

## Incomplete phase separation in mixed monolayers

A. Weinstein and S. A. Safran

*Department of Materials and Interfaces, The Weizmann Institute of Science, Rehovot 76 100, Israel*

(Received 30 September 1996; revised manuscript received 23 July 1997)

We propose that phase separation in a mixed, two-component, substrate in the presence of adsorbing molecules can be incomplete, with an equilibrium finite domain size. The free energy of the system is shown to decrease near interfaces between the two substrate components, as a result of mismatch between the natural spacing of the adsorbate molecules and the periodic potential of the substrate lattice. These systems are of current experimental interest in the context of surface induced freezing, where ice nucleation of varying efficiency is achieved by mixed monolayers of two types of amphiphiles above supercooled water.  
[S1063-651X(98)50905-1]

PACS number(s): 64.60.Qb, 64.70.Rh, 64.75.+g

While there have been many theoretical studies of the structure and phase behavior of single-component monolayers, there have been far fewer studies of the more realistic case of ordered monolayers composed of a mixture of amphiphilic molecules. In practical applications, mixed systems are ubiquitous; from a fundamental point of view, the composition degree of freedom in these systems allows a richer variety of behavior and function than that shown by the simpler, single-component system. Understanding how the composition can be tuned to control the properties of the system is therefore of great interest and utility.

Here we present a theoretical study of the role of mixing in determining the structure and phase behavior of Langmuir monolayers. The case we focus on is where each component in the monolayer shows crystalline ordering, but the molecules underneath the monolayer are coupled, with nearly commensurate ordering, to only one of the components (e.g., due to very weak chemical interactions with the second one). We show how this selective coupling can lead to a modulated, two-dimensional, structure where the domains of each component are finite in extent, as opposed to the usual case of macroscopic (in the thermodynamic limit, infinite) domains in a phase separated monolayer. The incomplete separation is explained by the existence of a short range attraction between different domains which, as we calculate from a microscopic model, is induced by the misfitting structure of the adjacent ordered layer of liquid molecules. Filling regions of high incommensurability by the noninteractive component reduces the misfit cost in energy, and this “mismatch effect” effectively reduces the interfacial tension and can result in finite domains of each species in the monolayer. It is important to note that, while standard treatments [1–3] of incommensurability effects in crystal structures have mostly been restricted to the case where each layer is composed of a single component, the present study of a mixed substrate provides insight into the generic physics of the competition between phase separation and ordering in incommensurate systems.

The work is motivated by recent experiments where binary mixtures of alcohols with perfluoroalcohols [4] or diols with alkanes [5] were used to induce ice nucleation. It was previously demonstrated [6] that monolayers of long chain alcohols, covering the surface of water, serve as excellent

nucleators for ice crystallization and significantly diminish the large supercooling possible in water. The phenomenon is related to the highly ordered two-dimensional structure [7] of the alcohol monolayer which closely matches that of ice, and the nucleation properties depend strongly [8] on the lattice mismatch between the alcohol monolayer and ice as well as on the crystallinity of the monolayer and its spatial extent [9]. In order to more carefully control the crystallization, recent experiments have studied mixed monolayers of good and poor nucleators (e.g., diols with alkanes) in various ratios. Direct measurements of the monolayers structure [4,5] show that phase separation in these systems is not macroscopic in the sense that each phase forms finite domains whose average extent is composition dependent in the dilute regime. This observation is supported by the behavior of the minimal supercooling temperature which decreases with the concentration of the good nucleator, presumably indicating a decreasing average domain size and, hence, a smaller number of domains which are above the size of a critical nucleus for crystallization.

As a model system we consider [Fig. 1(a)] a two-dimensional layer, composed of two species, **A** and **B**, above a layer of a third molecule, **C** (the adsorbate). In this picture **A** and **B** play the role of good and poor nucleators respectively and **C** represents the first layer of water molecules. We consider the case where, in the absence of **C**, the **A/B** mixture tends to phase separate into **A**-rich and **B**-rich regions which are typically of macroscopic size. In the **A**-rich region the molecules form a highly ordered two-dimensional crystal that imposes an effective periodic potential, of repeat distance  $a$ , on the adsorbing molecules [Fig. 1(b)]. Such a potential is not associated with the **B** region which, in our model, is assumed to have no interaction with the **C** layer. The misfit parameter is defined by  $\delta \equiv 2\pi(c-a)/a$ , where  $c$  is the lattice spacing between ordered **C** molecules in the absence of a substrate. In the previously studied [2] cases of a substrate with only one type of species (e.g., **A**), the system remains in a commensurate phase for small  $\delta$  (i.e., the lattice of **C** molecules has period  $a$ ). Above the critical misfit,  $\delta > \delta_c$ , various incommensurate structures occur which are characterized, near the transition [1], by large commensurate **C** domains separated by narrow domain walls where the molecules are incommensurate.

