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INTRODUCTION TO WETTING PHENOMENA*

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In these lectures the field of wetting phenomena is introduced from the point of view of statistical physics. The phase transition from partial to complete wetting is discussed and examples of relevant experiments in binary liquid mixtures are given. Cahn's concept of critical-point wetting is examined in detail. Finally, a connection is drawn between wetting near bulk criticality and the universality classes of surface critical phenomena.

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1. Situation and motivation

This survey aims at providing a pedagogical treatment of selected recent advances in the field of wetting phenomena and, in particular, wetting phase transitions. While the viewpoint is that of statistical physics, the strongly interdisciplinary character of the field should be stressed. Also in chemistry, biology, and several applied sciences wetting phenomena receive a lot of attention. One fascinating example is in biology, where the liquid behaviour of embryonic tissue is a subject of much recent interest. The tissue spreading in embryos strongly resembles basic wetting behaviour of immiscible liquids (Steinberg and Poole 1982, Steinberg 1993). This analogy has recently inspired joint research of physicists, biologists and physicians (Forgacs *et al.* 1991).

In spite of the common occurrence of wetting phenomena in daily life and their great relevance for technological applications, the popularization of modern developments in this field has been rather limited. Articles by experts that are quite accessible for nonspecialists include Moldover and

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Cahn's pioneering experimental investigation of the wetting phase transition, as published in *Science* (1980), and de Gennes' article about the spreading of a liquid drop in *Pour la Science* (1984). More recently, in *Nature,* Heslot *et al.* (1989) described their experimental discovery of molecular layering in the spreading of liquid drops. The formation of mist, dew, and breath figures was extensively treated by Beysens and Knobler in *La Recherche* (1992).

For our purposes it is convenient to distinguish two periods in wetting research in physics and physical chemistry. Before 1977, wetting phenomena were studied with emphasis on the characterization of the adhesion properties (such as the contact angles, for example) as a function of the structure and composition of solid substrata and liquid adsorbates. In this context, the work of Zisman (1964) and his collaborators must be mentioned. Also the Russian School (Deryagin and co-workers) has done important pioneering work on the subject. References can be found in de Gennes' review on the statics and dynamics of wetting phenomena (1985). Then, in 1977, the transition from partial wetting (nonzero contact angle) to complete wetting (zero contact angle), was recognized to be a (first-order) surface phase transition by Cahn, in Landau theory (1977), and by Ebner and Saam, in density-functional theory (1977). From then on, the emphasis has been shifted towards the investigation of phase transitions and critical phenomena associated with wetting.

One point of particular interest, and which was the main theme of Cahn's pioneering paper (1977), is the role of the bulk critical point (of the adsorbate) in wetting phenomena. This issue is relevant not only to fundamental experimental and theoretical physics, but is also important for applied science. This is illustrated by Cahn's application in metallurgy (1979) of his discovery of "critical-point wetting" (1977). Concerning this application, experiments that examine the growth of composites as a function of the wetting behaviour, which is apparently controlled by the temperature distance from a bulk critical point, were described by Grugel and Hellawell (1981). In 1987 Delannay *et al.* reviewed the wetting of solids by molten metals and its relation to the preparation of metal-matrix composites.

Between 1977 and 1981, it was established that the wetting phase transition may be continuous (or "critical") instead of first-order. Sullivan found a critical wetting phase transition in density-functional theory (1979, 1981). Abraham accomplished an exact calculation of a critical wetting transition in the two-dimensional Ising model (1980). On the experimental side, the wetting phase transition demonstrated by Moldover and Cahn (1980) in simple ternary liquid mixtures appeared to be of first-order character. Systematic insight into the different theoretical possibilities, including multicritical transitions, was gained after the derivation of global phase diagrams for wetting by Nakanishi and Fisher (1982).

Among the previous reviews of the field the following are of particular relevance to topics addressed in this survey. An introduction to three-phase equilibria and wetting transitions, including contact line phenomena and line tension, is given in Rowlinson and Widom's book *Molecular Theory of Capillarity* (1984). An extensive and systematic classification of multilayer adsorption phenomena was developed by Pandit *et al.* (1982). A short review with emphasis on early experimental results was presented by Moldover and Schmidt (1984). The review by de Gennes (1985) aims at a unified picture of the physical chemistry, statistical physics and fluid dynamics of the spreading of liquids on solids. Sullivan and Telo da Gama (1986) focussed on wetting transitions and multilayer adsorption at solid-fluid and fluid-fluid interfaces. The lecture of Fisher (1986a) on interface wandering in adsorbed and bulk phases, pure and impure, offers a systematic introduction to the scaling theory of interfacial phase transitions. A thorough survey of the statistical mechanics of wetting phenomena, a summary of experimental results, and an extensive bibliography are contained in Dietrich's review (1988).

The Les Houches volume on *Liquids at Interfaces* presents tutorial articles on wetting and related interfacial phenomena. In particular, Evans (1990a) discussed microscopic theories of simple fluids and their interfaces, Cazabat (1990) dealt with experimental aspects of partial wetting, complete wetting and wetting films, Schick (1990) gave an introduction to the statistical mechanics of wetting and summarized the theoretical and experimental state of the art, and Beysens (1990) reviewed experiments on wetting and adsorption, restricting attention to fluid and fluid mixture interfaces. In recent reviews, Evans focussed on fluids adsorbed in narrow pores (1990b), Forgács *et al.* (1991) treated interfaces in ordered and disordered systems, and Léger and Joanny (1992) dealt with liquid spreading. The recent Les Houches volume on *Dynamical Phenomena at Interfaces, Surfaces and Membranes* (1993), which contains the aforementioned biological contribution by Steinberg, features a number of wetting-related reports that illustrate the interdisciplinary character of the subject.

Clearly, the field of wetting phenomena has been — and continues to be — very active and has been reviewed from various angles in the last ten years. However, some gaps have not yet been filled. For example, a thorough discussion of critical-point wetting, involving a critical analysis of Cahn's controversial argument, is missing and will be developed here. Another *raison d'être* for this survey is the new perspective that has been added to the field by the advance, since 1990, of the study of the line tension at wetting. The surprising diversity of thermodynamic singularities associated with this excess free energy has revealed that interesting critical phenomena occur at first-order wetting transitions. Since the experimentally accessible wetting transitions to date are (almost) always of first order, this finding merits special attention. A thorough discussion of the line tension at wetting has been published recently as a review article (Indekeu 1994), and will therefore not be included here.

2. Partial wetting versus complete wetting

In order to introduce the basic phenomena and terminology, we consider the following simple setting. Suppose we have a solid container S filled with liquid L and vapour V at two-phase coexistence, as in Fig. 1. We distinguish three interfaces: liquid-vapour, solid-liquid, and solid-vapour. The associated surface free energies are $\gamma_{\rm LV}$, $\gamma_{\rm SL}$, and $\gamma_{\rm SV}$. The figure shows that there is a tendency towards wetting rather than drying. Indeed, out of the two adsorbed phases, liquid and vapour, the solid substrate prefers the liquid and disfavours the vapour. This is evident from the rise of the liquid near the wall: the contact angle θ is less than 90°. Experimentally, the contact angle must be measured close enough to the wall, that is, within a few percent of the capillary length a_0 (Rowlinson and Widom 1984). This length is a measure of the distance over which the liquid-vapour interface is curved, and results from the competition of surface tension and gravity. It is defined as

$$a_0 = \sqrt{\frac{2\gamma_{\rm LV}}{g\Delta\rho}}\,, \tag{2.1}$$

where g is the gravitational acceleration and $\Delta\rho$ is the density difference of liquid and vapour. Typical values of a_0 are of the order of one millimeter.

Preferential adsorption of the liquid phase is expressed by the inequality

$$\gamma_{\rm SL} < \gamma_{\rm SV}\,. \tag{2.2}$$

Fig. 1 shows that, although the vapour phase is disfavoured, a direct wall-vapour contact is still tolerated. However, when the preference for adsorption of the liquid would be further increased (for example, by changing the temperature), the vapour may become excluded from contact with the wall. This possibility is shown in Fig. 2. There, a liquid layer has intruded between solid and vapour. This is termed complete wetting, whereas the previous situation (Fig. 1) represents partial wetting. The thickness of the liquid wetting layer in the case of complete wetting is typically a few hundred Å, and is a result of the competition between gravity and intermolecular forces (Kayser *et al.* 1985, 1986). For complete wetting the inequality (2.2) is, of course, a fortiori satisfied. Moreover, at complete wetting a solid-vapour interface does not exist anymore as a single entity in thermodynamic equilibrium, but consists of the combination of two separate interfaces. The equilibrium surface free energy of the solid-vapour interface is consequently defined as

$$\gamma_{\mathrm{SV}} \equiv \gamma_{\mathrm{SL}} + \gamma_{\mathrm{LV}}\,, \quad \text{at complete wetting}. \tag{2.3}$$

This is called Antonov's rule. For partial wetting, on the other hand, we have the strict inequality

$$\gamma_{\mathrm{SV}} < \gamma_{\mathrm{SL}} + \gamma_{\mathrm{LV}}\,, \tag{2.4}$$

which expresses that although a solid-liquid contact is preferred, a solid-vapour interface has lower free energy than the combination of solid-liquid and liquid-vapour interfaces. In the case of partial wetting Young's law expresses the mechanical equilibrium of the forces (per unit length) that the interfaces exert on the contact line along which they meet. (Recall that surface free energies are energies per unit area and thus forces per unit length.) Balancing the components of these forces along the direction parallel to the substrate and perpendicular to the contact line (*i.e.*, the vertical direction in Fig. 1) leads to

$$\gamma_{\mathrm{SV}} = \gamma_{\mathrm{SL}} + \gamma_{\mathrm{LV}} \cos\theta\,. \tag{2.5}$$

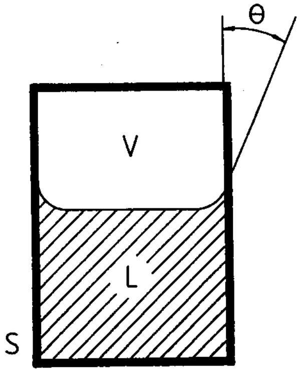

Fig. 1. Partial wetting of the solid container wall (S) by liquid (L), at liquid-vapour coexistence. The angle θ is the contact angle.

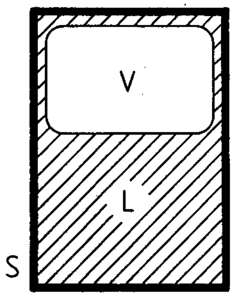

Fig. 2. Complete wetting: a liquid film separates solid and vapour.

