|\sigma_1|\cdot a\xi/k_BT$, $y = (\varphi/\varphi_\beta)^{1/2}$, $x = z/\xi$, and $\eta^2 = [\ln(\varphi_0/\varphi_\beta) + 1]/\ln\varphi_\alpha$ makes it possible to represent the functional (23) in the form

$$\frac{\sigma - \sigma_0}{|\sigma_1|\varphi_\beta} = -y_s^2 + \gamma^{-1}\int_0^\infty dx\left[y^6 - 2y^4 + \eta^2y^3 + \left(\frac{dy}{dx}\right)^2\right], \qquad (24)$$

where ξ is the correlation radius of the concentration fluctuations in solution for $\varphi_0 = \varphi_\beta$ and φ_α and φ_β are the equilibrium compositions of the dilute and concentrated phases respectively.

Next we obtain from the scheme described in Section II

$$\left(\frac{dy}{dx}\right)^2 = y^6 - 2y^4 + \eta^2y^2, \qquad (25)$$

$$-2y_s = \frac{2}{\gamma}\left(\frac{dy}{dx}\right)\Big|_{x=0} = -\frac{2}{\gamma}(y_s^6 - 2y_s^4 + \eta^2y_s^2)^{1/2}. \qquad (26)$$

It follows from Eqn.(26) that the real surface concentrations y_s can be obtained if the condition $1 - \eta^2 + \gamma^2 \geqslant 0$ is satisfied. Since η^2 is determined by the concentration of the solution, the length of the polymer chain, and temperature, it follows that, for a specified value of η, one can select substrates for which $\gamma \gg \gamma^* = (\eta^2 - 1)^{1/2}$ and $\varphi_s/\varphi_\beta = y_s^2 \simeq 1 + \gamma$, i.e. near the wall the concentration of the segments corresponds to a semidilute solution of the polymer and the "tail" of the profile extends into the bulk phase where the concentration is low. (For $\gamma < \gamma^*$, the energy of the interaction of the macromolecule where the substrate surface is low and cannot compensate for the energy expenditure on the creation of the concentration gradient, adsorption is an energetically unfavourable process.)

Detailed consideration of the density profile of the segments near the substrate surface[67,68] established that, over small distances $z < \xi$, the distribution of the concentration is determined solely by the energy of adhesion of the segments to the surface and that, for $\gamma \gg \gamma^*$, the concentration of the segments falls rapidly on moving away from the substrate. The distribution of the concentration in the central and "tail" parts of the profile depends significantly on η.

For $\eta^2 < 9/8$, a point of inflexion appears on the concentration profile and a fairly extended plateau is formed. The width of the plateau increases as the bulk-phase concentration of the polymer solution approaches values corresponding to the coexistence curve. For long distances from the substrate surface, the concentration of the segments tends exponentially towards the bulk-phase value. Thus the relations discovered in the study of the influence of the surface on homogeneous systems near the critical temperature[18] were also manifested in polymer solutions.

By expanding the local free energy density near T_c in series in terms of the order parameter $\psi = (\varphi - \varphi_c)/\varphi_c$, the functional of the free energy of the polymer system was transformed[32] into a form which has been investigated in detail within the framework of the phenomenological theory. For a polymer solution, we have

$$F_p[\psi(z)] = D^{-1}N^{-1}\left\{\int_0^D \mathrm{d}z\left[\frac{a^2}{24}N^{1/4}\left(\frac{\mathrm{d}\psi}{\mathrm{d}z}\right)^2 + \right.\right.$$
$$\left.\left. + \frac{1}{2}\left(\frac{\chi_c - \chi}{\chi_c}\right)\psi^2 + \frac{1}{12}N^{-1/4}\psi^4 - h\psi\right] - h_1\psi_s - \frac{1}{2}g\psi_s^2\right\}. \quad (27)$$

In the case of a polymer blend with equal sizes of chains of different kind, we have the expression

$$F_{cm}[\psi(z)] = D^{-1}N^{-1}\left\{\int_0^D \mathrm{d}z\left[\frac{a^2}{24}N\left(\frac{\mathrm{d}\psi}{\mathrm{d}z}\right)^2 + \right.\right.$$
$$\left.\left. + \frac{1}{2}\left(\frac{\chi_c - \chi}{\chi_c}\right)\psi^2 + \frac{1}{12}\psi^4 - h\psi\right] - h_1\psi_s - \frac{1}{2}g\psi_s^2\right\}. \quad (28)$$

In Eqns.(27) and (28), χ is the Flory–Huggins parameter,[7] χ_c is the value of χ at the critical point, and $D \to \infty$.

Thus the results of the study of the influence of the substrate surface on the phase transitions in immiscible liquids can be extended also to polymer systems. The presence of larger multipliers before the gradient terms in Eqns.(27) and (28) ($N^{1/2}$ and N respectively) compared with Eqn.(2) does not alter qualitatively the results presented in Figs.5 and 6. All the features discussed in Sections III and IV are retained on the phase diagrams of semi-infinite polymer systems. They reflect the possibility of wetting, of the transition from weak to strong adsorption in the single-phase region, and of the existence of surface spinodal curves and the associated wetting in the metastable region of the bulk of the system at a temperature below T_W. We may note that, in contrast to binary liquid mixtures for which the metastability limit is hardly attainable experimentally,[71] in polymer systems (and especially in polymer blends[72,73]) a labile state is really observed for large macromolecules ($N \to \infty$). If an analogous systems arises also in wetting polymer films, then there is a possibility of the experimental observation of the metastable and unstable wetting states.

Only the temperature range near the critical value was investigated by Nakanishi and Pincus,[32] but the parameter h_1 selected was too large, which led to the conclusion that critical wetting cannot be observed in polymer systems. The problem of the wetting of the substrate surface by polymer blends has been analysed in detail.[74] We shall consider the conditions for the occurrence of critical wetting. As we have seen above, a wetting transition of the second kind occurs when, on moving along the coexistence curve from the region of low miscibility of the components, the surface concentration increases continuously and reaches the concentration of the wetting phase. Since the region in which critical wetting occurs is bounded by the tricritical wetting point (Section IV and Fig.5*a*), it is possible to determine the concentration of the blend $\varphi_{T_W^1}$ at which the conditions $\partial^2\sigma/\partial\varphi_s^2 = 0$ and $\varphi_s = \varphi_\beta$ hold simultaneously. For a mixture of macromolecules with $N_A = N_B = N$, it was found that[74]

$$\varphi_{T_W^1} \cong -\frac{a}{g(18N)^{1/4}}. \quad (29)$$

The condition $\varphi_s = \varphi_\beta$ indicates a planar concentration profile near the substrate surface ($\mathrm{d}\varphi/\mathrm{d}z|_{z=0} = 0$). Consequently the parameter h_1 at the point T_W^1 can be estimated from Eqns.(4), (9), and (29):

$$h_{1,T_W^1} = -g\varphi_s = -g\varphi_\beta = -g(1 - \varphi_{T_W^1}) \approx -g + a(18N)^{-1/4}.$$

Then, a wetting transition of the first kind always appears for $h_1 > h_{1,T_W^1}$ and $\varphi < \varphi_{T_W^1}$, while a continuous transition is possible for $h_1 < h_{1,T_W^1}$ and $\varphi_{T_W^1} < \varphi < \varphi_c$. By altering the concentration along the branches of the binodal curve, we find the critical wetting condition for a fixed values of $h_1 < h_{1,T_W^1}$:[74]

$$\varphi_{cw} = 1 + h_1/g.$$

Thus polymer blends are good objects for the observation of critical wetting, since, by altering the chain length, it is possible to vary h_{1,T_W^1}.

