- [14] M. Schick and P. Taborek, Phys. Rev. B46 (1992).
- [15] M.S. Pettersen and W.F. Saam, J. Low Temp. Phys. 90, 159 (1993).
- [16] M. Schick and O.E. Vilches, preprint (1993).

Presented at the Discussion Meeting of the Deutsche Bunsen-Gesellschaft für Physikalische Chemie "Phase Transitions at Interfaces" in Bad Herrenalb, September 22nd to 24th, 1993

E 8569

Critical Point Wetting from Binary Polymer Mixtures

Ullrich Steiner, Erika Eiser, Andrzej Budkowski¹), Lewis Fetters²), and Jacob Klein³)

Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel

Key Words: Liquids / Polymers / Polymer Mixtures / Surfaces / Wetting

Critical point wetting generally occurs whenever a binary fluid system in the demixed region of phase space, in contact with a surface, approaches its critical temperature. For the case of polymeric mixtures the segmental interaction parameter, which determines the interfacial tension between the coexisting phases, can be very low even far from the critical point. This suggests that polymer blends should be likely candidates to exhibit complete wetting even far below the critical point. Using nuclear reaction analysis, we have now observed such complete wetting behaviour from two different classes of binary polymer mixtures. These are mixtures of statistical olefinic copolymers, with slightly different chemical microstructures; and an isotopic pair of deuterated and protonated polymers. In the former case we have been able to follow the growth with time t of the wetting layer thickness *l*; our results indicate $l \sim \log t$.

1. Introduction

A two-component liquid mixture (A and B say) with an upper critical solution temperature will separate, below its critical temperature T_c , into two coexisting phases, α (rich in A, say) and β (rich in B). Any surface in contact with such a mixture may be either partially or completely wetted by one of the phases. If A is the surface-preferred component, then complete wetting implies that the α -phase forms a macroscopic layer at the surface, completely excluding the β -phase [1]. In such a binary mixture the nature of the wetting is determined by the relation

$$\gamma_{\alpha\beta} \ge \gamma_{s\beta} - \gamma_{s\alpha} \tag{1}$$

Here γ_{ii} are the interfacial energies, where i, j refer to the α phase, the β -phase or to the surface phase s. Equality in Eq. (1) leads to complete wetting in the sense described above. Inequality implies partial wetting: i.e. that there must be an energetically cheaper way to cover the surface than by a macroscopic wetting layer of the α -phase [1]. In 1977 Cahn presented his seminal argument for the existence of critical point wetting [2]. He assumed that the nature of the surface interactions was short ranged, and that the difference in the interaction energies $\gamma_{s\alpha}$ and $\gamma_{s\beta}$ originated in, and was proportional to the difference in compositions of the α and β phases, more specifically in the difference in content of the A component. Since the wall is not a 'critical component' this difference varies as the length of the tie-line (between the coexisting compositions) at the appropriate temperature $T < T_c$, the critical temperature. This is illustrated in Fig. 1. Thus this difference scales as

$$(\gamma_{s\beta} - \gamma_{s\alpha}) \propto (T_c - T)^{\varepsilon}$$
⁽²⁾

where ε is a surface spinodal exponent whose value is ca. 0.8. At the same time the interfacial energy scales as

$$\gamma_{\alpha\beta} \propto (T_{\rm c} - T)^{2\nu} \tag{3}$$

where 2v is a bulk critical exponent whose value is ca. 1.3. Thus as T_c is approached the interfacial energy $\gamma_{\alpha\beta}$ will





The difference in volume fraction of the surface-preferred component A between the two coexisting phases at a temperature $T < T_c$ is given by the length of the tieline as shown. Near $T_{\rm c}$ this varies with temperature as given in Eq. (2)

^[13] J.O. Indekeu, Physica A 183, 439 (1992).

¹) On leave from Jagellonian University, Cracow, Poland.

²⁾ Exxon Research and Engineering Co., Annandale, N.J. 08801, USA.