The angle θ is the contact angle, shown in Fig. 1. Note that this law can also serve as the thermodynamic definition of the contact angle, when the surface free energies are known, but no direct observation of θ is made. Indeed, in view of (2.2) and (2.4) we can always find an angle $0 < \theta < 90°$ so that (2.5) holds. Clearly, complete wetting corresponds to $\theta = 0$. Young's law needs to be generalized as soon as the surface tension of the interface between the two adsorbed phases is anisotropic. This is the case, for example, when crystalline, or liquid-crystalline adsorbates are involved (de Coninck and Dunlop 1987).

In thermodynamic equilibrium we must have

$$\gamma_{\rm SV} \leq \gamma_{\rm SL} + \gamma_{\rm LV}\,, \tag{2.6}$$

and

$$\gamma_{\rm SL} \leq \gamma_{\rm SV} + \gamma_{\rm LV}\,. \tag{2.7}$$

Indeed, suppose that, for example, (2.6) is not obeyed. Then the supposed free energy $\gamma_{\rm SV}$ of the solid-vapour interface can be lowered to the sum $\gamma_{\rm SL} + \gamma_{\rm LV}$ by the intrusion of a liquid wetting layer between solid and vapour. Consequently, after equilibrium has been reached, (2.6) is restored. Out of equilibrium, however, violations of (2.6) or (2.7) are common. They result in a positive spreading coefficient S^*, with

$$S^* \equiv \gamma^*_{\rm SV} - (\gamma_{\rm SL} + \gamma_{\rm LV})\,, \tag{2.8}$$

where $\gamma^*_{\rm SV}$ is the free energy of any possible state in which the substrate is dry. This may be a metastable state, and in such cases $\gamma^*_{\rm SV} > \gamma_{\rm SV}$, where the latter always denotes the equilibrium value. (Likewise, $S^* \geq S$.) The consequences of $S^* > 0$ are studied in the dynamics of wetting (de Gennes 1985, 1990, Léger and Silberzan 1990).

The phase transition from partial to complete wetting can be discussed in terms of the equilibrium spreading coefficient S as follows. Note that $S \leq 0$, in view of (2.6). Using Young's law (2.5) we obtain

$$S = \gamma_{\rm LV}(\cos\theta - 1)\,, \tag{2.9}$$

so that for partial wetting $S < 0$, and for complete wetting $S = 0$. The wetting transition can now be characterized by the way in which S tends to zero, or, equivalently, the way in which $\cos\theta$ tends to 1. A typical case is sketched in Fig. 3. The singularity in S at the wetting temperature $T_{\rm w}$ can be written, for $T \to T_{\rm w}^-$, as

$$-S \propto (T_{\rm w} - T)^{2-\alpha_s}\,, \tag{2.10}$$

or, equivalently,

$$\theta \propto (T_{\rm w} - T)^{(2-\alpha_s)/2}\,, \tag{2.11}$$

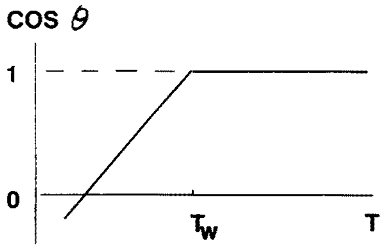

Fig. 3. Sketch of $\cos\theta$ versus temperature in the vicinity of a first-order wetting transition.

where α_s is the surface specific heat exponent. If S vanishes with a discontinuous first derivative (as it appears in Fig. 3), the wetting transition is of first order and $\alpha_s = 1$. On the other hand, if $\alpha_s < 1$ the transition is smoother and said to be continuous, or critical. Experimentally, first-order wetting transitions are the rule.

What we have said so far concerning a wetting transition can be simply reformulated to apply to a drying transition, which (if it exists) takes place at $\theta = 180°$. We will adopt the following terminology, used by many authors:

$$\begin{aligned} &\text{complete wetting} &&\Longleftrightarrow\ \theta = 0\,,\\ &\text{partial wetting} &&\Longleftrightarrow\ 0 < \theta < 90°\,,\\ &\text{partial drying} &&\Longleftrightarrow\ 90° < \theta < 180°\,,\\ &\text{complete drying} &&\Longleftrightarrow\ \theta = 180°\,. \end{aligned}$$

For the "neutral" case ($\theta = 90°$), there is no preferential adsorption and thus no tendency towards wetting or drying. For a somewhat different terminology, see Schick (1990).

Wetting and drying have a literal meaning when the adsorbate consists of liquid and vapour. In more general situations, for adsorbed liquid mixtures, binary alloys, Ising magnets, *etc.*, this literal meaning is lost and it is a matter of definition what one calls wetting or drying. Sometimes (in Ising models) the two are equivalent by symmetry, and one then simply uses "wetting" when referring to "wetting and/or drying". Furthermore, for adsorbed solids, "wetting" means coating.

Simple observations of liquid droplets and vapour bubbles at substrata can be adequate for distinguishing partial wetting from complete wetting, and can provide qualitative information concerning the possible presence of wetting phase transitions in systems as simple as one-component fluids at walls. However, the quantitative location of the transition as a function of temperature, for example, requires careful experimental work and relies on accurate measurements of, say, the contact angle. Very few experiments exist on transitions from partial to complete wetting in one-component adsorbates at solid substrata (Dietrich 1988). In these simple systems there is essentially only one control variable (the temperature T) that can induce a wetting transition, and it often happens that the wetting behaviour is not very sensitive to changes in T.

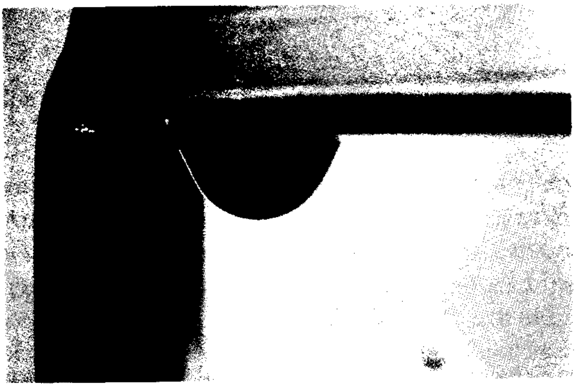

Fig. 4. Partial wetting of the liquid-vapour interface by the methanol-rich phase in the liquid mixture of methanol, cyclohexane, and water (with addition of a dye).

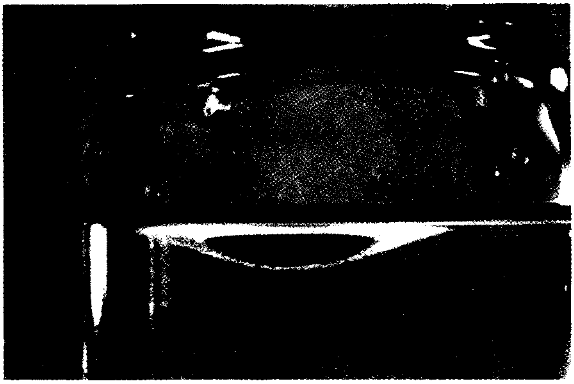

Fig. 5. Complete wetting: a lenticular film of the wetting phase spreads at the liquid-vapour interface. The water concentration is lower than in the mixture of Fig. 4.

In contrast, many thorough investigations of wetting transitions have been made in adsorbed liquid mixtures. Observations of adsorbed droplets are an adequate means of distinguishing partial and complete wetting in these systems. This has been demonstrated convincingly in the seminal experiments of Moldover and Cahn (1980). Binary mixtures of methanol and cyclohexane, with the addition of a small amount of water, display complete wetting at very low water content and partial wetting above a certain (low) water concentration. The wetting phase is the heavier methanol-rich phase, which forms a layer on top of the lighter cyclohexane-rich phase, at the interface with air or vapour. After shaking the mixture in a glass container, either articulate droplets (distinctly marked off against the background) are suspended from the upper interface (Fig. 4), or a broad lenticular film develops (Fig. 5). The former corresponds to partial wetting and the contact angle θ can be measured (Moldover and Cahn 1980). The latter is the signature of complete wetting ($\theta = 0$) and under those circumstances there are no suspended droplets. These observations are easy to make and the mixtures can be prepared quickly without special care. It is one of the favourite "classroom" experiments on wetting. (Usually, one adds a dye to make the wetting phase strikingly visible.) Strictly speaking, suspended droplets and lenticular films are metastable and slowly diffuse away into the lower bulk liquid phase, but the time required for equilibration is of the order of a week. Achieving equilibrium wetting layer thicknesses in liquid mixtures is a notorious problem (Kayser *et al.* 1986).

It is well known that equilibration is fast in one-component systems, and this makes them suitable for reliable wetting experiments, in principle. However, we have already mentioned that, in practice, the experimentalist has to face the serious problem, that the wetting properties of one-component systems at substrata vary only weakly with adjustable parameters, such as the temperature. Many fluids are "triple-point wetters" on many substrata (Pandit and Fisher 1983, Dietrich 1988). That is, complete wetting occurs already from the triple point on and persists until the critical point. On the other hand, if partial wetting is found it is likely that the contact angle decreases only slowly with increasing temperature and that the supposed wetting transition takes place at rather high temperatures and correspondingly high pressures (always assuming liquid-vapour coexistence). Experiments in liquid mixtures are more rewarding, in spite of the equilibration problem, because drastic phenomenological changes can occur under ambient conditions of p and T, as a function of a concentration, for example. Also, some oil-water-surfactant systems display a wetting transition at a readily accessible temperature. The transition can be recorded by direct eye observation, by varying T at fixed overall concentration (Robert and Jeng 1988).

From a fundamental point of view, wetting transitions in one-component adsorbates deserve special attention and, indeed, most of the theoretical work up to now has been devoted to them. On the experimental side there seems to be no widely accepted precise determination of a wetting transition in a one-component fluid at a wall, under the strict condition of liquid-vapour coexistence. However, under the less stringent condition of liquid-air coexistence, at ambient pressure, wetting transition temperatures for one-component adsorbed liquids have been measured already long ago (Bigelow *et al.* 1947). Indeed, as reviewed by Zisman (1964), and emphasized at a Faraday Meeting by Henderson (1986) and Moldover (1986), molten pure compounds (fatty acids, for example) on so-called high-energy surfaces (metals, glass, *etc.*) at atmospheric pressure (in air) were studied by Bigelow *et al.* (1947). These authors found that at a certain temperature T_w, the condition of zero contact angle is reached (that is, $\theta > 0$ for $T < T_w$, and $\theta = 0$ for $T > T_w$). Of course, the interpretation in terms of a surface phase transition was not known until 30 years later. Let us mention two results of this beautiful early work. Firstly, for octanoic acid on a platinum foil, $T_w = 23°\mathrm{C}$ (the melting point of this liquid is at $T_m = 17°\mathrm{C}$, and the boiling point at $T_b = 240°\mathrm{C}$). Secondly, for octadecanoic acid on a platinum foil, $T_w = 106°\mathrm{C}$ ($T_m = 70°\mathrm{C}$ and $T_b = 383°\mathrm{C}$). These adsorbed liquids belong to the category of "autophobic liquids" (Zisman 1964). They show nonzero contact angles (for $T < T_w$) on surfaces with which they have previously been in contact, and on which, as a result of this contact, an adsorbed oriented monolayer has formed.