Despite the considerable progress in the theoretical analysis of the problem, there have been no complete experimental investigations of wetting transitions in polymer systems. There are literature data indicating the appearance of thick adsorption polymer layers in adsorption from a poor solvent.[62,63] The adsorption of poly(methyl methacrylate), polystyrene, and their copolymers from a mixture of carbon tetrachloride (an effective solvent) and heptane (a non-solvent) on quartz particles has been investigated in fair detail.[75] With increase in heptane concentration near the limit of stability of the homogeneous solution, a sharp increase in the adsorption of polystyrene copolymers with a high styrene content was observed. There was a parallel variation also of the volume of the deposit of the disperse phase particles. These factors indicate the formation of extended adsorption layers on the surface of the quartz particles. The influence of temperature on the adsorption of the polymer near the phase transition point in the bulk of the polystyrene–cyclohexane system has been investigated.[76] The appearance of a peak on the temperature variation of the ellipticity coefficient of the light reflected from the solution–vapour boundary at polymer concentrations above the critical value was attributed[76] to the formation of a wetting film of the solvent. The examples quoted confirmed to some extent the results of the theoretical consideration of the problem. At the same time, systematic investigations of the wetting phenomena arising under PT conditions in the bulk of polymer systems have still to be carried out.

An important application of the theory discussed above involved the calculation of the interaction forces between surfaces coated by adsorption layers of macromolecules. An undoubted advantage of the theory consists in the fact that all the data necessary for the calculations (information about the sizes of the unperturbed polymer chains, adsorption, and the concentrations of the equilibrium phases) can be obtained by studying the volume properties of the solution. Such calculations have been performed[68] for the specific polystyrene–cyclohexane system and have been compared to the results of an experimental study of the interaction forces between mica plates coated by adsorption layers of polystyrene in cyclohexane.[77,79] It was found that the calculations reproduce satisfactorily the experimentally observed inhomogeneous character of the variation of the forces and make it possible to estimate the distances over which attraction between the plates begins to be manifested and is then replaced by repulsion. Since the profile of the forces is a reflection of the distribution of the concentration of the chain segments near

the substrate surface, it follows that attraction over a distance exceeding the size of the unperturbed polymer coil arises as a consequence of the increase in the polystyrene concentration in the zone corresponding to the overlap of the concentration profiles up to values in the range $\varphi_\alpha < \varphi < \varphi_\beta$. In this case, strong interactions between segments of the adsorbed chains, characteristic of the two-phase region of the system, take place, and the plates attract one another. When the plates have shifted so much that φ becomes greater than φ_β, the attraction is replaced by repulsion. Although fine details of the forces profile are fairly satisfactorily predicted by the theory, there is no complete agreement between the absolute values of the forces. This is probably because of the neglect of the possibility of the formation of bridges as a result of the binding of the macromolecule to both plates (it has been shown[80] that the formation of a small number of bridges can become the main source of the interaction between the adsorption layers).

The theory of PT in semi-infinite polymer solutions creates a satisfactory basis for the discussion of the extensive experimental data[81] on interfacial adsorption layers whose stability is fairly high, which has in fact been demonstrated.[82] We shall consider the phase diagram of a polymer solution (Fig.7), in which a boundary between regions differing in the degree of adsorption of the polymer (*PW*) and the gel formation region (shaded) was observed. Suppose that the surface activity of the polymer is fairly high so that $\varphi_s > \varphi_g > \varphi_0$ (φ_g is the concentration at which gel formation takes place). If the concentration of the solution is lower than the values corresponding to the *PW* line, the degree of adsorption is low, but as soon as the concentration exceeds these values, the degree of adsorption becomes high ($\varphi_s > \varphi_\beta$) and a plateau appears on the concentration profile [where $\varphi(z) \simeq \varphi_\beta$], whose extent increases as φ_0 approaches φ_α. If the concentration on the plateau exceeds the gel formation concentration, then a film of gel arises at the interface. The thickness of this film corresponds to the width of the plateau and in the vicinity of φ_α greatly exceeds the size of the unperturbed polymer coil.

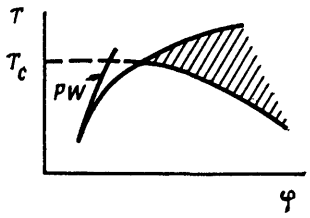


Figure 7. Phase diagram for a semi-infinite polymer solution.[82] The composition region in which gel formation takes place is shown shaded.

VI. THE ROLE OF LONG-RANGE FORCES IN WETTING TRANSITIONS

The theories of the surface transitions in semi-infinite systems considered were constructed taking into account surface forces with a small radius of action. This approach presupposes the existence of a non-specific dependence of the contact energy F_s on the composition of the surface layer and precludes an adequate description of real systems in which the zone of action of surface forces is known[45,83] not to be restricted to a monolayer. The approach to real conditions requires the analysis of the long-range action of the substrate. At the present time, theoretical studies have been carried out on continuous,[33,84–90] lattice,[31,60,91–95] and effective models of the layer.[96–100] Surface transitions in one-component systems and binary liquid mixtures are discussed within the framework of these models. An important aspect of such studies is the search for a relation beween the parameters of the microscopic interactions occurring in the system and the type of the surface transition. The introduction of the potential of the interaction between molecules in the bulk phase makes it possible to remove the limitation associated with the gradient form of the local free energy density and to describe the properties of the inhomogeneous liquid by considering the interaction occurring at the molecular level.

Careful analysis of this question, resorting to different models, showed that the type of the wetting transition is extremely sensitive to the form of the pair interaction potential. When the attraction of the molecule by the wall and by the surrounding molecules is described by potentials which decrease exponentially with increase in the distance between them, one can observe the appearance of wetting transitions of the first and second kind.[84,85] If the attraction between the molecules in the bulk phase operates over distances greater than the surface forces, a transition of the first kind occurs; otherwise we have a transition of the second kind (critical wetting). This model has been investigated in detail.[87] Much attention has been devoted to the modelling of the interactions in the system using the Lennard-Jones potentials.[31,60,85,86,89,90,101] In this case only a wetting transition of the first kind occurs and the features characteristic of it appear. It is noteworthy that the specific features of the microscopic interactions are manifested in the laws according to which the thickness of the layer increases as the system approaches saturation: $\hat{l} \propto |\ln|\Delta\mu||$ for forces with a small radius of action and $\hat{l} \propto |\Delta\mu|^{-1/3}$ for long-range forces.[31]

The interaction potentials between the molecules of the liquid and the substrate $V(z)$ and between the adsorbed molecules and the bulk of the liquid $U(z)$ have been described[89,93–96] by a more general expression

$$V(z) = -\left[\sum_{i=3}^{M} \gamma_{wi}/z^i\right], \quad U(z) = -\left[\sum_{i=3}^{M} \gamma_{fi}/z^i\right].$$

Depending on the coefficients γ_{fi} and γ_{wi}, in these systems it is possible to differentiate critical wetting, a wetting transition of the first kind, and other types of surface transitions. The important role of the terms γ_{f4}/z_4 and γ_{w4}/z^4 in the occurrence of critical wetting has been demonstrated in a study,[96] where an analytical expression was obtained for the separatrix separating the regions of the first- and second-order wetting transitions. The results[89,90,93–96,102] have shown that the fine details of the microscopic interactions are reflected in the macroscopic behaviour of the semi-infinite system: whether or not the wetting layer grows continuously or abruptly with increase in temperature and as the latter approaches T_c depends on the many-particle interactions and the structure of the substrate. Naturally, it follows from some of the above studies[89,94,96] that, in order to be able to predict the type of transition in each specific system, it is essential to have detailed information about it and the determination of such information constitutes an extremely complex problem. In their turn, experimental studies of the wetting transitions can prove an extremely valuable source of information about the microscopic interactions.