³) To whom correspondence should be addressed.

always decrease faster than the difference $(\gamma_{s\beta} - \gamma_{s\alpha})$, so that sufficiently close to the critical temperature the inequality in Eq. (1) will become an equality and complete wetting will occur. This is Cahn's argument for critical point wetting. It relies for its generality on the existence of short range surface forces alone, but it has been found to hold in most binary liquid mixtures examined to date, and has provided stimulation of much theoretical work [3-6].

The above discussion applies to binary mixtures of small or monomeric species. In the case of polymer mixtures, an interesting situation arises with respect to the question of complete wetting. This is because of the connectivity of the large number N (typically $10^3 - 10^4$) of monomers on each chain, which suppresses the contribution of translational entropy in the mixing of two different polymers. The classical Flory-Huggins expression for the free energy of mixing $\Delta F_{\rm M}$ of different polymers A and B shows this clearly [7, 8]:

$$\Delta F_{\rm M}/k_{\rm B}T = (\phi_{\rm A}/N_{\rm A})\ln\phi_{\rm A} + (\phi_{\rm B}/N_{\rm B})\ln\phi_{\rm B} + \chi\phi_{\rm A}\phi_{\rm B} \qquad (4)$$

Here ϕ represents the volume fractions (where $\phi_A + \phi_B = 1$) and N the degrees of polymerisation (the subscripts relating to the respective polymers), while χ is the segmental interaction parameter. The first two terms on the R.H.S. are due to the translational entropy of mixing of the chains, and are reduced by factors of order N relative to that in corresponding small molecule mixtures. This results in critical interaction parameters χ_c that are themselves very small: $\chi_c \sim 1/N$. This is the central point: it implies that even deep into the two phase region of the phase diagram the condition $1 \gg \chi \gg \chi_c$ may hold. Since the interfacial tension between two coexisting polymer phases (α and β , or A-rich and Apoor respectively) varies as the interaction between the A and B monomers, this implies that $\gamma_{\alpha\beta}$ can be very small even deep into the two phase region. Finally, we recall that, when short-ranged forces are dominant, the interactions of the surface with the two phases is a function of their respective monomer surface concentrations only, and independent of N. Therefore the argument leading to Eq. (2) remains valid. (To make contact with later experimental results, we note at this point that, for the case where dispersive forces dominate the segmental interactions, $\chi k_{\rm B} T$ is essentially independent of the temperature T, so that $\chi \propto 1/T$. Such a dependence also implies an upper critical solution temperature (UCST).)

Relative to mixtures of monomeric species that are far in the immiscible region, then, the surface interaction difference $(\gamma_{s\beta} - \gamma_{s\alpha})$ remains essentially unchanged for polymers. At the same time the interfacial energy $\gamma_{\alpha\beta}$ can be very low. Taken together, these conditions mean that for polymeric mixtures the inequality (1) can become an equality even very far from T_c , an implication first pointed out by Binder and coworkers [9]. Thus polymeric mixtures should readily exhibit complete wetting behaviour. Nonetheless, until very recently such behaviour has never been observed. Investigations of surface composition in binary polymer mixtures have shown only partial wetting, or surface enrichment, as in the case of isotopic blends [10] or of mixtures of compatible polymers with specific interactions [11]. In this lecture we describe a recent study of the surface compositions in samples of two polymeric mixtures: an isotopic mixture of microstructurally identical chains where the segmental interactions arise from the slight differences between deuterated and protonated species; and a binary mixture of random copolymers which differ slightly in their microstructure. In the former case we demonstrate for the first time the existence of a wetting-like layer in such an isotopic blend. In the second system we show unambiguously the growth with time - to macroscopic thickness - of a wetting layer of one of the two phases in the mixture, from a coexisting composition of the other phase [12].