Whether a liquid will wet a solid substrate completely ($\theta = 0$), or partially ($\theta > 0$), apparently depends to a large extent only on the relative magnitude of the liquid-vapour tension γ_{LV} and the so-called "critical surface tension" γ_c associated with the solid (Zisman 1964). One finds $\theta > 0$ as long as $\gamma_{\mathrm{LV}} > \gamma_c$, and $\theta = 0$ for $\gamma_{\mathrm{LV}} < \gamma_c$. This remarkable empirical finding is due to Zisman and co-workers (1964). A theoretical explanation is far from obvious. For the case of van der Waals forces, the pertinent arguments have been reviewed by de Gennes (1985). We summarize them here. In terms of the work of adhesion $\mathcal{W}_{\mathrm{SL}}$ required to separate solid and liquid by introducing a vapour between them, we have (Israelachvili 1985)

$$\mathcal{W}_{\mathrm{SL}} = \gamma_{\mathrm{SV}} + \gamma_{\mathrm{LV}} - \gamma_{\mathrm{SL}}\,, \tag{2.12}$$

which is often referred to as Dupré's equation. Analogously, the work of cohesion of the liquid $\mathcal{W}_{\mathrm{LL}}$ required to separate the liquid in two parts by introducing a vapour in between, is given by

$$\mathcal{W}_{\mathrm{LL}} = 2\gamma_{\mathrm{LV}}\,. \tag{2.13}$$

(The usual definitions invoke vacuum instead of vapour, a distinction we may neglect for dilute vapour phases.) Using (2.5) we can now write

$$\cos\theta = \frac{\mathcal{W}_{\mathrm{SL}}}{\gamma_{\mathrm{LV}}} - 1\,, \tag{2.14}$$

which is the so-called Young-Dupré equation. Invoking the dielectric polarizability per unit volume $\mathcal{P}$, and assuming (to a first approximation) $\mathcal{W}_{AB} \propto \mathcal{P}_A \mathcal{P}_B$ (Israelachvili 1985), one obtains

$$\cos\theta = 2\sqrt{\frac{\gamma_c}{\gamma_{\mathrm{LV}}}} - 1\,, \tag{2.15}$$

where $\gamma_c \propto \mathcal{P}_{\mathrm{S}}^2$, which indeed depends only on the solid. We emphasize that these arguments are crude and are only meant to provide some theoretical basis for the purely empirical parameter γ_c.

Zisman's criterion immediately leads us to expect partial wetting of water on teflon, for example, since $\gamma_c \approx 18$ ergs/cm^2 for teflon (1 erg $= 10^{-7}$ J) and $\gamma_{\mathrm{LV}} \approx 73$ ergs/cm^2 at room temperature. On the other hand, for liquid CO_2 on teflon, for example, complete wetting should be expected. Indeed, the surface tension γ_{LV} of CO_2 is only about 15 ergs/cm^2 at the triple point ($p_t \approx 5$ atm, $T_t \approx -56°$C), and decreases with increasing T to zero at the critical point ($p_c \approx 73$ atm, $T_c \approx 31°$C). At 20°C, $\gamma_{\mathrm{LV}} = 1.16$ ergs/cm^2 (Gas Encyclopaedia 1976). We conclude $\gamma_{\mathrm{LV}} < \gamma_c$, and thus $\theta = 0$ according to the criterion. In order to make simple and qualitative observations of the wetting behaviour in these systems, for didactical purposes, one may use a pressure-cell and a rotatable substrate (Indekeu 1990).

Close to the bulk critical point of the fluid the liquid-vapour interface is only weakly curved near a vertical wall, so that it appears to the eye that the contact angle approaches 90° when the critical point is neared. The usual explanation for this is the vanishing of the capillary length a_0, defined in (2.1). Invoking the critical exponents of surface tension and bulk order parameter, $\mu \approx 1.26$ and $\beta \approx 0.33$, respectively, we obtain from (2.1)

$$a_0 \propto (T_c - T)^{(\mu-\beta)/2}\,, \tag{2.16}$$

and $(\mu - \beta)/2 \approx 0.47$. Therefore, the length scale over which the interface is curved goes to zero at T_c. So, to the eye $\theta \to 90°$, whereas actually $\theta = 0$ up to T_c (complete wetting).

Observations of CO_2 on teflon, at room temperature and $p \approx 57$atm, during condensation, show the formation of a liquid film underneath a (horizontal) substrate. The planar projection of a suspended droplet (Fig. 6) appears to meet the substrate tangentially ($\theta = 0$, that is, complete wetting). Its shape is strikingly similar to that of the analogous object in the liquid mixture (Fig. 5). On the other hand, during evaporation, one sees vapour bubbles clinging under an immersed substrate. Experiments making use of hanging drops or sessile bubbles have been discussed by Adamson (1982). Bubbles tend to settle near irregularities or grooves in the substrate surface, and appear round (Fig. 7). (The vapour bubble spans the supplement of the contact angle, 180° – θ, which equals 180° at complete wetting.) The size (and lifetime) of sessile bubbles can be controlled by delicately changing the pressure. After a suitable increase in pressure they shrink away.

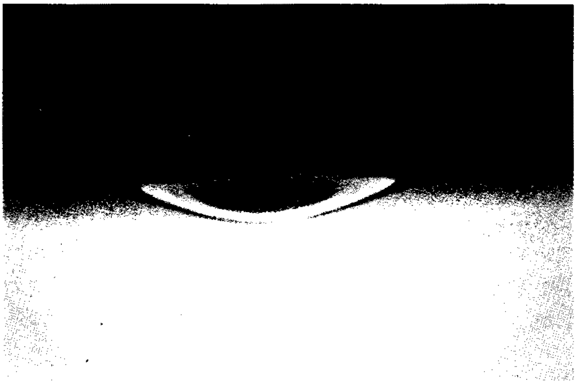

Fig. 6. Complete wetting of a teflon substrate by suspended liquid CO_2, at liquid-vapour coexistence. Note the similarity with the shape in Fig. 5.

Fig. 7. Spherical vapour bubble of CO_2 under a teflon substrate immersed in liquid CO_2: complete wetting by liquid.

For water on teflon one observes the qualitatively different case of partial wetting (featuring hemispherical liquid droplets and hemispherical vapour bubbles). Note that the equilibrium contact angle, θ_E, corresponding to θ as defined by (2.5), is seldom observed in practice, due to contact angle hysteresis. Under static conditions, the observed θ lies between two limiting values, the advancing contact angle (θ_A) and the receding one (θ_R) (Zisman 1964, de Gennes 1985). If one goes beyond these limits, the contact line starts to move with a certain velocity and interacts with defects on the substrate surface, as studied in the dynamics of wetting (Raphaël and de Gennes 1989). Both θ_A and θ_R can be observed, for example, with the tilting plate method, using a rotatable substrate (Adamson 1982, Adam and Jessop 1925, Fowkes and Harkins 1940, Speece *et al.* 1957). Apparent contact angles are easily read with a precision of one degree. However, as surface tension and contact angle are very sensitive to impurities and substrate roughness, reproducible experiments require great care.

The surface roughness parameter is defined as

$$R_a = \frac{1}{L}\int_0^L |h(x) - \bar{h}|dx\,, \tag{2.17}$$

where $h(x)$ denotes the height function describing the surface along a straight path of length L (of the order of 1 mm in practice), and $\bar{h}$ is the average height along the path. For teflon, fairly smooth surfaces [for example, with $R_a \approx 0.04\mu\text{m}$ (Indekeu 1990)] can be obtained by abrading and polishing, using a sequence of powders with grains down to less than a micron in size, or by other techniques (Fox and Zisman 1950, Neumann *et al.* 1971). To a first approximation contact angles on rough and smooth surfaces can be related by a simple geometrical argument (Zisman 1964). For a rough surface the actual area A is larger than its planar projection $A_{\|}$ by a factor $b \geq 1$, and Young's law reads

$$b\gamma_{\mathrm{SV}} \approx b\gamma_{\mathrm{SL}} + \gamma_{\mathrm{LV}}\cos\theta\,, \tag{2.18}$$

so that

$$\cos\theta_{\mathbf{rough}} \approx b\cos\theta_{\mathbf{smooth}}\,. \tag{2.19}$$

This suggests that contact angles are decreased (assuming $\theta < 90°$) and wetting is promoted by roughness.

In order to get a notion of measured contact angles and contact angle hysteresis, let us examine published results for the teflon-water-air system. For sessile water drops on clean and smooth (heat-pressed) teflon, Fox and Zisman (1950) reported $\theta_A = 108°$. According to Zisman (1964) $\theta_A = \theta_R = \theta_E$ in these measurements, owing to the extreme purity and substrate smoothness. Employing Fox and Zisman's technique, Schwartz *et al.* (1964) reproduced the value $\theta_E = 108°30'$ for water on clean and smooth teflon. With a different method and using rougher teflon surfaces they investigated contact angle hysteresis. From a determination of the critical line force necessary to initiate the motion of the three-phase contact line, they deduced $\theta_A = 118°47'$ and $\theta_R = 95°17'$, for water-air menisci inside a clean teflon capillary. Dann (1970) reported the advancing angle for water on teflon using sessile-drop (or captive-bubble) methods as $\theta_A = 112°$, a value generally reproducible within about ±3°. For water on flow-smoothed (heat-pressed) teflon, using a captive-bubble method, Hu and Adamson (1977) reported $\theta_A = 98°$ (see also Adamson 1982). This value is significantly smaller than those reported by Fox and Zisman (1950) and Dann (1970). Hu and Adamson suggested that this discrepancy may be due to a roughness effect or to the creation of polar sites on the surface by flow-smoothing. They added that they could reproduce the more usual value $\theta = 109°$ for unpolished teflon. Clearly, unequivocal contact-angle determinations are difficult.