Next we shall consider, on the basis of the results of a number of studies,[21,91,92,103,105] what new contributions are made by long-range forces, compared with the forces with a small radius of action, to the

wetting transitions. As we have demonstrated above, in the latter case the presence of the substrate always initiates wetting in the vicinity of the critical temperature. We shall compare the phase diagrams presented in Fig.5 with the diagrams constructed[91,92] on the assumption that weak long-range forces exist, diminishing on moving away from the substrate surface in accordance with the law $h_{LR} \propto z^{-(m+1)}$ (where $m = 2, 3$), and there are short-range interaction forces between the molecules of the liquid (Fig.8). We shall assume that these forces promote the wetting of the substrate by phase β for $h_1 > 0$. The diagrams have many features in common: they reflect the presence of ordinary, special, and extraordinary transitions determined by the effective parameters of the interaction of the molecules of the liquid at the wall g^*; the type of behaviour of the wetting lines near T_c is the same. However, significant differences are also manifested. Fig.8 shows that, near T_c for $h_1^* < 0$ and $g^* = 0$, and $g^* > 0$, the wetting transitions, which in the case of short-range forces of the interaction of the substrate are characterised by the formation of a wetting layer (phase α) of infinite thickness (in the absence of gravitational field), now become transitions accompanied by the appearance of layers having a finite thickness (*PD*). Furthermore, for $g^* < 0$, the critical wetting transitions are transformed into wetting transitions of the first kind and the wetting of the substrate by the second phase is fully suppressed.

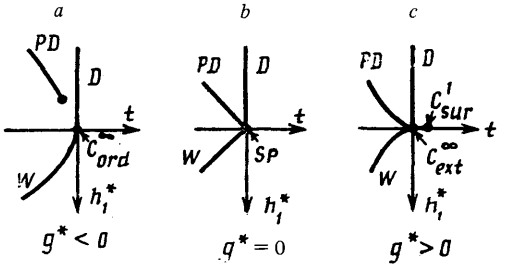


Figure 8. Phase diagram for a semi-infinite system with weak long-range forces in the substrate[92] (the legend is given in the caption to Fig.5 and further explanation can be found in the text).

The breakdown of the symmetry of the phase diagrams, characteristic of short-range potentials of the substrate (Fig.5), can find an explanation within the framework of the phenomenological theory if account is taken of the long-range effect of the substrate by including in Eqn.(2) the term[21,91,92,103–105]

$$\int_0^l [-h_{LR}(z)\,\psi(z)]\,dz, \quad l \to \infty .$$

This leads to an additional change in the interfacial free energy by the amount $\Delta\sigma = Al^{-m}$. Next, if the long-range forces cooperate with the forces of the direct interaction of the liquid molecules with the wall, then, for $h_1 > 0$, $\Delta\sigma$ is positive and the formation of a wetting layer with an infinite thickness ($l = \infty$) ensures a minimum in the free energy of the system. In this situation a macroscopic layer arises only as a result of a transition of the first kind. On the other hand, if the interactions of the substrate with the nearest layer of molecules are favourable for the other phase ($h_1 < 0$), then $\Delta\sigma < 0$ and at $t \neq 0$ the macroscopic layer of this phase never corresponds to the conditions for a minimum in the interfacial free energy, i.e. the long-range forces suppress the wetting transition. In this case critical wetting occurs at T_c.

The inhibition of the wetting transitions by long-range forces makes it possible to understand the results of experimental studies in which there was no wetting in the vicinity of T_c. On the basis of the phase diagram illustrated in Fig.8*a*, Franck and co-workers[55,56] interpreted the results of the study of such transitions in the nitromethane–carbon disulphide system on a chemically modified glass surface. It was assumed that, with increase in the number of methyl groups on the surface, the parameter h_1 diminishes monotonically, while the sign of the long-range potential of the substrate remains unaltered. The experimentally observed increase in the wetting transition temperature and its approach to the critical temperature with decrease in the polarity of the glass can then be accounted for with the aid of the phase diagram in Fig.8*a*. Indeed, when $h_1^* \to 0^+$, then we also have $t_W \to 0$. If the degree of modification of the glass surface increases so much that the preferential adsorption of carbon disulphide begins, the long-range and short-range forces compete with one another, promoting the disposition of different phases near the substrate and there is no wetting.

With increase in long-range forces, new effects appear on the phase diagrams:[92] a sequence of wetting transitions arises near T_c and wetting layers with different concentration profiles are observed in different temperature ranges. The parameter g^* plays a significant role under these conditions.

An important problem in the experimental investigation of wetting transitions is the quality of the substrate surface. In the theoretical study of this question, the wall is assumed to be ideally smooth, so that the interactions between the substrate and the liquid molecule depend solely on the coordination at right angles to the surface. However, the imperfection of the surface or the presence of impurities, both in the material itself and adsorbed on the latter, lead to random variations in the energy of the interaction of the molecules with the substrate in the plane of its surface. A recent analysis of experimental data has shown[106] that the inconstancy of the wetting energy (even when the best of the available substrates are used) influences significantly the adsorption isotherm near the two-dimensional liquid–vapour critical point. The study of this process in relation to wetting transitions[107,108] has shown that the random energy inhomogeneity of the wall does not affect the critical wetting transition and promotes a continuous variation of the degree of adsorption when the system passes from the weak adsorption region to the strong adsorption region (on intersection of the *PW* line on the phase diagrams).