2. Materials and Experimental

Materials

Two types of binary polymer systems were investigated. An isotopic mixture of perdeuterated polystyrene (dPS) and protonated polystyrene (hPS), of similar molecular weights M (or degrees of polymerisation N), obtained and characterised by Polymer Laboratories (UK); and statistical copolymers of ethyl-ethylene (EE) and ethylene (E) monomers, $EE_{x_i}E_{1-x_i}$, where the monomers are arranged randomly along the polymer chain. The relative amount x_i of ethyl-ethylene monomers, $EE = -(C_2H_3(C_2H_5)) -$, can be varied to any value $0 \le x_i \le 1$. In this sense the molecules (and thereby their interactions) may be viewed as continuously 'tunable' between essentially pure polyethylene and pure poly(ethyl ethylene). Some of these random copolymers were partially deuterated (to an extent e), a prerequisite of our analytic technique as described below. The miscibility of a mixture of such copolymers depends very sensitively on the difference in the x_i , as well as on the difference in deuteration [13, 14]. The precise characteristics of the polymers used are indicated at the beginning of each section. It is noteworthy that mixtures of different x_i values (and extent of deuteration, e) can exhibit similar critical temperatures. As the material with the higher ethyl-ethylene content (i.e. higher x_i value) is preferentially adsorbed at the free surface, this allows studies of systems with different effective surface interactions, while bulk miscibility is nearly unchanged.

Experimental

Samples were prepared by spin coating a film from toluene on a polished silicon wafer. When bilayer samples were required, a second film was spin coated onto mica and then float-mounted onto the first film. The samples were annealed in vacuum and subsequently quenched and stored at a temperature below their glass transition temperatures (of $100 \,^{\circ}$ C for the PS samples, and ca. $-40 \,^{\circ}$ C for the olefinic copolymers) until their composition-depth profiles could be analysed.

The composition-depth profile $\phi(z)$ of the samples following different annealing times was determined using

nuclear reaction analysis (NRA). The method as used in these studies, which is capable of high resolution spatial profiling of deuterated species, is described in detail elsewhere [15, 16]. In brief: an energetic ³He beam of the appropriate energy impinges on the polymer sample and the nuclear reaction ${}^{3}\text{He} + {}^{2}\text{H} \rightarrow {}^{1}\text{H} + {}^{4}\text{He} + 18.35 \text{ MeV}$ takes place. The energy of the outgoing α -particles (⁴He) reveals the deuterium distribution in the sample: the incident ³He particles lose energy due to inelastic electronic processes as they penetrate the sample, so that the energy of the resulting α -particles depends on the depth in the sample at which the nuclear reaction occurred. These α -particles lose additional energy on the way to the detector, and the overall energy spectrum can be related to the depth in which the reaction has taken place and to the local ²H concentration at that depth. A schematic figure illustrating the geometry is shown in Fig. 2.



The geometry of the NRA used to profile the composition-depth characteristics of the deuterated polymer chains in these experiments. The magnetic field allows through only the required particles. (b) A magnified scale of the sample. The energy loss ΔE_4 reveals the depth at which the reaction occured (adapted from Ref. [15])

3. Results and Discussion

a) Determination of Phase Coexistence

To understand the nature of wetting from a binary mixture it is necessary that we know where it is in phase space and therefore that we determine its phase-coexistence characteristics. This was done for all the samples described in this study, using mainly the approach of Ref. [17]. In this, a layer some hundreds of nm thick of one of the pure components (B say) is spin cast on the silicon wafer, and a similar layer of the other component (A) is laid on top. It is possible to ensure that surface enrichment or wetting effects do not perturb the final phase configuration; for example, by arranging for the surface-preferred phase to be near the surface to start with. At temperatures above T_s , but below T_{c} , the two components will interdiffuse until the phases on either side of the original interface have reached their coexisting compositions ϕ_1 and ϕ_2 . At this point net bulk transport ceases. Determination of these limiting coexisting compositions at different temperatures, $T < T_c$, yields the phase coexistence diagram directly. A typical profile for coexisting phases of the binary pair of olefinic copolymers designated d88 (x = 0.88, e = 0.37,



(a) Equilibrium composition-depth profile for the d88/h78 couple on silicon at 90 °C, showing the coexisting compositions ϕ_1 and ϕ_2 . (b) The corresponding phase-equilibrium diagram for this pair

N = 1610/h78 (x = 0.78, e = 0, N = 1290) is shown in Fig. 3. Also shown is the corresponding phase coexistence diagram, showing that for this pair the critical temperature is $T_c = 126 \pm 3$ °C.