Let us again consider a pure one-component adsorbate at its vapour pressure, and in contact with a solid substrate, and let us assume that there is preferential adsorption of vapour (that is, $\theta > 90°$). A question which has led to lively discussions among experts, is whether or not complete drying by vapour (that is, $\theta = 180°$) is possible. Apparently, the experimental results on (multi-component) solid-liquid-air systems at ambient pressure all indicate that there is a maximum contact angle θ_{max} associated with liquid droplets, and that $\theta_{\mathrm{max}} < 180°$ (Shafrin and Zisman 1964). Our present question, however, is different in the important respect that we can bring the liquid and vapour phases close together in density by approaching the bulk critical point of the one-component adsorbate. Then, according to Cahn (1977), we should expect one of the two adsorbed phases to exclude the other from contact with the substrate. That is, we should expect either complete wetting by liquid or complete drying by vapour. Apparently, while the former commonly occurs (presupposing the liquid is preferentially adsorbed), the latter is elusive in real experiments. Why?

This question can be answered in terms of effective forces between surfaces (or interfaces). In terms of the work of adhesion (Zisman 1964, Israelachvili 1985) of liquid on solid, using the Young-Dupré equation (2.14), we have

$$\mathcal{W}_{\mathrm{SVL}} = \gamma_{\mathrm{LV}}(1 + \cos\theta)\,, \tag{2.20}$$

where we write $\mathcal{W}_{\mathrm{SVL}}$ rather than $\mathcal{W}_{\mathrm{SL}}$ to emphasize the presence of the third medium, the vapour phase. Complete drying results when, in equilibrium, $\mathcal{W}_{\mathrm{SVL}} = 0$, implying the spontaneous separation of solid and liquid phases by a vapour layer of macroscopic thickness. We will now argue that *(i)* this phenomenon is theoretically possible and has been observed in computer simulations, but *(ii)* it is unlikely to occur in real systems with van der Waals forces.

Theoretically, in systems with interparticle interactions of finite range complete drying results when the attraction between a molecule of the fluid and a molecule of the solid is sufficiently weak compared with the mutual attraction of molecules in the fluid. Computer simulations using truncated Lennard-Jones potentials confirm this (see Indekeu and Nijmeijer 1993, and references therein). However, in real systems with van der Waals forces the long-range tail of the intermolecular attraction leads to an effective long-range interaction between the interfaces that bound the adsorbed layer. Consequently, the surface free energy acquires an important dependence on the thickness l of the adsorbed layer, which, to a good approximation, is described by

$$\gamma_{\mathrm{SL}}(l) = \gamma_{\mathrm{SV}} + \gamma_{\mathrm{LV}} + A_{\mathrm{SVL}}\, l^{-2}\,, \quad \text{for large } l\,, \tag{2.21}$$

assuming non-retarded van der Waals forces. Since the equilibrium state corresponds to the minimum of $\gamma_{\mathrm{SL}}(l)$, a macroscopic vapour layer ($l = \infty$) will be stable only if $A_{\mathrm{SVL}} > 0$. This amplitude A is proportional to the so-called Hamaker constant, which is expressed in terms of the frequency-dependent dielectric functions of the media (Dzyaloshinskii *et al.* 1961, Visser 1972, Israelachvili 1985). To a first approximation (de Gennes 1981), A_{SVL} can be expressed in terms of the static polarizabilities per unit volume, $\mathcal{P}$, in the different phases,

$$A_{\mathrm{SVL}} \approx c(\mathcal{P}_{\mathrm{S}} - \mathcal{P}_{\mathrm{V}})(\mathcal{P}_{\mathrm{V}} - \mathcal{P}_{\mathrm{L}})\,, \tag{2.22}$$

where $c > 0$. Now, since the liquid is denser than the vapour, $\mathcal{P}_{\mathrm{L}} > \mathcal{P}_{\mathrm{V}}$. Furthermore, in general, and certainly for dilute vapour phases, $\mathcal{P}_{\mathrm{S}} > \mathcal{P}_{\mathrm{V}}$ is to be expected. Indeed, not only is the vapour normally (much) less dense than the solid, but also the polarizability per molecule tends to be lower in the adsorbate, since the latter is still in the fluid state at a temperature and pressure for which the substrate material is already in the solid state. (The polarizability (squared) per molecule is roughly proportional to the triple point temperature, since $k_{\mathrm{B}}T_{\mathrm{t}}/\epsilon$ is typically of order 1. Here, ϵ is the well-depth of the intermolecular potential, and, to a first approximation, ϵ is proportional to the product of the polarizabilities of the interacting particles.)

In conclusion, $A_{\mathrm{SVL}} < 0$, as a rule. Consequently, at most a finite vapour film, of thickness l_e, may be adsorbed from a liquid approaching liquid-vapour coexistence. The Dupré equation now becomes

$$\mathcal{W}_{\mathrm{SVL}} = \gamma_{\mathrm{LV}} + \gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}}(l_e) = -A_{\mathrm{SVL}}\, l_e^{-2} > 0\,, \tag{2.23}$$

so that, recalling (2.20), the contact angle can never quite reach 180°. The presupposed tendency towards drying in this system is thus counteracted by the net effect of the tails of the long-range van der Waals forces. This competition is referred to as the antagonistic case by de Gennes (1983).

In systems of this type, neither complete drying, nor complete wetting can develop (Nightingale and Indekeu 1985).

In sum, to a first approximation, a necessary condition for complete drying appears to be that the polarizability per unit volume in the vapour phase exceeds the polarizability per unit volume in the substrate. This seems impossible to realize, unless, perhaps, exceptional solids and very dense vapour phases are contemplated. The latter may be achieved, but only in the close neighbourhood of the liquid-vapour critical point, T_c. So, whereas complete wetting is common and often occurs in the whole range $T_t \leq T \leq T_c$, complete drying poses an extraordinary experimental challenge.

3. Critical-point wetting

In this Chapter we will be interested in wetting transitions in model systems with short-range interactions. The paradigm is the nearest-neighbour Ising model. We will focus primarily on what happens in the vicinity of the bulk critical point T_c, and scrutinize Cahn's argument, which states that complete wetting (or drying) is necessary near T_c: critical-point wetting (Cahn 1977). We will ask if Cahn's argument is supported by scaling theory, and if it is valid in the Landau theory that Cahn used (1977). Next, we will address model systems with special symmetries that lead to qualitatively different wetting behaviour near T_c. These models are physically relevant to a specific variety of grain boundaries. Finally, we will conclude with a classification scheme relating wetting behaviour near T_c to universality classes of surface critical phenomena at T_c.

Let us first deal with ordinary wetting problems and consider the usual setting in which an adsorbate is in contact with a substrate or, more generally, a spectator phase. These problems belong to the category "wetting at walls", where the term "wall" is to be understood in a very broad sense. Forgetting about short-range forces for a moment, the examples we have in mind are a liquid-vapour system at a solid substrate, a two-phase binary liquid mixture in contact with its vapour, a three-phase liquid mixture in which one of the phases serves as spectator phase, a ferromagnet with a surface against air or vacuum, etc. In all these examples, the important characteristic is that one of the phases plays a passive role and can be effectively replaced by a surface field that acts at the interface against the other two phases. The latter define the adsorbate and we will generally assume that these phases are close to their critical point, where they become identical in bulk.

Most realistic systems feature forces that decay algebraically with the distance between the particles. A familiar example is the r^{-6} decay of intermolecular potentials in systems of van der Waals type, such as ordinary liquids. In order to obtain the potential energy that a single particle experiences at a distance z from a wall or spectator phase, one essentially has to integrate, over d dimensions, the r^{-6} potential. This gives z^{-3} in $d = 3$. Because this represents a fairly slow decay, van der Waals forces are termed long-range forces from the viewpoint of surface and wetting phenomena. In general, we will therefore consider all algebraically decaying potentials to be of long range. In contrast, strictly local interactions, as in a nearest-neighbour Ising model, or interactions that decay exponentially fast, will be termed short-range forces. In nature, short-range forces in this sense arise when algebraic potentials are screened by some sufficiently short screening length (de Gennes 1985).

Systems with surfaces or interfaces are, of course, inhomogeneous, and as a result, the order parameter m (density, concentration, magnetization, ...) becomes a function of position. This function is called the order parameter profile $m(z)$, where z measures the distance from the substrate or spectator phase, into the adsorbate. (To a first approximation, we will ignore fluctuations in the directions parallel to the substrate surface.) In systems with short-range forces, the problem category "wetting at walls" is characterized by a semi-infinite adsorbate and a surface field H_1 (Nakanishi and Fisher 1982). In the language of the Ising model (Abraham 1986) the relevant Hamiltonian (with spins $s_i = \pm 1$) reads

$$\mathcal{H}(\{s\}) = -J_{\mathrm{B}} \sum_{\langle ij \rangle} s_i s_j - J_{\parallel} \sum_{\langle ij \rangle \in \Gamma} s_i s_j - H_1 \sum_{i \in \Gamma} s_i \,, \tag{3.1}$$

where J_{B} is the bulk nearest-neighbour coupling, $J_{\parallel}$ the surface nearest-neighbour coupling (the surface is denoted by Γ), and H_1 the surface field. The corresponding spin lattice is shown in Fig. 8.

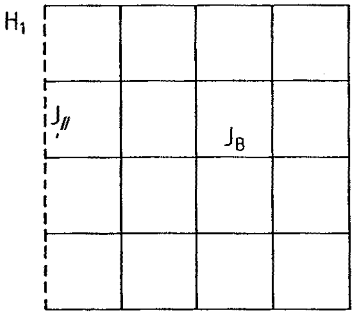

Fig. 8. Spin lattice for a semi-infinite system with a surface (dashed bonds), suitable for modelling wetting at walls.

A concise discussion of critical-point wetting at walls runs as follows. Consider a wall with surface field $H_1 > 0$. The adsorbate is at two-phase coexistence, and we denote the phases by + and −. The wall favours the + phase (because $H_1 > 0$), and thus the preferred state is one in which the bulk adsorbate is in the + phase. It is characterized by a surface free energy γ_+. If, however, we impose the disfavoured state, in which the bulk adsorbate is in the − phase, the surface free energy is denoted by γ_-^*, where the star indicates that this state need not be an equilibrium state. Clearly, $\Delta\gamma^* \equiv \gamma_-^* - \gamma_+ > 0$. We say that there is preferential adsorption of the + phase. Besides γ_+ and γ_-^* there is a third actor in the play, namely the surface tension of a +− interface infinitely far from any wall, γ_0.