VII. FLUCTUATIONS IN THE WETTING LAYERS AND CRITICAL PARAMETERS OF WETTING TRANSITIONS

In considering the wetting phenomena, we neglected previously the fluctuations in the wetting film. The underestimation of the role of fluctuations in describing the PT in the bulk phase makes the results obtained using classical theories inaccurate in the vicinity of T_c.[1–3,5] Only for systems where there are strong interactions between the molecules over long distances and for polymer blends[109–111] (with the exception of a narrow temperature range near T_c) are the conclusions based on the average field theory reliable. Appreciable interest has arisen recently in the study of fluctuations in wetting layers[30,74,87,88,97–100,112,129] and in the elucidation of their influence on the stability of the layer. Attention has been concentrated on the study of capillary waves arising at the boundaries of the wetting layer. At the same time, the appearance of fluctuations of another kind, capable of preventing the formation of a wetting layer of

the denser phase at the boundary with the vapour, has also been noted.[39,112]

Below we shall consider briefly the fluctuations in the wetting films formed when a gas is adsorbed on a substrate. The presence of the film limits the fluctuations at the film–vapour boundary, but, under the conditions of the continuous increase in the thickness of the film (for critical wetting or for an increase in concentration up to saturation), the influence of the substrate weakens and the adsorption layer terminates as the almost free liquid-vapour interface. Many characteristics of the wetting transitions, including the critical phenomena, can be explained within the framework of the model of the layer with effective interactions between the surfaces bounding the film.[97–100,113–122] In this model, the surface fluctuations are described as the deviations $\delta(x, y)$ of the position of the free boundary of the film, corresponding to its local thickness $l(x, y)$, from the equilibrium thickness $\hat{l}$: $l(x, y) = \hat{l} + \delta(x, y)$, where x and y are coordinates in a plane parallel to the substrate surface. The functional of the free energy of the film assumes the form[113–118]

$$F[l] = \int dx\,dy\left[\frac{1}{2}\sigma_{\alpha\beta}(\nabla l)^2 + V(l)\right] = F[\hat{l}] + \\ + \int dx\,dy\left[\frac{1}{2}\sigma_{\alpha\beta}(\nabla\delta)^2 + \frac{1}{2}\left(\frac{\partial^2 V(l)}{\partial l^2}\right)_{\hat{l}}\delta^2 + O(\delta^3)\right].$$

The first term describes the change in free energy as a result of the increase in the surface area as a result of the fluctations in $l(x, y)$: $V(l)$ is the effective potential of the film (it determines whether or not the attraction or repulsion of the free surface of the film by the well depends on the potentials of the interactions of the molecules with the substrate). If the attraction between the surfaces bounding the film is fairly strong and retains the free film surface at a certain distance l from the wall, then the change in conditions is accompanied by a continuous decrease in this attraction. We shall assume that the substrate is impermeable to the molecules of the liquid. Then the potential $V(l)$ of the wetting films formed from the single-phase systems depends on the extent to which the vapour has failed to reach saturation and in the case of surface forces with small radius of action has the following form:[115–119,123]

$$V(l) = A\exp(-\tau l) + |\Delta\mu|\,l, \tag{30}$$

while in the case of long-range forces we have[115–118]

$$V(l) = Bl^{-m} + |\Delta\mu|\,l, \tag{31}$$

where A, B, and τ are coefficients and $\Delta\mu$ is the deviation of the chemical potential from its value on the coexistence curve. Wetting in model systems whose potential $V(l)$ is described by Eqns.(30) and (31) takes place for positive values of the coefficients A and B, whereupon $\Delta\mu \to 0$.

In the model considered, the dependence of the equilibrium film thickness $\hat{l}$, the correlation radius of the surface fluctuations $\xi_{\|}$, and the interfacial free energy on the degree of unsaturation can be found from the relations

$$\left.\frac{\partial V(l)}{\partial l}\right|_{\hat{l}} = 0;\ \sigma_{\alpha\beta}(\xi_{\|})^{-2} = \frac{\partial^2 V(l)}{\partial l^2};$$
$$\sigma_s = V(\hat{l}). \tag{32}$$

The character of the variation of these quantities for $\Delta\mu \to 0$ makes it possible to determine the critical parameters of the wetting transition β_s, $\nu_{\|}$, and α_s:

$$\hat{l} \propto |\Delta\mu|^{\beta_s};\ \xi_{\|} \propto |\Delta\mu|^{-\nu_{\|}};\ \sigma_s \propto |\Delta\mu|^{2-\alpha_s} \tag{33}$$

For systems where only small-radius interaction forces exist, it follows from Eqns.(30), (32), and (33) that $\beta_s = 0$, $\nu_{\|} = 1/2$, and $\alpha_s = 1$; if the intensity of the interactions between the liquid molecules and the substrate diminishes in accordance with a power law, the critical parameters depend on the parameter m in Eqn.(31):

$$\beta_s = -(m+1)^{-1};\quad \nu_{\|} = (m+2)/(2m+2),$$
$$\alpha_s = (m+2)/(m+1)$$

[for non-lagging van der Waals forces ($m = 2$), we have $\beta_s = -1/3$, $\nu_{\|} = 2/3$, and $\alpha_s = 4/3$ [114–118,123]]. Thus the appearance of a macroscopic wetting layer on the substrate surface as the coexistence curve is approached is accompanied by an increase in fluctuations on the free surface of the layer. This factor indicates the similarity of the behaviour of the systems in the wetting transitions to the behaviour of the bulk-phase systems near the critical point.

The question arises whether the growing fluctuations alter the results obtained within the framework of the average field theory for surface wetting transitions. An answer may be obtained by estimating with the aid of a suitable hyperscaling relation,[116,118] for example:

$$(d-1)\nu_{\|} = 2 - \alpha_s \tag{34}$$

the limiting number of dimensions d^* of the space.[1–3] The character of the variation of the quantities $\hat{l}$, $\xi_{\|}$, and σ_s as a function of $\Delta\mu$ is predicted correctly by the average field theory, provided that the number of dimensions of the space in which the transition is investigated is greater than d^*. By substituting in Eqn.(34) the values of $\nu_{\|}$ and α_s quoted above, it is possible to find d^*. For the modelling of the interactions in the film by means of the potential defined by Eqn.(30), we have $\nu_{\|} = 1/2$ and $\alpha_s = 1$, so that $d^* = 3$. Additional analysis of this case showed[117] that, for a three-dimensional space, the average field theory yields the correct values of the wetting parameters. Under the conditions of long-range action, the quantity d^* is extremely sensitive to the character of the variation of the forces: $d^*(m) = (3m + 2)/(m + 2)$, but, for finite values of m, the quantity $d^*(m) < 3$ (long-range forces diminish d^*, as for the critical phenomena in the bulk phase). Thus the average field theory describes correctly the influence of the substrate surface on total wetting transitions.

Critical wetting is also accompanied by an increase in surface fluctuations. The parameter $\nu_{\|}$ in the temperature variation of the correlation radius, calculated in accordance with the average field theory for models in which the existence of only forces with a small radius of action is postulated, is 1, while $d^* = 3$.[116,124] However, in critical wetting the role of fluctuations is more significant; $\nu_{\|}$ loses its universality and depends on the dimensionless parameter $\omega = k_B T(4\pi\sigma_{\alpha\beta}\xi_{\|}^2)^{-1}$. Three ranges of ω values have been differentiated:[119–122,125] $\omega < 1/2$ with $\nu_{\|} = (1 - \omega)^{-1}$, $1/2 < \omega < 2$ with $\nu_{\|} = (2^{1/2} - \omega^{1/2})^{-2}$, and $\omega > 2$ with $\nu_{\|} = \infty$. It has been suggested[122,128] that, for pure liquids, their binary mixtures, and polymer systems (as well as other systems which belong to this class of universality), the parameters ω near T_c refer to the second region (according to Moldover,[13] $\omega \simeq 0.8$). If the fluctuations in the wetting films are small, then $\nu_{\|} = 1$. The transition from the classical forms of critical conditions, obtained on the basis of the average field theory, to the non-classical form occurs when the correlation radius of the surface fluctuations is equal to to 5–6 molecular diameters.[129] The experimental confirmation of the relations described in real systems, where long-range forces play an important role, is hardly feasible.