In addition to this method, it is also possible to determine the coexistence compositions ϕ_1 and ϕ_2 by making use of a 'single layer' approach. In this, a mixture of initial mean composition in the two phase region (for $T < T_c$) undergoes a phase separation where each of the phases segregates to a different interface. The thickness of the respective phases is then regulated by the overall amount of the two components, and their compositions are simply the coexistence values for that temperature. Examples of this are shown later (Fig. 6).

b) Growth of a Wetting Layer from the One-Phase Region

In the classic Moldover-Cahn experiment [18] a wetting layer of one liquid phase grows at a surface from another liquid phase within which it is in coexistence. We have emulated this for a binary polymer system by studying the formation of a layer of one polymeric phase growing - to macroscopic dimensions - from a coexisting composition of the other phase. To achieve this, we employed a "selfregulating" geometry [12]: a film of the deuterated EE_xE_{1-x} copolymer d88 is placed on the silicon substrate and covered with an h78 (x = 0.78, e = 0, N = 1290) film. Initially, the d88 - h78 interface broadens to a interfacial width comparable to the bulk correlation length; the materials partially interdiffuse until the two layers attain the composition of the coexisting phases ϕ_1 and ϕ_2 , as described for determination of coexistence in the previous section. As d88 is preferentially adsorbed at the free surface, a d88 surface peak forms, as soon as there is a finite d88 concentration (ϕ) at the surface. As the d88 in the region adjacent to the surface approaches its value on the coexistence curve, the surface peak grows. For $\phi \approx \phi_1$, the surface layer attains a thickness which is macroscopic in the sense of being larger than the other length scales in the system (such as the radius of gyration or the correlation length). This layer continues to grow until, in principle, the entire surface-preferred (d88-rich) phase is incorporated into the wetting layer, as expected in the case of complete wetting (always



h78/d88 bilayers following annealing of $t = 0 \min$ (a), $t = 30 \min$ (b) and t = 3 days (c) at 110 °C

assuming the substrate is not itself wetted). This behaviour is reproduced in Fig. 4, which shows the h78/d88 bilayer as prepared, after 30 min; and after 3 days at 110 °C (16 °C below the critical point of this mixture, $T_c = 126$ °C).

Complete phase inversion can be attained after long enough times. This demonstrates unambiguously the complete wetting of the polymer-air interface by the phase rich in the d88 component as it grows from the phase rich in the h78 component. In addition, we are able to follow the growth of this layer in time, on a time scale from 30 min to 1 week. The width *l* of the wetting layer may be defined by the distance between the points of inflection of the profile at the air interface and at the interface where the wetting layer falls off. Experimentally, we find that the dependence of l on time t is best fitted by a logarithmic variation, $l \sim \log t$, as shown in Fig. 5a. (A log l vs. log t plot, on the other hand, appears to show a systematic curvature; while this may be attributed for example to different power-law regimes, the data is not sufficient to justify further analysis along these lines.)

While there is ample theoretical work on the equilibrium properties of wetting, there are few publications on the build-up of wetting layers. The discussion by Lipowsky and Huse [19], and by Jones [20], treats the case of a wetting layer of one phase growing at a surface by diffusion from a coexisting composition of the other. The following reproduces their argument, while the sketch in Fig. 5b illustrates the geometry. The surface excess of the wetting layer $\Gamma = A_1$ is created by diffusion of the surface active component from the region adjacent to the wetted surface. Conservation of material requires $A_1 = A_2$, the area of the depleted region from which the surface active component was incorporated into the wetting layer.