Now there are two important cases. The first is $\Delta\gamma^* < \gamma_0$, implying partial wetting. The second corresponds to all possible alternatives to the inequality $\Delta\gamma^* < \gamma_0$. These are *(i)* the disfavoured state is unstable (in which case γ_-^* is not well defined), *(ii)* the disfavoured state is metastable (in which case $\Delta\gamma^* > \gamma_0$, along the well-defined metastable continuation of the disfavoured state in a theory of mean-field type), and *(iii)* we are right at the wetting transition, so that $\Delta\gamma^* = \gamma_0$. For all these alternatives, in thermodynamic equilibrium, $\Delta\gamma = \gamma_0$. Indeed, the disfavoured state yields to the combination of the preferred state and a +− interface far from the wall, with surface free energy $\gamma_+ + \gamma_0$. Equilibration thus leads to complete wetting.

What happens when the temperature T approaches T_c? The critical behaviour of γ_0 is given by

$$\gamma_0 \propto (T_c - T)^\mu \,, \tag{3.2}$$

with $\mu \approx 1.26$. What can we say about the critical behaviour of $\Delta\gamma^*$? In thermodynamic equilibrium, we must have $\Delta\gamma \leq \gamma_0$. This does not tell us if, at some temperature, there is going to be a wetting transition. However, if we have recourse to a mean-field approximation we can follow metastable continuations of stable states, and ask what the critical behaviour of the metastable continuation $\Delta\gamma^*$ is. This is what Cahn's argument is all about (Cahn 1977). Explicit calculations in Landau theory (a theory of the mean-field type) show that

$$\Delta\gamma^* \text{ does not vanish at } T_c\,. \tag{3.3}$$

This result differs from earlier speculations ($\Delta\gamma^* \propto (T_c - T)^\beta$, or $\Delta\gamma^* \propto (T_c - T)^{\beta_1}$), but the previously proposed conclusion (Cahn 1977) is not changed. Approaching T_c, partial wetting must yield to complete wetting, in view of (3.2) and (3.3). For wetting at walls, critical-point wetting is thus the rule, at least as far as the predictions of the Landau theory can be trusted.

After this concise discussion, we will have a more detailed look at the Landau theory, and at pertinent scaling arguments. We begin with the latter. From the very beginning an appealing "scaling" argument for critical-point wetting has been proposed (Cahn 1977). However, it is not a genuine scaling argument, and a proper discussion within scaling theory has been given by Pandit *et al.* (1982). What does scaling theory predict? Near bulk criticality, *i.e.*, for small $t \equiv (T_c - T)/T_c$, and, furthermore, for small h_1 (> 0), with $h_1 = H_1/k_B T_c$,

$$\gamma(t, h_1) = l^{-(d-1)} \gamma(l^{y_T} t, l^{y'_H} h_1) , \tag{3.4}$$

where l is a positive length-rescaling factor. This generalized homogeneity relation applies to γ_+ as well as to γ_-, but only for the thermodynamic <u>equilibrium</u> values. Thus, γ_-^* is to be replaced by $\gamma_- \equiv \min\{\gamma_-^*, \gamma_+ + \gamma_0\}$. The exponent $d-1$ is the surface dimensionality. The positive exponent y_T is the thermal critical exponent, and equals the inverse correlation length exponent ($y_T = 1/\nu$). The positive exponent y'_H is the surface ordering field (or "magnetic") exponent. The surface tension γ_0 obeys an analogous relation,

$$\gamma_0(t) = l^{-(d-1)} \gamma_0(l^{y_T} t) . \tag{3.5}$$

Now we choose $l = t^{-1/y_T}$. Note that $\mu = (d-1)/y_T$, by hyperscaling. Furthermore, the critical behaviour of the surface order parameter m_1 ($\propto \partial\gamma/\partial h_1$) in zero surface field is described by the critical exponent $\beta_1 = (d - 1 - y'_H)/y_T$. Note that $\beta_1 < \mu$. It follows that

$$\gamma_0 = A t^{\mu} , \tag{3.6}$$

$$\Delta\gamma = A t^{\mu} \mathcal{X}(h_1 t^{-\Delta_1}) , \tag{3.7}$$

where $\Delta_1 = \mu - \beta_1 > 0$, and $\Delta\gamma \equiv \min\{\Delta\gamma^*, \gamma_0\}$. The scaling function $\mathcal{X}$, which is by Young's law the cosine of the contact angle θ, satisfies $| \mathcal{X}(x) | \leq 1$ (equilibrium), and $\mathcal{X}(x) \propto x$, for $x \to 0$. Therefore,

$$\Delta\gamma \propto h_1 t^{\beta_1} , \quad \underline{\text{provided}} \quad h_1 \ll t^{\Delta_1} . \tag{3.8}$$

This result (Pandit *et al.* 1982) is very different from what was assumed in Cahn's argument (1977), namely $\Delta\gamma \propto t^{\beta}$. Firstly, $\beta \approx 0.3$ (for $d = 3$) is to be replaced by β_1. This is a minor point, because both are smaller than $\mu \approx 1.3$. Secondly, we are not allowed to take $t \to 0$ at fixed h_1 in (3.8). This restriction is very important, and was clearly stated by Pandit *et al.* (1982), but appears to have been largely ignored in later works. Finally, (3.8) concerns $\Delta\gamma$ and not the metastable continuation $\Delta\gamma^*$ assumed in Cahn's argument. (For accurate values of bulk critical exponents, see Le Guillou and Zinn-Justin (1989), and for values of surface critical exponents, see the reviews by Binder (1983) and Diehl (1986). For example, $\mu = 1.260 \pm 0.0015$ for $d = 3$.)

Clearly, from scaling theory alone a wetting transition cannot be predicted, and critical-point wetting cannot be argued. Indeed, a simple counterexample that satisfies all the pertinent scaling relations but produces no wetting transition, is the choice $\mathcal{X}(x) = \tanh x$. This gives $\Delta\gamma < \gamma_0$ for all $T < T_c$ (no wetting transition). Scaling theory does not give $\mathcal{X}(x)$. Explicit model calculations or approximation schemes (*e.g.*, Landau theory) are required. A wetting transition is then seen to correspond to a singularity in $\mathcal{X}(x)$ at some point x_0, with $\mathcal{X}(x) < 1$, for $x < x_0$, and $\mathcal{X}(x) = 1$, for $x \geq x_0$ (Pandit *et al.* 1982). If a wetting transition is known to occur at some point (T, h_1), scaling theory predicts how the wetting phase boundary, given by $x = x_0$, behaves near T_c, in terms of the critical exponent Δ_1. Assuming $\Delta_1 > 0$ (since the surface field is a relevant perturbation), we obtain critical-point wetting. That is, $(h_1)_W \to 0$ for $T_W \to T_c$, where the subscript W refers to the wetting phase boundary.

We now turn to the Landau theory, which provides an explicit approximation for the scaling function $\mathcal{X}(x)$, and serves as an ideal testing ground for arguments à la Cahn. In the phenomenological Landau theory, wetting at walls is represented by the surface free-energy functional (Cahn 1977, Nakanishi and Fisher 1982)

$$\gamma[m] = \int_1^\infty \left\{ \frac{c^2}{4} \left(\frac{dm}{dz} \right)^2 + f(m(z)) \right\} dz + \gamma_s(m_1) , \tag{3.9}$$

of the order-parameter profile $m(z)$, for $z \geq 1$. The substrate is at $z = 1$. The value of m at the substrate is denoted by $m_1 \equiv m(z = 1)$. For the reduced (*i.e.*, divided by $k_B T_c$) bulk free-energy density the usual quartic polynomial is assumed,

$$f(m) = a_0 + a_2\, m^2 + a_4\, m^4 . \tag{3.10}$$

(An external field is not included and liquid-vapour symmetry is assumed, so that $a_1 = a_3 = 0$.) The usual procedure is to take $a_4 = 1$, $a_2 = 2A^2(T - T_c)/T_c$, and a_0 such that $\min[f(m)] = 0$. At two-phase coexistence $(T \leq T_c)$, the bulk order parameter $m_b \equiv m(z = \infty)$ is then given by $m_b = \pm m_0$, where

$$m_0 = A \left(1 - \frac{T}{T_c} \right)^{1/2} . \tag{3.11}$$

For the substrate-adsorbate energy the usual form

$$\gamma_s(m_1) = -\, h_1\, m_1 - g\, \frac{m_1^2}{2} \tag{3.12}$$

is chosen, with h_1 the surface field and g the surface-coupling enhancement ($g < 0$ is typical for fluids at walls, whereas also $g \geq 0$ is possible for magnets). The Landau theory can be derived starting from the Ising model and performing approximations of the mean-field type (Maritan *et al.* 1991). In particular, $g > 0$ corresponds to the case of $J_{\|}$ being significantly stronger than J_B. A physical example of this is surface ferromagnetism above the bulk Curie temperature (Weller *et al.* 1985).

In the Landau theory one calculates the $m(z)$ that minimizes $\gamma[m]$. This leads to the "Euler-Lagrange equation" (in the language of mechanics)

$$\frac{c^2}{2}\frac{d^2m}{dz^2} = \frac{df}{dm}, \tag{3.13}$$

and the boundary conditions

$$\frac{c^2}{2}\left.\frac{dm}{dz}\right|_1 = -h_1 - g\,m_1\,, \tag{3.14}$$

$$m(\infty) = m_b = \pm m_0\,. \tag{3.15}$$

The sign in (3.15) depends on which phase is imposed in bulk. Note that integration of (3.13) gives the "constant of the motion"

$$E = \frac{c^2}{4}\left(\frac{dm}{dz}\right)^2 - f(m) = 0\,, \tag{3.16}$$

where the constant E is indeed zero in view of (3.15). When this is substituted in (3.9), one obtains

$$\gamma[m] = c\int_{m_b}^{m_1} dm\, f(m)^{1/2} - h_1 m_1 - \frac{g m_1^2}{2}\,, \tag{3.17}$$

where $m_1 \geq m_b$ is assumed. Otherwise, the integration limits must be interchanged. From (3.16) and (3.17) it is easy to see that $\gamma[m]$ can be calculated in terms of integrals or areas in the phase-portrait plane (that is, in the plane of dm/dz versus m). This naturally leads to *equal-areas rules* for obtaining the location of the surface phase transitions (Cahn 1977, de Gennes 1985).

The surface free energies γ_+ and γ_-^* are well defined as long as they correspond to profiles that represent (local) minima of $\gamma[m]$. An explicit calculation of $\Delta\gamma^*$ and γ_0 gives

$$\frac{\Delta\gamma^*}{\gamma_0} = \tfrac{1}{16}\{[\kappa^2 + 4(1+\phi)]^{3/2} - [\kappa^2 + 4(1-\phi)]^{3/2}\} + \tfrac{3}{4}\phi\kappa\,, \tag{3.18}$$

$$\gamma_0 = \tfrac{4}{3}cm_0^3\,, \tag{3.19}$$

where $\phi = h_1/cm_0^2$, and $\kappa = g/cm_0$.