Under the conditions of the existence of long-range forces, the critical behaviour of three-dimensional systems is independent of the surface tension and surface fluctuations do not alter the average field

regime.[99,119] For potentials of the type $V(l) = A(T - T_{cW})l^{-n} + Bl^{-m}(A, B > 0, m > n > 0)$, we have $\beta_s = -1/(m-n)$ and $\nu_{\|} = (m+2)/2(m-n)$. So far the problem of the experimental confirmation of the theory remains open.

VIII. CRITICAL ADSORPTION

The picture of the influence of the surface on PT in two-component systems must be supplemented by considering the adsorption of the components from a homogeneous mixture having the critical composition. It has been established that in the vicinity of T_c an anomalous increase in the degree of adsorption of one of the mixture components on the surface of the wall is observed. This phenomenon is called critical adsorption. Its essential feature reduces to the following. Under the conditions of the preferential interaction of one of the components with the wall, the composition of a mixture of liquids changes over distances from the wall surface comparable to the correlation radius of the fluctuations in the bulk phase. Since the approach to T_c induces a sharp increase in the fluctuations in the system, within a certain concentration and temperature range near the critical point, an extended region should arise at the substrate surface in which the mixture composition differs from the bulk-phase composition. The closer the system is to the critical point, the wider the layer of liquid in which the composition is modified.

The critical adsorption phenomenon, first observed by Rusanov and co-workers,[130-132] has become the subject of intense theoretical and experimental studies. It is possible to distinguish two theoretical approaches to the consideration of critical adsorption in two-component systems. The first of these is based on the thermodynamic Gibbs relation for adsorption:[133]

$$\Gamma_{B(A)} = -\left(\frac{\partial\sigma}{\partial\mu}\right)_T = -\left(\frac{\partial\sigma}{\partial\varphi}\right)_T\left(\frac{\partial\varphi}{\partial\mu}\right)_T, \tag{35}$$

(where $\Gamma_{B(A)}$ is the relative degree of adsorption) and requires knowledge of the equation of state and of the character of the variation of the surface tension as a function of mixture composition and temperature in the critical region. In modern theories of critical phenomena,[1-3] the dependence of the chemical potential on composition is described by the expression $|\mu - \mu_c| \simeq |\varphi - \varphi_c|^{4.8}$, where μ_c is the critical potential of component B in the mixture at the critical point. The studies by Widom and co-workers[134-138] have led to the conclusion that, in the vicinity of the critical point, the surface tension is a monotonic function of composition, increasing with increase in the concentration of the component with a higher value of σ. At the critical temperature, the form of the function $\sigma(\varphi)$ is analogous to the form of the critical isotherm for a one-component liquid. The form of the dependence of the surface tension on concentration has been established:[133,138]

$$|\sigma - \sigma_c| \propto |\varphi - \varphi_c|^{\mu/\beta}, \mu/\beta \cong 3.9. \tag{36}$$

When the classical values of the critical parameters $\mu = 3/2$ and $\beta = 1/2$ are used, the concentration dependence of the deviation of the surface tension from its value at the critical point σ_c becomes more pronounced:[133,134]

$$|\sigma - \sigma_c| \propto |\varphi - \varphi_c|^3 \ln[|\varphi - \varphi_c|^{-1}]. \tag{37}$$

The experimental data for the nitrobenzene–hexane,[131] nitroethane–3-methylpentane,[137] and isobutytric acid–water[137,138] systems agree with the principal theoretical conclusions concerning the character of the variation of σ with concentration. However, the inadequate accuracy of the methods for the measurement of surface tension and the methodological difficulties arising in measurements in the critical region makes it impossible to determine which of the relations (36) and (37) holds.

The temperature dependence of the degree of adsorption near T_c can be obtained from Eqns.(35)–(37):

$$\Gamma_{B(A)} \propto |t|^{\beta-\nu} = |t|^{-0.3}, \tag{38}$$

$$\Gamma_{B(A)} \propto \ln|t^{-1}|, \tag{39}$$

where ν is the critical exponent in the temperature variation of the correlation ranges of the volume fluctuations. (The classical form of the equation of state $|\mu - \mu_c| \propto |\varphi - \varphi_c|^3$ is used in the derivation of the last relation.)

The second way of investigating critical adsorption is associated with the elucidation of the concentration profile at the interface beween the binary liquids with the critical composition and the wall. This procedure can be used in the analysis of the liquid–vapour and liquid–solid interfaces. A wide variety of theoretical approaches are adopted for the investigation of the form of the concentration profile: the average field theory,[134-136] scaling,[139] the renormalised group method,[140-142] and the method of functional expansions.[143-145] We may note that in the case under consideration an approximation is used according to which the existence of surface forces with a small radius of action is postulated. This approximation is entirely justified, since, with increase in the correlation radius, the wall has no influence over long distances ($z > \xi$).

The average field theory postulates a slow decrease in the concentration of the adsorbed component with increase in the distance from the surface:[133,134,143]

$$\Delta\varphi(z) = \varphi(z) - \varphi_c \propto z^{-1}. \tag{40}$$

More realistic models, constructed either on the basis of the equations of state for two-component liquids, reflecting the real features of the critical systems,[133,135,140,143,144] or using modern theories of critical phenomena,[139-142] yield a different form of the concentration profile. According to a number of workers,[139-142] one of the mixture components is adsorbed preferentially at the boundary with the substrate at the critical point, the decrease in the concentration of this component on moving away from the wall obeying the law

$$\Delta\varphi(z) \propto z^{-\beta/\nu}. \tag{41}$$

If the experimental temperature differs from T_c, then Eqn.(41) holds only within the limits of the correlation radius and is then replaced by another equation according to which the composition changes faster:

$$\Delta\varphi(z) \propto \exp(-z/\xi), \quad z \gg \xi. \tag{42}$$

The excess concentration of the adsorbed component can be determined by analysing the profile

$$\Gamma \propto \int_0^\infty \Delta\varphi(z)\,dz. \tag{43}$$

In order to elucidate the character of the temperature variation of the degree of adsorption, one introduces the hypothesis that, over distances exceeding the molecular size a, Eqns.(41) and (42) hold, while in the range $0 < z < a$ the concentration is constant and $\varphi(z) = \varphi_s$. In this case, the surface excess is described by an expression of the type

$$\Gamma = a\varphi_s\left[\frac{2\nu-\beta}{\nu-\beta}\left(\frac{\xi}{a}\right)^{1-\beta/\nu} - \frac{\beta}{\nu-\beta}\right] \propto |t|^{\beta-\nu}. \tag{44}$$

(For a liquid–vapour interface, a similar discussion has been published elsewhere.[133-136,143-145])

The critical liquid–vapour[130–132,146–150] and critical liquid–solid wall[151–155] interfaces are studied experimentally with the aid of a wide variety of optical methods. In the studies quoted above, an anomalous behaviour of structure-centred parameters in the vicinity of the critical point has been noted. In the study of the surface of the nitrobenzene–hexane binary mixture having a nearly critical composition, a sharp increase in the ellipticity coefficient was observed in the vicinity of T_c.[130,142] Ellipsometric studies of the liquid–vapour interfaces in various critical mixtures have been continued.[150] Rusanov and Pshenitsyn,[130] Peliti and Leibler,[142] and Schmidt and Moldover[150] concluded that the observed anomalies are caused solely by surface phenomena and indicate an increase in the degree of adsorption in the critical region. Critical adsorption of the components of the nitrobenzene–hexane mixture on a glass surface has been investigated by the fluorescence method.[151] The increase in the fluorescence intensity near the critical point is explained by the selective interaction of nitrobenzene with glass. It has been established[152–154] that an increase in the intensity of the reflection of light from the interface between glass and a mixture of nitromethane with carbon disulphide is due to the critical adsorption of nitromethane; the change in the polarity of the glass induced by making it hydrophobic promoted the preferential interaction of carbon disulphide with the substrate and the consequent decrease in the reflection coefficient.