The surface excess Γ can also be expressed in terms of the thickness of the wetting layer $l \sim \Gamma$. The assumption here is that the wetting layer is in equilibrium with the concentration ϕ_d of the adjacent depleted zone. In that case the functional dependence of l on ϕ_d has been derived by Cahn [2], for the case of $\phi_d \approx \phi_1$ ($\phi_d < \phi_1$):

$$l = -\text{const.} \ln \left(1 - [\phi_{\rm d}/\phi_{\rm 1}]\right)$$
 (5)

The prefactor in Eq. (5) is of order of the correlation length in the mixture. Since the process is assumed diffusion controlled, the width of the depleted layer is of order $(Dt)^{1/2}$; thus the depleted area may be approximated as

$$A_2 \approx (Dt)^{1/2} (\phi_1 - \phi_d)$$
 (6)



Fig. 5

(a) Variation of layer thickness with time for the profiles of Fig. 4. (b) Schematic illustration of diffusion-limited growth of a wetting layer

Recalling $A_2 = A_1 = \Gamma \approx l$, we find, by eliminating ϕ_d from Eqs. (5) and (6), that at short times $l(t) \sim (Dt)^{1/2}$, while at long times

$$l(t) \sim \ln(t) \tag{7}$$

While Eq. (5) appears to be in agreement with our experimental result, it does not, unfortunately, accurately describe our experimental system. Because of the relatively high value of D and the finite thickness of the polymer films, the spatial extent of the depleted well $(Dt)^{1/2}$ very soon exceeds the width of the layer of composition ϕ_1 . This occurs already at the shortest times of measurement (ca. 30 min), so that the conservation conditions leading to Eq. (7) are not valid in our system [21].

A more realistic description of the build-up of the wetting layer in our geometry has to take into account the finite size of our system, and in particular the "reservoir" (this is the d88-rich phase next to the silicon substrate). It is likely that the growth rate of the d88-rich wetting layer at the surface is limited by diffusion of material from this reservoir into the coexisting d88-poor phase adjacent to it (Fig. 4). A detailed description of wetting in such finite-sized systems has yet to come.

c) Surface Segregation from the Two Phase Regime

In a second series of experiments thick monolayers of d86 (x = 0.86, e = 0.4, N = 1520) and h75 (x = 0.75, e = 0, N = 1267) mixtures were used with a d86 content varying from 5% to 40%. The phase coexistence diagram of this mixture shows $T_c = 176 \pm 3$ °C. The depth profiles of samples of three initial compositions 20%, 30% and 40% and after annealing for 1 day at 150 °C are shown in Fig. 6. For concentrations $\phi_{\infty} < \phi_1$, thermodynamic equilibrium is characterized by a peak with maximum d86 concentration $\phi_{max} < \phi_2$ and with a width smaller than the spatial extent of the polymer molecules. By analyzing the surface excess (the area under the peak) as a function of ϕ_{∞} , the surface interaction parameters for this mixture can be obtained [9].

For initial concentrations $\phi_{ini} > \phi_1$ (i.e. in the two phase regime), the sample will undergo spinodal decomposition.

Due to the surface activity of d86, the subsequent growth of the spinodal domains takes place in surface-directed manner and at equilibrium the composition profile is characterized by a macroscopically thick layer (in the sense of being larger than any microscopic or correlation length in the system) of the d86-rich phase in contact with a "bulk" phase of composition ϕ_1 (d86-poor). Similar results have been reported [22] on the mixture PS/brominated-PS.

d) Surface Segregation from Isotopic Mixtures

Wetting from isotopic liquid mixtures presents a special interest: this is because the bulk and surface interactions of isotopic mixtures can be modeled more easily than in systems where more complex chemical interactions are involved. The investigation of wetting from isotopic mixtures can thus be used to examine theoretical models of wetting transitions. For small molecules the interactions between molecules due to isotopic differences alone are generally far too small to lead to phase separation at accessible temperatures. Thus wetting from such mixtures in the sense we are discussing is not possible. For the case of polymers these small interactions – manifested in small values of χ – are greatly magnified per polymer chain due to the large values of N [7, 8]. Phase separation in bulk isotopic polymer mixtures is therefore accessible and has indeed been studied [23], as has surface-directed spinodal decomposition [24]. Here we report the observation of surface phase segregation resulting in the formation of macroscopic 'wetting-like' layers.