The basic phase diagrams have been obtained in the well-known paper by Nakanishi and Fisher (1982), and have often been reviewed. Since they provide an important reference frame, we repeat them here, but restrict ourselves to two-phase coexistence in bulk (*i.e.*, omitting the prewetting phenomena and the surface transitions above T_c). The wetting phase boundary is given by $\Delta\gamma^*/\gamma_0 = 1$, and the drying phase boundary by $\Delta\gamma^*/\gamma_0 = -1$. The two are related by trivial symmetry ($h_1 \to -h_1$). Typical results are shown in Fig. 9.

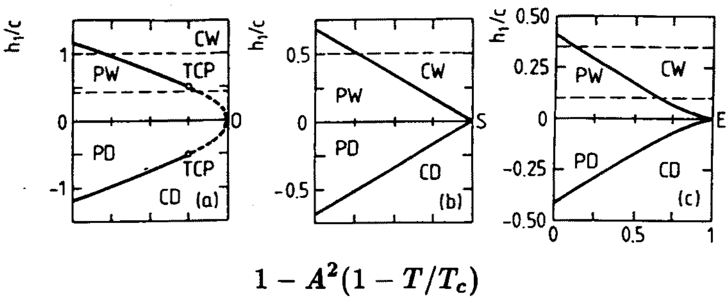

Fig. 9. Wetting (and drying) phase boundaries in the (h_1, T)-plane, separating partial wetting (PW) from complete wetting (CW). (a) $g < 0$ (*e.g.*, $g/c = -1$ for the present calculation). At the tricritical point TCP first-order wetting (solid line) changes to critical wetting (dashed line). At $h_1 = 0$ and $T = T_c$, the Ordinary transition (O) takes place. (b) $g = 0$. First-order transitions. At $h_1 = 0$ and $T = T_c$: Special transition (S). (c) $g > 0$ (*e.g.*, $g/c = 1$). First-order transitions. At $h_1 = 0$ and $T = T_c$: Extraordinary transition (E). (Thin horizontal dashed lines are relevant to Fig. 10.)

It is interesting at this point to present $\Delta\gamma^*$ and γ_0 versus temperature, for typical cases. This is done in Fig. 10. Note that $\Delta\gamma^*$ does not approach zero, for $T \to T_c$. To the contrary, for $t \to 0$,

$$\text{either}\quad \Delta\gamma^* \quad \text{ceases to exist,} \tag{3.20}$$

$$\text{or}\quad \Delta\gamma \to \text{constant} \neq 0\,. \tag{3.21}$$

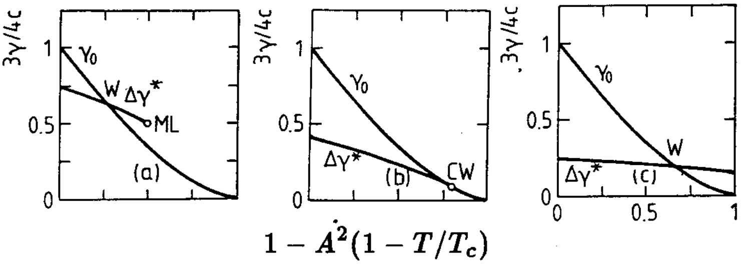

Fig. 10. $\Delta\gamma^*$ and γ_0 versus temperature for fixed h_1 and g. (a) $g/c = 0$ and $h_1/c = 0.5$ (see Fig. 9b). $\Delta\gamma^*$ can be continued beyond first-order wetting (W) but ceases to exist at the metastability limit (ML). Similar behaviour is found for, *e.g.*, $g/c = -1$ (Fig. 9a) and $h_1/c = 1$, and, *e.g.*, $g/c = 1$ (Fig. 9c). (b) $g/c = -1$ and $h_1/c = 0.45$ (Fig. 9a). $\Delta\gamma^*$ merges with γ_0 in a cusp (*i.e.*, with coincident tangents) and ceases to exist, right at critical wetting (CW). (c) $g/c = 1$ and $h_1/c = 0.1$ (Fig. 9c). $\Delta\gamma^*$ is nonzero at T_c.

Furthermore, for the equilibrium states we find, in all cases,

$$\Delta\gamma = \gamma_0 \propto t^{\mu}\,, \quad \text{for} \quad 0 \le t \le t_W\,, \tag{3.22}$$

where $t_W = (T_c - T_W)/T_c > 0$. A "global" wetting phase diagram is shown in Fig. 11. It is a convolution of the standard phase diagrams of Fig. 9, using the scaling variables instead of the thermodynamic ones. If we let T approach T_c, at fixed h_1 and g, we move away from the origin along a parabola

$$|\,\phi\,| = (|\,h_1\,|\,c/g^2)\kappa^2\,. \tag{3.23}$$

We always encounter a wetting transition, the character of which can be critical, tricritical (at TCP in Fig. 11), or first-order. The phase boundary for critical wetting is given by $|\,\phi\,| = -\kappa$ and $\kappa < -2$. The tricritical point is at $|\,\phi\,| = 2$ and $\kappa = -2$. The disfavoured profile ceases to exist beyond the critical wetting transition, and beyond the metastability limit associated with first-order wetting. This metastability limit is found by inspection of (3.18) and is given by

$$|\,\phi\,| = 1 + \frac{\kappa^2}{4}\,, \quad \text{with} \quad \kappa > -2\,. \tag{3.24}$$

At this limit a local minimum of $\gamma[m]$, the (metastable) disfavoured profile, is annihilated by a local maximum of $\gamma[m]$. Therefore, beyond this limit γ_-^* and hence $\Delta\gamma^*$ no longer exist (in fact, they are undetermined). Note that for $g > 0$ <u>and</u> $| h_1 | c/g^2 < 1/4$, we can continue γ^*_- to T_c and in that case, for $t \to 0$,

$$\Delta\gamma^* \to \frac{g^3}{12c^2}\left\{\left[1+\frac{4h_1c}{g^2}\right]^{3/2} - \left[1-\frac{4h_1c}{g^2}\right]^{3/2} + \frac{12h_1c}{g^2}\right\} \neq 0\,. \qquad (3.25)$$

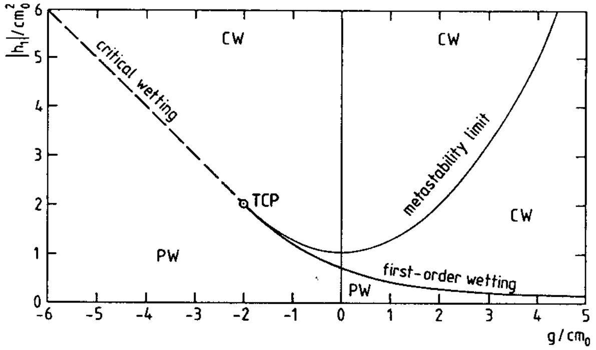

Fig. 11. Global phase diagram of wetting at walls. The wetting phase boundary (first-order or critical) separates partial wetting (PW) from complete wetting (CW).

In order to make contact with (3.7) and (3.8), and to identify the mean-field values for β_1 and Δ_1, we distinguish the following cases.

(a) $g = 0$. We obtain from (3.18), with $\kappa = 0$, that $\Delta\gamma^*/\gamma_0$ is a function of ϕ alone. Comparison with (3.7) implies $\Delta_1 = 1$, in view of (3.11). Furthermore, for small ϕ, $\Delta\gamma \sim 2h_1m_0$, implying $\beta_1 = 1/2$, by comparison with (3.8). This case corresponds to the "Special" surface transition (see further).

(b) $g < 0$. The critical point is then approached in the limit $\kappa \to -\infty$. We obtain

$$\Delta\gamma^*/\gamma_0 = \tfrac{3}{2}\phi/ \mid \kappa \mid + \mathcal{O}(\mid \kappa \mid^{-3})\,. \qquad (3.26)$$

Rewriting this as $\Delta\gamma^* \sim 2c(h_1/ \mid g \mid)m_0^2$, we find $\Delta_1 = 1/2$ and $\beta_1 = 1$. This corresponds to the "Ordinary" surface transition.

(c) $g > 0$. In this case we let $\kappa \to \infty$, and obtain

$$\frac{\Delta\gamma^*}{\gamma_0} = \tfrac{3}{2}\phi\kappa + \mathcal{O}(\kappa^{-1})\,, \qquad (3.27)$$

so that $\Delta_1 = 3/2$ and $\beta_1 = 0$. This corresponds to the "Extraordinary" transition. We remark that in this case the exponent β_1 is in fact better defined in a different way, namely so that it describes the vanishing of the singular part of the surface order parameter, relative to a regular and finite background contribution. This gives $\beta_1 = 2$ (Bray and Moore 1977, Binder 1983).

As an aside, we note that for small ϕ and arbitrary κ,

$$\Delta\gamma^* = h_1 m_0(\kappa + (\kappa^2 + 4)^{1/2}) + \mathcal{O}(\phi^3)\,, \tag{3.28}$$

In general, and especially for $g \geq 0$, $\Delta\gamma^*$ is well approximated by the first term in this expansion, as far as the location of the wetting transition is concerned. However, the transition always comes out first-order in this approximation. For the phase boundary, see Indekeu (1991).

Concerning the different surface transitions that are possible at T_c, we remind the reader about the basic notions in the Ising model context. For reviews, see Binder (1983) and Diehl (1986). For the semi-infinite Ising model described by the Hamiltonian (3.1) and illustrated in Fig. 8, we distinguish two main cases: $H_1 = 0$ and $H_1 \neq 0$. For $H_1 = 0$ we further distinguish the Ordinary, Special, and Extraordinary transitions. The case $H_1 \neq 0$ is similar to the Extraordinary transition, and is therefore sometimes given the same name (Bray and Moore 1977), although nowadays the term "Normal transition" is preferred. The reason for this is that most real systems lack the special symmetry that corresponds to $H_1 = 0$. The surface phase diagram for $H_1 = 0$ is shown schematically in Fig. 12 .

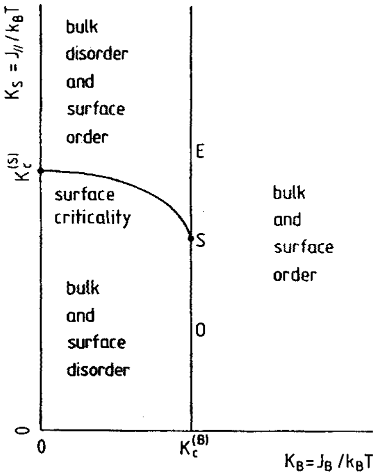

Fig. 12. Surface phase diagram of the semi-infinite Ising model in zero surface field (and zero bulk field). The bulk is ordered for $K_B > K_c^{(B)}$, and is critical at $K_B = K_c^{(B)}$. The surface is critical on the line extending from $K_S = K_c^{(S)}$ at $K_B = 0$ (criticality of an isolated surface) to the Special transition point S.