Although there is convincing evidence for the anomalously high degree of adsorption in the critical region, a quantitative interpretation of the experimental results presents certain difficulties. Firstly, it is necessary to establish the relation between the parameters measured experimentally and the degree of adsorption[146,149] and the distribution of concentration in space.[76,148,150,155] Secondly the conclusion about the temperature variation of the degree of adsorption or about the concentration profile must be based on a comparison of relations fairly similar in form: $\Gamma \propto \ln(t^{-1})$ and $\Gamma \propto (t)^{-0.3}$, $\Delta\varphi(z) \propto z^{-1}$ and $\Delta\varphi(z) \propto z^{-1/2}$. These factors are apparently the cause of the ambiguous interpretation of the experimental data. Thus a logarithmic temperature dependence of the degree of adsorption of cyclohexane at the interface with vapour from solutions in aniline has been established.[146,147] It has been found[149] that the critical adsorption parameter is 0.35 ± 0.15, but at the same time there is a temperature range in which the results are described satisfactorily by linear relation between Γ and $\ln(t^{-1})$. On the basis of a study of the temperature variation of the ellipticity coefficient of the light reflected from the interface between the vapour and a solution of polystyrene in cyclohexane, it has been demonstrated[75] that, for the critical adsorption of the solvent, the concentration profile corresponds to Eqns.(41) and (42). The data of Heidel and Findenegg[148] also agree with the model for which Eqns.(41) and (42) are valid, but the $\Delta\varphi(z) \propto z^{-1}$ relation cannot be fully excluded. The application of the methods for the solution of the converse ellipsometric problem developed recently may prove useful for the final elucidation of the question of the distribution of concentration in the adsorption layer under the conditions of critical adsorption, together with an increase in experimental accuracy.[156]

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It follows from the data presented that the presence of the wall leads to the appearance of a whole range of transitions near the surface. The study of the physics of phase transitions and of the physical chemistry of surfaces has ensured during the last 5–10 years rapid progress in the theory of transitions induced by the presence of the wall. In a brief review, it is impossible to reflect fully all the fine details of the models used in the consideration of various aspects of wetting transitions and to discuss comprehensively all the theoretical results obtained with their aid. Preference has been given to the clearest data reflecting important aspects of the phenomenon.

The experimental study of the problem requires considerable effort associated both with the preparation of the objects of study and with the careful thermostatic control of the system, on the one hand, and with the long equilibration time, on the other. So far there are no experimental data on wetting transitions in polymer systems, although certain hopes for the attainment of a combination of the interactions between the components which is manifested in the form of critical wetting are in fact associated with precisely these systems. There are scanty data concerning the existence in a homogeneous system of regions characterised by significantly different degrees of adsorption of the mixture components on the substrate. There have been no studies whatever of labile states of the surface layer. These and other questions require comprehensive consideration.

REFERENCES

1. H.E.Stanley, "Introduction to Phase Transitions and Critical Phenomena" (Translated into Russian), Izd. Mir, Moscow, 1973.
2. S.Ma, "Modern Theory of Critical Phenomena" (Translated into Russian), Izd. Mir, Moscow, 1980.
3. A.Z.Patashinskii and V.L.Pokrovskii, "Fluktuatsionnaya Teoriya Fazovykh Perekhodov" (Fluctuation Theory of Phase Transitions), Izd. Nauka, Moscow, 1982.
4. B.Chu, Ber. Bunsenges. Phys. Chem., 1972, **76**, 202.
5. M.A.Anisimov, Uspekhi Fiz. Nauk, 1974, **114**, 249.
6. A.Kumar, H.R.Krishnamurthy, and E.S.R.Gopal, Phys. Repts., 1983, **98**, 57.
7. P.Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca–New York, 1953.
8. P.G.de Gennes, "Scaling Ideas in Polymer Physics" (Translated into Russian), Izd. Mir, Moscow, 1982.
9. S.P.Papkov, "Studneobraznoe Sostoyanie Polimerov" (The Gel State of Polymers), Izd. Khimiya, Moscow, 1974.
10. S.P.Papkov, "Ravnovesie Faz v Sisteme Polimer–Rastvoritel" (Phase Equilibrium in a Polymer–Solvent System), Izd. Khimiya, Moscow, 1981.
11. A.E.Nesterov and Yu.F.Lipatov, "Termodinamika Rastvorov i Smesei Polimerov" (Thermodynamics of Polymer Solutions and Blends), Izd. Naukova Dumka, Kiev, 1984.
12. C.Houessou, P.Guenoun, R.Gastaud, et al., Phys. Rev. A, 1985, **32**, 1818.
13. M.R.Moldover, Phys. Rev. A, 1985, **31**, 1022.
14. L.D.Landau and E.M.Lifshits, "Statisticheskaya Fizika" (Statistical Physics), Izd. Nauka, Moscow, 1976, Part 1.
15. N.S.Karpinskaya, Fiz. Tverd. Tela, 1979, **21**, 1160.
16. M.I.Kaganov and M.S.Karpinskaya, Zhur. Eksper. Teor. Fiz., 1979, **76**, 2143.
17. V.L.Ginzburg and A.A.Sobyanin, Uspekhi Fiz. Khim., 1976, **120**, 153.
18. J.W.Cahn, J. Chem. Phys., 1977, **66**, 3367.
19. C.Ebner and W.F.Saam, Phys. Rev. Lett., 1977, **38**, 1486.