To study wetting from a binary isotopic mixture, we repeated the experiment outlined in the previous section, using a mixture of deuterated polystyrene dPS (N = 17411) and its protonated analog hPS (N = 17308). High molecular weight isotopic mixtures of polystyrene are known to phase separate [23], exhibiting an upper critical solution temperature [17]. For this mixture, a critical temperature of ca. 221 °C has been calculated. Figure 7 shows single films of hPS/dPS mixtures, ca. 1.6 µm thick, containing 5% – 40% of dPS, after annealing for 1 week at 218 °C. While, for dPS concentrations < 30%, only a narrow layer enriched in dPS can be observed, there is a pronounced wet-



h75/d86 mixtures of initial d86 composition: (a) 20%, (b) 30% and (c) 40%, after + day at 150 °C



h75/d86 mixtures of initial d86 composition: (a) 20%, (b) 30% and (c) 40%, after 1 day at 150 °C

ting-like layer at the free surface for samples containing more than 30% dPS.

It has to be pointed out, however, that this result is not obtained consistently every time the experiment is performed. This is most probably due, indirectly, to the low diffusion coefficient of this hPS/dPS system. While for the olefinic copolymers described in the previous sections $D \sim 10^{-10} - 10^{-12} \text{ cm}^2/\text{s}$, and the buildup of the wetting layer over ~ 100 nm takes place on the time scale of 1 week, the diffusion coefficient for the hPS/dPS mixture is several orders of magnitude lower, $D \approx 10^{-19} \text{ cm}^2/\text{s}$. For this reason, buildup of the wetting layer for the hPS/dPS mixture may in general take place over time scales which are beyond our experimental possibilities. However, NRA profiling unannealed spin-cast films of this dPS/hPS mixture reveal nonhomogeneous initial composition profiles, probably resulting from some variation in the spin-casting conditions. We believe that the reason why wetting-like layers, as shown in Fig. 7, are not obtained reproducibly each time has to do with this. Films with a 'favorable' initial composition variation, that is, one where some of the surfacefavoured (dPS) component is present at the surface already in the as-cast film, may reach equilibrium more quickly as compared to a homogeneous sample. Nonetheless, while this by no means constitutes a complete study of wetting from isotopic mixtures, our results suggest that wetting from isotopic mixtures may be observed and studied.

Finally, we should sound a word of caution concerning the interpretation of the nature of the macroscopic layers of surface-preferred phase shown in Figs. 6 and 7. While the growing wetting layer shown in Fig. 4 is unambiguously due to complete wetting of the polymer-air interface by the d88-rich phase growing from the h78-rich one, the formation of a thick surface-preferred phase can in principle occur also from a binary mixture which only partially wets the surface (i.e. in conditions where *inequality* applies in Eq. (1)). The reason for this is illustrated in Fig. 8. Fig. 8a shows a surface with a microscopic layer rich in the surface active component, in equilibrium with the phase (of composition ϕ_1 poor in this component. This corresponds to partial wetting, and is a configuration that would be stable in a large ('semi-infinite') system. Implicit (though far away and therefore not seen) in Fig. 8a is a reservoir of the ϕ_2

phase with which the ϕ_1 phase is in equilibrium. The corresponding situation for a small system is illustrated in Fig. 8b. One may envisage, however, that even for the case of partial wetting (inequality in Eq. (1)) the system would like to eliminate one of the interfaces, and revert to a situation where the entire phase rich in the surface-preferred component resides at that surface. While for large systems it is difficult to envisage how such a phase inversion (which requires transition through an energetically unfavourable state) could occur in accessible times, this may be possible for small systems, as schematically indicated in Fig. 8c. Very recently this phenomenon of surface phase inversion has been studied in detail [25]. Thus the profiles shown in Figs. 6 and 7 may not necessarily correspond to complete wetting as in Fig. 4, but could be related rather to such an effect.