Note that varying the temperature T corresponds to moving along a straight line through the origin. For fixed and small $J_{\|}/J_B$, the surface is disordered at the bulk critical point (segment O: Ordinary transition). On the other hand, for fixed and large $J_{\|}/J_B$, we encounter surface criticality (the onset of spontaneous surface order) at a temperature above bulk criticality. Bulk criticality is then achieved in the presence of a spontaneously ordered surface (segment E: Extraordinary transition). For one particular choice of $J_{\|}/J_B (> 1)$, surface and bulk become critical simultaneously. This happens at the multicritical point S (Special transition).

Finally, for $H_1 \neq 0$, as is the case in standard wetting problems (fluids at walls, liquid mixtures at walls, or magnets at surfaces, ...), the surface is "ordered" at the bulk critical point, because of the presence of the symmetry breaking surface field. However, this is field-induced or imposed order, whereas true long-range or spontaneous surface order is only possible for $H_1 = 0$ (for critical remarks about proper terminology, see Fisher [1986b]). One must be careful here, because some experts consider imposed order to be a form of disorder.

Before coming to the conclusions of this Chapter we comment briefly on the status of the Landau theory in the research on wetting phenomena. The Landau theory is of mean-field type and consequently misses effects of fluctuations which may lead to quantitative and even qualitative changes in phase diagrams, the order of phase transitions (first-order or continuous), critical exponents, *etc.* An important parameter in this respect is the upper critical dimension d_{uc}. This is the dimension above which the mean-field theory can be trusted, even quantitatively. For bulk critical phenomena (in the Ising universality class, for example) $d_{uc} = 4$, implying that bulk critical phenomena in real systems ($d \leq 3$) are not correctly described by mean-field theory.

For wetting and other interfacial phenomena the mean-field theory is in a better position than for bulk phenomena. To begin with, $d_{uc} = 3$ for complete wetting and critical wetting in the presence of short-range forces (as in Ising models, or in continuum fluids with a potential cutoff as in most computer simulations, or in real metals where the screening effect of the electrons can significantly reduce the amplitude of the Van der Waals interaction [Maggs and Ashcroft 1987]). By complete wetting we mean here the continuous phase transition associated with the divergence of the wetting layer thickness upon approach of two-phase coexistence from the one-phase region (Lipowsky 1985). By critical wetting we mean, as before, a continuous wetting transition along two-phase coexistence. By analogy with bulk phenomena, one would expect that right at d_{uc} the pertinent critical exponents are still correctly given by mean-field theory. Interestingly, this is not the case. In $d = 3$ important and complicated (non-universal) corrections to the mean-field exponents have been predicted by renormalization group methods (Brézin *et al.* 1983). Although these corrections have apparently not yet been seen in simulations of the Ising model (Binder and Landau 1988, Binder *et al.* 1989), they show up in simulations of interface-displacement models (Gompper and Kroll 1988), and of the Solid-on-Solid limit of the Ising model (Gompper *et al.* 1990), and should definitely be there according to a recent scrutiny of renormalization group predictions (Fisher and Jin 1991, 1992).

The physical explanation for the breakdown of mean-field theory in three and less dimensions lies in the thermal roughness of the (liquid-vapour) interface that arises from divergent capillary wave fluctuations at long wavelengths. The roughness is described by the length $L_\perp$, perpendicular to the interface, which is found to behave as $L_\parallel^{(3-d)/2}$, for $d < 3$, where $L_\parallel$ is the in-plane or parallel length of the interface. In $d = 3$, $L_\perp \propto (\ln L_\parallel)^{1/2}$. Thus, the interface is rough in $d \leq 3$. Mean-field theory corresponds to setting $L_\perp$ equal to a finite length, imposing a smooth interface. For a comprehensive review, see Fisher (1986a).

Next, $d_{uc} < 3$ for complete and critical wetting in the presence of long-range intermolecular forces (with power-law decay as in Van der Waals systems). The physical origin for this is that intermolecular forces that decay as $r^{-(d+\sigma)}$ (*e.g.*, $\sigma = 3$ for non-retarded Van der Waals forces in $d = 3$) produce a long-ranged surface free energy contribution $l^{-(\sigma-1)}$ for a wetting layer of thickness l (in the approach to complete wetting). This must be compared with the fluctuation-induced entropic repulsion of the interface by the wall. This repulsion arises because the capillary waves "collide" with the wall at large wavelengths. In a simple interface displacement model, this contribution is of order gradient squared, *i.e.*, $(L_\perp/L_\parallel)^2$. On a perpendicular length scale $L_\perp$ of order l, this gives $l^{-2(d-1)/(3-d)}$, for $d < 3$. If this term is of shorter range than the intermolecular term, we can ignore roughness and use mean-field theory. Thus, $d_{uc} = 3 - 4/(\sigma + 1)$, which is less than 3. For $d > d_{uc}$ (mean-field regime) the critical exponents depend on the range of the intermolecular forces; for $d < d_{uc}$ (fluctuation regime) they depend on the dimensionality. Analogous arguments apply for critical wetting. See Fisher (1986a) for a review.

The great merit and predictive power of mean-field theories for wetting phenomena, and in particular the Landau theory, even when applied to the (short-range) Ising model, is strikingly demonstrated in the extensive Monte Carlo simulations of $d = 3$ Ising models (Binder and Landau 1988, Binder *et al.* 1989). These studies confirm in detail the wealth of first-order, critical and tricritical wetting transitions, as well as prewetting phenomena, predicted by the Landau theory.

Discussion

(1) What is the role of the bulk critical point in wetting phenomena at walls?

In general, wetting phenomena and wetting phase transitions depend sensitively on non-universal characteristics (such as details of the intermolecular forces), and the principal role of the bulk critical point is nothing more than to delimit the range of thermodynamic variables (temperature, ...) over which wetting phenomena can be defined. (A possible exception to this is complete drying by vapour, a phenomenon which, if it exists at all, is expected to occur in the immediate vicinity of the bulk critical point, as argued in the Introduction.) However, near bulk criticality wetting phenomena acquire universal characteristics. Cahn's discovery of complete wetting near critical points exemplifies a universality of this kind. It is of interest to investigate which is the pertinent universality class. Cahn (1977) implicitly suggested the universality class of bulk critical phenomena. (Indeed, he invoked the bulk β exponent for describing the critical behaviour of the difference of surface free energies $\Delta\gamma$. Furthermore, the surface tension exponent μ is determined by the dimension d and the bulk correlation exponent ν: $\mu = (d-1)\nu$.) We will propose a different universality class, namely that of the Normal surface transition (which is, for all practical purposes, the same as the Extraordinary surface transition).

(2) Is complete wetting necessary near bulk criticality?

For wetting at walls as described by the Ising model with a surface field H_1, or, more phenomenologically, by the Landau theory with $h_1 \neq 0$, we have found no exceptions to complete wetting near the bulk critical point (T_c). We tend to conclude that complete wetting is necessary near bulk criticality for wetting at walls or other spectator phases with short-range substrate-adsorbate forces that can effectively be characterized by $h_1 \neq 0$.

(3) Is Cahn's argument (or a later version thereof) supported by scaling theory?

The argument assumes that a difference of surface free energies, $\Delta\gamma$, vanishes as a positive power of the temperature distance from the bulk critical point. An exponent is assumed (β, β_1, or 1, ...) which is smaller in magnitude than the critical exponent μ of the surface tension. This cannot be supported by scaling theory. Firstly, as Pandit *et al.* (1982) remarked, scaling theory deals with thermodynamic equilibrium and not with the metastable states (of a mean-field theory). Secondly, these authors showed that β_1 does play a role, but in the limit of zero surface field ($h_1 \to 0$), and not in the limit of bulk criticality ($T \to T_c$). Scaling theory does not make a prediction in this latter limit, unless the occurrence of a wetting transition is given a priori.

(4) Is the argument valid in the Landau theory?

In the Landau theory for wetting (Cahn 1977, Nakanishi and Fisher 1982), we checked explicitly that the difference of surface free energies $\Delta\gamma^*$ does not vanish at the critical point. Although this is in fact opposite to what the usual argument assumes, Cahn's conclusion of critical-point wetting is a fortiori true! Indeed, in hindsight one could make the argument stronger: "Since γ_0 vanishes at T_c, but $\Delta\gamma^*$ does not, critical-point wetting is necessary."

Concerning questions (3) and (4), specialists may wonder why we have bothered to scrutinize this "old" burden. The reason will become clear when we study critical-point wetting in other categories of wetting problems, *e.g.*, special varieties of grain boundaries (and where we shall meet important cases for which $\Delta\gamma^* \to 0$). But besides that, a scrutiny of Cahn's pioneering conjectures is far from a waste of time if one realizes that it is difficult to think of a paper on wetting phenomena that has been as stimulating and influential as his one of 1977.

4. Wetting at neutral grain boundaries

Our second category of wetting problems, after wetting at walls, is "wetting at grain boundaries". A physical example is the pinning of an antiphase boundary at a grain boundary in a binary alloy crystal (Cénédèse *et al.* 1988). This is illustrated in Fig. 13. Basically, problems in this category concern two semi-infinite adsorbates that meet at a defect plane with defect coupling H_2.