20. K.Binder, "Phase Transitions and Critical Phenomena" (Edited by C.Domb and J.L.Lebowitz), Acad. Press., London–New York, 1983, pp.1, 467.
21. P.-G.de Gennes, Rev. Modern Phys., 1985, **57**, 827.
22. T.C.Lubensky and M.H.Rubin, Phys. Rev. B, 1975, **12**, 3885.
23. H.Nakanishi and M.E.Fisher, Phys. Rev. Lett., 1982, **49**, 1565.
24. D.L.Mills, Phys. Rev. B, 1973, **8**, 4424.
25. K.Binder and P.C.Hohenberg, Phys. Rev. B, 1974, **9**, 2194.
26. H.A.Coccatto, J. Phys. A, 1986, **19**, 751.
27. M.E.Costas, C.Varea, and A.Robledo, Phys. Rev. Lett., 1983, **51**, 2394.
28. E.D.Shchukin, A.V.Pertsov, and E.A.Amelina, Kolloid. Khim., 1982.
29. J.W.Cahn and J.E.Hilliard, J. Chem. Phys., 1958, **28**, 258.
30. E.Hauge and M. Schick, Phys. Rev. B, 1983, **27**, 4288.
31. R.Pandit, M. Schick, and M. Wortis, Phys. Rev. B, 1982, **26**, 5112.
32. H.Nakanishi and P.Pincus, J. Chem. Phys., 1983, **79**, 997.
33. P.Tarazona, M.M.Telo da Gama, and R.Evans, Mol. Phys., 1983, **49**, 283, 301.
34. A.K.Sen and C.Ebner, Phys. Rev. B, 1986, **33**, 5076.
35. J.W.Schmidt and M.R.Moldover, J. Chem. Phys., 1986, **84**, 4563.
36. M.R.Moldover and J.W.Cahn, Science, 1980, **207**, T35.
37. V.Vani, S.Guha, E.S.R.Gopal, and S.M.Rao, Phys. Lett. A, 1983, **99**, 441.
38. O.D.Kwon, D.Beaglehole, W.W.Webb, et al., Phys. Rev. Lett., 1982, **48**, 185.
39. D.Beaglehole, J. Phys. Chem., 1983, **87**, 4749.
40. J.W.Schmidt and M.R.Moldover, J. Chem. Phys., 1983, **79**, 379.
41. M.R.Moldover and J.W.Schmidt, Physica D, 1984, **12**, 351.
42. X.-L.Wu, M. Schlossman, and C.Franck, Phys. Rev. B, 1986, **33**, 402.
43. D.W.Pohl and W.I.Goldburg, Phys. Rev. Lett., 1982, **48**, 1111.
44. D.Beysens and D.Esteve, Phys. Rev. Lett., 1985, **54**, 2123.
45. B.V.Deryagin, N.V.Churaev, and V.M.Muller, "Poverkhnostnye Sily" (Surface Forces), Izd. Nauka, Moscow, 1986.
46. B.Widom, J. Chem. Phys., 1978, **68**, 3878.
47. P.-G.de Gennes, J. Phys. Lett. (France), 1981, **42**, L337.
48. P.Tarazona, M.M.Telo da Gama, and M.Robert, J. Chem. Phys., 1987, **86**, 1521.
49. R.F.Kayser, Phys. Rev. Lett., 1986, **56**, 1831.
50. R.F.Kayser, Phys. Rev. B, 1986, **34**, 3254.
51. I.E.Dzyaloshinskii, E.M.Lifshits, and L.P.Pitaevskii, Uspekhi Fiz. Nauk, 1961, **73**, 381.
52. R.F.Kayser, M.R.Moldover, and J.W.Schmidt, J. Chem. Soc. Faraday Trans. II, 1986, **82**, 1701.
53. F.Guzman and J.W.Schmidt, J. Phys. Chem., 1987, **91**, 263.
54. L.Sigl and W.Fenzl, Phys. Rev. Lett., 1986, **57**, 2191.
55. D.J.Durian and C.Franck, Phys. Rev. Lett., 1987, **59**, 555.
56. K.Abeysurija, X.-L.Wu, and C. Franck, Phys. Rev. B, 1987, **35**, 6771.
57. S.Ross and R.Kornbrekke, J. Colloid Interface Sci., 1984, **99**, 446.
58. E.Bruno, C.Coccamo, and P.Tarazona, Phys. Rev. A, 1986, **34**, 2513; 1987, **35**, 1210.
59. D.E.Sullivan, J. Chem. Phys., 1981, **74**, 2604.
60. R.Pandit and M. Wortis, Phys. Rev. B, 1982, **25**, 3226.
61. T.J.Sluckin and J.T.Chalker, J. Phys. Lett. (France), 1984, **45**, L863.
62. Yu.S.Lipatov and L.N.Sergeeva, "Adsorbtsiya Polimerov" (Adsorption of Polymers), Izd.Naukova Dumka, Kiev, 1972.
63. Yu.S.Lipatov, "Mezhfaznye Yavleniya v Polimerakh" (Interfacial Phenomena in Polymers), Izd. Naukova Dumka, Kiev, 1980.
64. M.A.Cohen Stuart, T.Cosgrov, and B.Vincent, Adv. Colloid Interface Sci., 1986, **24**, 143.
65. G.Flier and J.Liklema, "Adsorption from Solution at the Solid/Liquid Interface" (Edited by G.G.Parfitt and C.H.Rochester) (Translated into Russian), Izd. Mir, Moscow, 1986, p.182.
66. P.-G.de Gennes, Adv. Colloid Interface Sci., 1987, **27**, 189.
67. J.Klein and P.Pincus, Macromolecules, 1982, **15**, 1129.
68. K.Ingersent, J.Klein, and P.Pincus, Macromolecules, 1986, **19**, 1374.
69. P.-G.de Gennes, Macromolecules, 1981, **14**, 1637.
70. P.-G.de Gennes, Macromolecules, 1982, **15**, 492.
71. J.W.Cahn, "Critical Phenomena in Alloys, Magnetics and Superconductors" (Edited by R.I.Jafer, R.E.Mills, and E.Ascher), McGraw-Hill, New York, 1971, p.41.
72. P.-G.de Gennes, J. Chem. Phys., 1980, **72**, 4756.
73. P.Pincus, J. Chem. Phys., 1981, **75**, 1996.
74. I.Schmidt and K.Binder, J. Phys. (France), 1985, **46**, 1631.
75. I.F.Guthrie and G.J.Howard, "Polymer Adsorption and Dispersion Stability" (Edited by E.D.Goddard and V.Vincent), Amer. Chem. Soc., Washington, 1984, p.297.
76. B.Heidel and G.H.Findenegg, J. Chem. Phys., 1987, **87**, 706.
77. J.Klein, J. Chem. Soc. Faraday Trans I, 1983, **79**, 99.
78. J.Klein and P.F.Luckham, Macromolecules, 1986, **19**, 2007.
79. J.N.Israelachvili, M.Tirrell, J.Klein, and Ya.Almog, Macromolecules, 1984, **17**, 204.
80. S.Granick, S.Pattell, and M.Tirrell, J. Chem. Phys., 1986, **85**, 5370.
81. V.N.Izmailova and P.A.Rebinder, "Strukturoobrazovanie v Belkovykh Sistemakh" (Structure Formation in Protein Systems), Izd.Nauka, Moscow, 1978.
82. M.W.Kim, D.G.Peiffer, and P.Pincus, J. Phys. Lett. (France), 1984, **45**, L953.
83. Yu.M.Malinskii, Uspekhi Khim., 1970, **39**, 1511 [Russ. Chem. Rev., 1970(8)].
84. G.F.Telezke, L.E.Scriven, and H.T.Davis, J. Chem. Phys., 1982, **77**, 5794; 1983, **78**, 1431.
85. P.Tarazona and R.Evans, Mol. Phys., 1983, **48**, 799.
86. R.Evans and P.Tarazona, J. Chem. Phys., 1984, **80**, 587.
87. T.Aukrust and E.H.Hauge, Physica A, 1987, **141**, 427.
88. J.K.Percus, J. Stat. Phys., 1987, **47**, 801.
89. D.M.Kroll and T.F.Meister, Phys. Rev. B, 1985, **31**, 392.
90. T.F.Meister and D.M.Kroll, Phys. Rev. A, 1985, **31**, 4055.
91. C.Ebner and W.F.Saam, Phys. Rev. B, 1987, **35**, 1822
92. C.Ebner and W.F.Saam, Phys. Rev. Lett., 1987, **58**, 587.
93. C.Ebner, W.F.Saam, and A.K.Sen, Phys. Rev. B, 1985, **31**, 6135.
94. C.Ebner, W.F.Saam, and A.K.Sen, Phys. Rev. B, 1985, **32**, 1558.
95. S.Dietrich and M.Schick, Phys. Rev. B, 1985, **32**, 4718.
96. S.Dietrich and M.Schick, Phys. Rev. B, 1986, **33**, 4952.
97. M.P.Nightingale, W.F.Saam, and M.Schick, Phys. Rev. Lett., 1983, **51**, 1275.
98. W.F.Saam, Surface Sci., 1983, **125**, 253.
99. M.P.Nightingale, W.F.Saam, and M.Schick, Phys. Rev. B, 1984, **30**, 3830.