Schematic composition-depth profiles of the surface-preferred component A of a coexisting binary mixture at temperature $T < T_c$, for which the coexisting compositions are ϕ_1 (A-poor) and ϕ_2 (A-rich) (see Fig. 1). (a) Partially wetting of the surface (at depth 0) from the A-poor phase, for a semi-infinite system (the ϕ_2 phase is far away). (b) Partial wetting from a small system, bounded on the right by a neutral surface as shown. (c) The configuration in (b) has inverted (see text)

4. Summary and Conclusions

The connectivity of polymer chains and the large number N of monomers on a typical chain results in a strong reduction (of order N) in the contribution of translational entropy to the mixing free energy $\Delta F_{\rm M}$. At the same time, the size and flexibility of the chains implies that they are strongly interpenetrated in the melt. This leads to an enthalpic contribution to $\Delta F_{\rm M}$ that is essentially the same as for monomeric mixtures. Taken together, these two features lead to critical interaction parameters χ_c that are very small, and to the possibility of coexisting phases characterised by values of $\chi \gg \chi_c$ that are still very small. As a conse-

quence of this, low interfacial energies between these coexisting phases are possible even at temperatures far from the critical temperature. Thus binary polymer mixtures should be good candidates to exhibit complete wetting behaviour, over a wide range of temperatures, at interfaces which favour one of the components. Using a high resolution composition-depth profiling method based on nuclear reaction analysis we have observed such wetting behaviour from mixtures of olefinic random copolymers, and also the formation of wetting-like layers from isotopic polymer mixtures. From an experimental point of view, in particular, the large size and low mobility of polymeric chains allow convenient studies of the spatial and time aspects of the wetting layers. Our results show that the growth with time t of such layers of thickness *l* from a finite size system obeys $l(t) \sim \ln t$, a slow variation which we believe is due to the diffusion-limited transport of surface-active material in our system.

We thank the German Israel Foundation (GIF), the US-Israel Binational Science Foundation, the Ministry of Science and Technology (Israel) and the Commission of the European Communities for partial support of this work. This lecture was presented at the Discussion Meeting on Phase Transitions at Interfaces at Bad Herrenalb, and J.K. thanks Professor Freyland and the other organisers for arranging a fruitful and enjoyable symposium.

References

- A particularly clear discussion is given by M. Schick, in: Liquids at interfaces, eds. by J. Charvolin, J.-F. Joanny, an Zinn-Justin, Les Houches Session XLVIII, pp. 419-497, North Holland, Amsterdam, 1990.
- [2] J.W. Cahn, J. Chem. Phys. 66, 3667 (1977).
- [3] P.G. de Gennes, Rev. Mod. Phys. 57, 827-863 (1985).
- [4] S. Dietrich, in: Phase transitions and critical phenomena, Vol. 12, p. 1-218, eds. by C. Domb and J. Lebowitz, Academic Press, London, 1988.
- [5] D. Beysens, in: NUSMG, NATO ASI, Les Houches, session XLVIII, liquids at interfaces, p. 499 – 548, eds. by J. Charvolin, J.F. Joanny, and J. Zinn-Justin, North-Holland, Amsterdam, 1990.
- [6] J.O. Indekeu, Physica A 177, 428-436 (1991).
- [7] P. J. Flory, Principles of polymer chemistry, Cornell University Press, Ithaca, 1953.