At the level of an Ising model description, the problem is that of the pinning of an interface at a defect plane (Abraham 1981). In general, there may be a surface field H_1 at the location of the defect plane. If $H_1 \neq 0$ the defect plane prefers one of the two phases, and the preferred state consists of the presence of that preferred phase on both sides of the defect plane. For a large variety of real grain boundaries H_1 will be present and the discussion of wetting phenomena then closely resembles that of wetting at walls, at least as far as the universal properties near the bulk critical point are concerned (Ebner *et al.* 1990). Our purpose here is to study a system with a different symmetry, and therefore we restrict attention to what we will call neutral grain boundaries, *i.e.*, those with $H_1 = 0$. Wetting at neutral grain boundaries is characterized by the Hamiltonian

$$\mathcal{H}(\{s\}) = -J_B^- \sum_{\langle ij\rangle} s_i s_j - J_\parallel^- \sum_{\langle ij\rangle \in \Gamma^-} s_i s_j - J_B^+ \sum_{\langle ij\rangle} s_i s_j - J_\parallel^+ \sum_{\langle ij\rangle \in \Gamma^+} s_i s_j - H_2 \sum_{i\in\Gamma^- j\in\Gamma^+} s_i s_j \,, \tag{4.1}$$

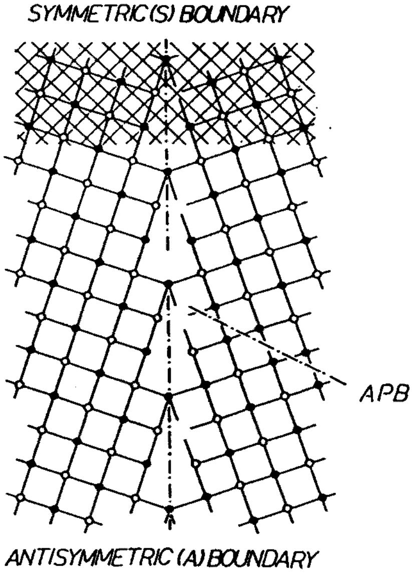

Fig. 13. A grain boundary between two ordered grains in a lattice gas model. An antiphase boundary (APB) in the right-hand grain joins the grain boundary at an angle (*i.e.*, the contact angle as determined by the generalized Young equation [de Coninck and Dunlop 1987]) and changes it from symmetric to antisymmetric. The underlying lattice is shown along the top. (Reproduced from Cénédèse *et al.* 1988)

where J_B is the bulk nearest-neighbour coupling, $J_{\|}$ the surface nearest-neighbour coupling (the defect plane or "surface" is denoted by Γ), and $H_2 \equiv J_D$ the nearest-neighbour defect coupling. The corresponding spin lattice is shown in Fig. 14. Note that the defect plane Γ is composed of two surfaces Γ^- and Γ^+. For the moment, we assume $J_B^- = J_B^+$. (The more general case will be studied later.) Furthermore, we assume $J_{\|}^- = J_{\|}^+$. Concerning the symmetry, we remark that the Hamiltonian of the Ising model for wetting at walls (see the preceding chapter) is not invariant under sign reversal of all spins, because a surface field H_1 is present. In contrast, the Hamiltonian (4.1) is invariant under this transformation.

A concise discussion of critical-point wetting at grain boundaries runs as follows. Consider a defect plane with defect coupling $H_2 > 0$. The adsorbate is at two-phase coexistence, and we denote the phases by + and −. The preferred state is one in which the bulk adsorbate is in the + phase on both sides of the defect plane, or, equivalently, in the − phase on both sides (because $H_2 > 0$). It is characterized by a surface free energy $\gamma_{++}(=\gamma_{--})$. If, however, we impose the disfavoured state, in which the bulk adsorbate is in the − phase on one side, and in the + phase on the other, the surface

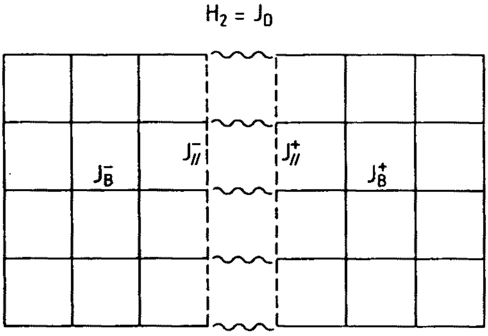

Fig. 14. Spin lattice for two semi-infinite systems meeting at a defect plane (with defect bonds (wiggly) and surface bonds (dashed)), suitable for modelling wetting at neutral grain boundaries.

free energy is denoted by $\gamma^*_{+-} (= \gamma^*_{-+})$, where, as before, the star denotes the possibility of a metastable state. Clearly, $\Delta\gamma^* \equiv \gamma^*_{+-} - \gamma_{++} > 0$. We say that there is preferential adsorption of equal phases on both sides of the defect plane. Besides γ_{++} and γ^*_{+-} we must, like for wetting at walls, consider the surface tension of a $+-$ interface infinitely far from any defect plane, γ_0.

Just like for wetting at walls, there are two important cases. The first is $\Delta\gamma^* = \Delta\gamma < \gamma_0$, corresponding to partial wetting. The second corresponds to all possible alternatives to the just mentioned inequality, which all imply $\Delta\gamma = \gamma_0$ in thermodynamic equilibrium. Indeed, the disfavoured state yields to the combination of the preferred state and a $+-$ interface far from the defect plane, with surface free energy $\gamma_{++} + \gamma_0$. This corresponds to complete wetting. Note that the transition can occur on either side of the defect plane, with equal probability.

What happens when the temperature T approaches T_c? The critical behaviour of γ_0 is given by

$$\gamma_0 \propto (T_c - T)^{\mu} , \tag{4.2}$$

as before. What can we say about the critical behaviour of $\Delta\gamma^*$? Explicit calculations in Landau theory, supplemented with scaling arguments that invoke the correct critical exponents, show that (Sevrin and Indekeu 1989)

$$\Delta\gamma^* = \Delta\gamma \propto (T_c - T)^{2\beta_1}, \tag{4.3}$$

We have $2\beta_1 \approx 1.5 > \mu \approx 1.3$, in $d = 3$. (In Landau theory, $2\beta_1 = 2$ and $\mu = 3/2$.) Consequently, if there is partial wetting to begin with at some $T < T_c$, partial wetting persists until T_c. There is no critical-point wetting.

This conclusion was also reached in earlier works (Abraham 1981, Cénédèse *et al.* 1988).

However, this is only half of the story. Explicit calculations in Landau theory (Sevrin and Indekeu 1989) show that (4.3) is only valid provided the surface order parameter m_1 vanishes at T_c. In other words, it holds only if the defect plane disorders at the bulk critical point. This is not always the case. Indeed, if the interactions parallel to the defect plane, $J_{\|}$, are sufficiently strongly enhanced relative to J_B, the defect plane remains spontaneously ordered at T_c, so that m_1 does not vanish. This is called the Extraordinary transition. (We assume here that the dimensionality of the bulk adsorbate is not too low. The surface dimensionality $d-1$ should namely exceed the lower critical dimension d_{lc}, which equals 1. For $d=3$, there is no problem.) Then,

$$\Delta\gamma^* \quad \text{does not vanish at} \quad T_c, \tag{4.4}$$

implying critical-point wetting!

5. Universality of critical-point wetting

It is well-known that wetting phenomena do not possess the degree of universality that is characteristic of bulk critical phenomena. Since wetting phenomena are essentially surface phenomena, perhaps they can possess the degree of universality that is characteristic of surface critical phenomena. This is seen in several situations indeed. An excellent example is the equivalence of pure surface criticality (in the bulk one-phase region above the bulk critical point) and prewetting criticality, proposed by Nakanishi and Fisher (1982) and checked by Nicolaides and Evans (1989). Sometimes wetting transitions constitute a novel universality class themselves. This is the case, for example, for critical wetting as studied by Sullivan (1979, 1981), and by Brézin *et al.* (1983). In other cases simple wetting phenomena are genuine critical phenomena but had not been recognized as such. Important work in this respect is Lipowsky's study (1985) of complete wetting as a critical phenomenon with a diverging correlation length. A quite different universal property of wetting phenomena was revealed already at an early stage, when Cahn (1977) discovered that complete wetting is "necessary" near bulk criticality. The precise kind of universality that plays a role there has remained controversial until quite recently. The calculations reviewed in the topics "wetting at walls", "wetting at neutral grain boundaries", and "wetting at triple junctions" (a topic which is not covered in these lectures, but which can be found in Indekeu and Nikas 1991) suggest the following answer.

Consider a wetting problem that can be formulated in terms of a suitable Ising model. This is possible in many cases. For example, in the case of the liquid mixtures of Moldover and Cahn (1980), one may represent the binary system methanol-cyclohexane by a semi-infinite Ising model, and the spectator vapour phase by a short-range surface field h_1 plus a long-range field h_{lr}, acting on the semi-infinite system. Varying the concentration of an additional component, in this case water, is equivalent to varying the temperature in the Ising model, and so on. The generic situation in these systems is that the effective surface field h_1, which is responsible for preferential adsorption of one of the phases, varies in some smooth fashion with, *e.g.*, temperature, and assumes a finite nonzero value at the bulk critical point of the adsorbate, T_c. Note that h_1 may at some temperature pass through zero, thereby reversing the preferential adsorption (Durian and Franck 1987), but there is in general no reason whatsoever for that temperature to coincide with T_c. Thus, the generic situation is that a nonzero surface field is present, below, at (and above) T_c. As a result the Ising model will have a nonzero surface order parameter m_1 (a surface magnetization, or density or concentration excess), also at T_c. This property shows up experimentally in the form of critical adsorption (Liu and Fisher 1989), or, for ferromagnets, in the form of surface magnetization at the Curie point. The calculations indicate that this feature ($m_1 \neq 0$ at T_c) is systematically associated with complete wetting in the two-phase region near (typically below) T_c.

In Ising model language, if $m_1 \neq 0$, the surface is often said to be "ordered". Unfortunately, this nomenclature is confusing, because many physicists have specific ideas about surface order in the context of which it would be quite contrary to say that the interface between a liquid mixture and its vapour is "ordered". In order to reduce and hopefully eliminate confusion, one should specify the kind of order that applies. In the presence of an ordering "field" (in the general sense) the order is "imposed". In absence of such fields, true long-range or "spontaneous" order is possible (and can be measured by examining the decay of a suitable net correlation function). The calculations now show that both "imposed" and "spontaneous" surface order, at T_c, are associated with complete wetting below T_c. Imposed order is generic for the standard wetting problems (fluids and magnets at surfaces or interfaces), whereas spontaneous order is possible in wetting problems in systems with internal defect planes like neutral grain boundaries, for example.

Conversely, if $m_1 \to 0$ for $T \to T_c$, the surface is said to be disordered at T_c, again in Ising model language. While this is highly exceptional (if not impossible) for standard systems, it is likely to occur in grain boundary wetting, at least for neutral grain boundaries. The calculations show that surface disorder at T_c (*i.e.*, the total absence of field-induced or spontaneous order) is associated with partial wetting below T_c.

The conclusion, as formulated in the language of surface critical phenomena, is that the Ordinary transition is strongly associated with partial wetting, and the Extraordinary transition with complete wetting. For convenience we have, following Bray and Moore (1977), generalized the term Extraordinary transition to the case of "imposed" order, although nowadays the term "Normal transition" is preferred for systems with $H_1 \neq 0$. In conclusion, we can classify wetting behaviour (partial or complete wetting) near T_c according to the surface transition that the system undergoes at T_c. The main universality classes of surface critical phenomena thus have a clear and strong association with wetting phenomena. In our opinion this connection illuminates the universality of wetting near critical points, and represents new progress on the important issue pioneered by Cahn (1977, 1979).

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