100. S.Dietrich, M.P.Nightingale, and M.Schick, Phys. Rev. B, 1985, **32**, 3182.
101. J.H.Sikkenk, J.O.Indekeu, J.M.J.van Leeuwen, and E.O.Vossnack, Phys. Rev. Lett., 1987, **59**, 98.
102. F.Van Swol and J.R.Henderson, J. Chem. Soc. Faraday Trans. II, 1986, **82**, 1685.
103. V.Privman, J. Chem. Phys., 1984, **81**, 2463.
104. P.-G.de Gennes, Compt. rend. Ser. 2, 1983, **297**, 9.
105. M.P.Nightingale and J.O.Indekeu, Phys. Rev. B, 1985, **32**, 3364.
106. R.E.Ekke, J Ma, A.D.Migone, and T.S.Sullivan, Phys. Rev. B, 1986, **33**, 1746.
107. G.Forgacs, H.Orland, and M.Schick, Phys. Rev. B, 1985, **32**, 4683.
108. R.Kariotis, J. Phys. A, 1986, **19**, L979.
109. P.-G.de Gennes, J. Phys. Lett. (France), 1977, **38**, L441.
110. J.F.Joanny, J. Phys. A, 1978, **11**, L117.
111. K.Binder, Phys. Rev. A, 1984, **29**, 341.
112. P.Tarazona and R.Evans, Mol. Phys., 1982, **47**, 1033.
113. P.Tarazona, R.Evans, and U.Marini-Bettolo Marconi, Mol. Phys., 1985, **54**, 1357.
114. D.M.Kroll and R.Lipowsky, Phys. Rev. B, 1983, **28**, 5273.
115. R.Lipowsky, D.M.Kroll, and R.K.P.Zia, Phys. Rev. B, 1983, **27**, 4499.
116. R.Lipowsky, Z. Phys. B, 1984, **55**, 335, 345.
117. R.Lipowsky, Phys. Rev. Lett., 1984, **52**, 1429.
118. R.Lipowsky, Phys. Rev. B, 1985, **32**, 1731.
119. D.S.Fisher and D.A.Huse, Phys. Rev. B, 1985, **32**, 247.
120. D.M.Kroll, R.Lipowsky, and R.K.P.Zia, Phys. Rev. B, 1985, **32**, 1862.
121. M.E.Fisher, J. Chem. Soc. Faraday Trans. II, 1986, **82**, 1569.
122. E.Brézin and T.Halpin-Healy, J. Phys. (France), 1987, **48**, 757.
123. R.Evans and P.Tarazona, Phys. Rev. Lett., 1984, **53**, 400.
124. E.Brézin, B.I.Halperin, and S.Leibler, J. Phys. (France), 1983, **44**, 775.
125. E.Brézin, B.I.Halperin, and S.Leibler, Phys. Rev. Lett., 1983, **50**, 1387.
126. J.R.Henderson, Phys. Rev. B, 1986, **33**, 614.
127. S.Chatterjee, V.Vani, S.Guha, and E.S.R.Gopal, J. Phys. (France), 1985, **46**, 1533.
128. K.Binder, D.P.Landau, and D.M.Kroll, Phys. Rev. Lett., 1986, **56**, 2272.
129. T.Halpin-Healy and E.Brezin, Phys. Rev. Lett., 1987, **58**, 1220.
130. A.I.Rusanov and V.I.Pshenitsyn, Dokl. Akad. Nauk SSSR, 1969, **187**, 619.
131. A.I.Rusanov, S.A.Levichev, and O.N.Mikhalenko, Zhur. Fiz. Khim., 1969, **43**, 2636 [Russ. J. Phys. Chem., 1969(10)].
132. V.I.Pshenitsyn and A.I.Rusanov, Zhur. Fiz. Khim., 1972, **46**, 1031 [Russ. J. Phys. Chem., 1972(4)].
133. J.S.Rowlinson and B.Widom, "Molecular Theory of Capillarity", Clarendon Press, Oxford, 1982.
134. B.Widom, J. Chem. Phys., 1977, **67**, 872.
135. B.Widom, Physica A, 1979, **95**, 1.
136. F.Ramos-Gomez and B.Widom, Physica A, 1980, **104**, 595.
137. M.P.Klosla and B.Widom, J. Colloid Interface Sci., 1980, **76**, 375.
138. N.Nagarajan, W.W.Webb, and B.Widom, J. Chem. Phys., 1982, **77**, 5771.
139. M.E.Fisher and P.-G.de Gennes, Compt. rend. Ser. B, 1978, **287**, 207.
140. E.Brézin and S.Leibler, Phys. Rev. B, 1983, **27**, 594.
141. S.Leibler and L.Peliti, J. Phys. C, 1982, **15**, L403.
142. L.Peliti and S.Leibler, J. Phys. C, 1983, **16**, 2635.
143. V.L.Kuz'min, F.M.Kuni, and A.I.Rusanov, Zhur. Fiz. Khim., 1972, **46**, 1801 [Russ. J. Phys. Chem., 1972(7)].
144. V.L.Kuz'min and B.I.Gorovits, "Sorbtsiya i Khromatografiya" (Sorption and Chromatography) (Edited by V.A.Tulupov), Izd. Nauka, Moscow, 1979, p.28.
145. V.L.Kuz'min and A.I.Rusanov, Kolloid. Zhur., 1984, **46**, 449.
146. D.Beaglehole, J. Chem. Phys., 1980, **78**, 3366.
147. D.Beaglehole, Phys. Lett. A, 1982, **91**, 237.
148. B.Heidel and G.H.Findenegg, J. Phys. Chem., 1984, **88**, 6575.
149. A.V.Mikhailov, V.L.Kuz'min, and A.I.Rusanov, Kolloid. Zhur., 1984, **46**, 481.
150. J.W.Schmidt and M.R.Moldover, J. Chem. Phys., 1985, **83**, 1829.
151. D.Beysens and S.Leibler, J. Phys. Lett. (France), 1982, **43**, L133.
152. C.Franck and S.E.Schnatterly, Phys. Rev. Lett., 1982, **48**, 763
153. M.Schlossman, X.-L.Wu, and C.Franck, Phys. Rev. B, 1985, **31**, 1478.
154. J.A.Dixon, M.Schlossman, X.-L.Wu, and C.Franck, Phys. Rev. B, 1985, **31**, 1509.
155. C.Zalczer, J. Phys. (France), 1986, **47**, 379.
156. J.C.Charmet and P.-G.de Gennes, J. Opt. Soc. Amer., 1983, **73**, 1977.

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