- [8] P.G. de Gennes, Scaling concepts in polymer physics, Cornell University Press, London, 1979.
- [9] I. Schmidt and K. Binder, J. Phys. (France) 46, 1631-1644 (1985).
- [10] R.A.L. Jones et al., Phys. Rev. Lett. 62, 280-283 (1989).
- [11] Q.S. Bhatia, D.H. Pan, and J. Koberstein, Macromolecules 21, 2166 (1988).
- [12] U. Steiner, J. Klein, E. Eiser, A. Budkowski, and L. J. Fetters, Science 258, 1126-1129 (1992).
- [13] A. Budkowski, J. Klein, E. Eiser, U. Steiner, and L.J. Fetters, Macromolecules 26, 3858 (1993).
- [14] W. W. Graessley, R. Krishnamoorti, N. P. Balsara, L. J. Fetters, D. J. Lohse, D. N. Schulz, and J. A. Sissano, Macromolecules 26, 1137-1143 (1993).
- [15] U.K. Chaturvedi, U. Steiner, O. Zak, G. Krausch, G. Schatz, and J. Klein, Appl. Phys. Lett. 56, 1228 (1990).
- [16] J. Klein, Science 250, 640 (1990).
- [17] A. Budkowski, U. Steiner, J. Klein, and G. Schatz, Europhys. Lett. 18, 705 (1992).
- [18] M. Moldover and J.W. Cahn, Science 207, 1073 (1980).
- [19] R. Lipowsky and D.A. Huse, Phys. Rev. Lett. 57, 353-356 (1986).
- [20] R.A.L. Jones Personal communication.
- [21] While there are no predictions for the case of wetting layer buildup for the precise situation corresponding to our geometry, there is a related theoretical study by Langer (Ann. Phys. (NY), Vol. 65, p. 53, 1971) which we recall in passing. This discusses how a series of one-dimensional spinodal domains evolve with time. This situation bears some resemblance to our experiments in the following sense. Starting with an array of equidistant spinodal domains of the same width, every second domain grows while the domain adjacent to it shrinks, both with a logarithmic time dependence, while the interdomain region at the coexisting composition retains a constant width. This is very reminiscent of the time-evolution of the adjacent domains in the profiles in Fig. 4, though the driving force for the growth of the wetting layer differs from that of the spinodal decomposition.
- [22] F. Bruder and R. Brenn, Phys. Rev. Lett. 69, 624-627 (1992).
- [23] F.S. Bates and G.D. Wignall, Phys. Rev. Lett. 57, 1429-1432 (1986).
- [24] R.A.L. Jones, L.J. Norton, E.J. Kramer, F. Bates, and P. Wiltzius, Phys. Rev. Lett. 66, 1326 (1991).
- [25] U. Steiner, J. Klein, and L. J. Fetters, to be published.

Presented at the Discussion Meeting of the E 8592 Deutsche Bunsen-Gesellschaft für Physikalische Chemie "Phase Transitions at Interfaces" in Bad Herrenalb, September 22nd to 24th, 1993

X-ray Studies of the Thickness and Roughness of Thin Adsorbed Fluid Layers

P.S. Pershan

Division of Applied Sciences and the Physics Department, Harvard U., Cambridge, MA 02138, USA

Key Words: Adsorption / Liquids / Surfaces / X-ray Scattering

This paper is a brief summary of a talk delivered at the "Discussion Meeting on Phase Transitions at Interfaces", Bad Herrenalb, Germany in September 1993 on the application of synchrotron X-ray scattering to the study of liquid surfaces. More complete discussion of much of this material can be found in the publications cited in the manuscript. The oral presentation was concerned with the application of X-ray specular reflectivity to study structure of the liquid/vapor interface for various liquids, including superfluid ⁴He, liquid gallium and thin liquid wetting layers of classical liquids adsorbed on solid surfaces. The effects that correlations between the height fluctuations on the top and bottom surfaces of thin adsorbed liquids have on the reflectivity and diffuse scattering from thin films will be discussed.

Work supported at Harvard by the following grants: NSF-DMR-91-13782, NSF-DMR-89-20490; and the NSLS is supported by DE-AC02-76CH00016.