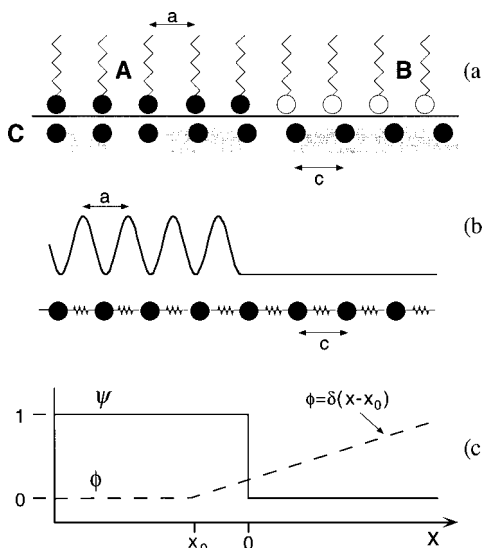


FIG. 1. (a) Mixed monolayer of **A** and **B** molecules above adsorbate **C** molecules. The natural lattice spacing is  $a$  for the **A** layer and  $c$  for the **C** layer. (b) The periodic potential imposed by **A** on the **C** layer and the harmonic interaction between the **C** molecules. The **B** molecules do not impose a potential on the adsorbate. (c) The composition of **A** molecules  $\psi$  and the phase of the **C** molecules  $\phi$  as a function of the distance from the **A/B** interface,  $x$ .

The presence of “neutral” **B** molecules enables the **C** molecules to vary their lattice spacing already in the transition region between **A** and **B** (Fig. 1) in order to more closely match their preferred spacing,  $c$ . As we show later, this profile results in a **reduction** in the net energy of the **C** layer, which physically means that a creation of **A/B** interfaces is favored by the **C** molecules. Consequently, even below the critical misfit ( $\delta < \delta_c$ ), a new modulated phase can arise in which finite sized **A** and **B** domains coexist in order to take advantage of the energy reduction of the misfitting layer near the **A/B** interfaces. The length scale of the domains is determined by the competition between this interfacial energy reduction and the conventional line tension, originating from **A/B** interactions, which favors large domains. For  $\delta > \delta_c$  there can be an additional fine structure of many nearly commensurate domains of **C** underneath the **A** regions.

We first use a coarse-grained, phenomenological approach and consider **A**-rich and **B**-rich patches of size  $d$  randomly mixed in a plane, as illustrated in Fig. 2(a). Note

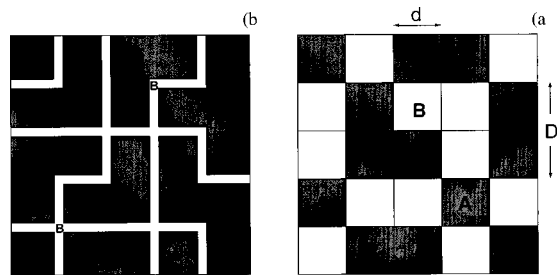


FIG. 2. (a) Random mixing of **A** and **B** domains with a minimal domain size  $d$ . The possibility for adjacent domains make the average domain size,  $D$ , larger. (b) At high volume fractions of **A** molecules, the **B** molecules are expected to order into thin films, separating **A** domains, in contrast to the picture in (a).

that, in contrast to the ordered phases (e.g., hexagonal or striped) commonly obtained in the presence of long-range forces [10], here only short-range interactions are considered and the structure expected is a disordered array of domains with various sizes and shapes. Denoting the volume fraction of **A**-rich domains by  $\Psi$ , the free-energy per unit area (in units of  $k_B T$ ) can be written as:

$$F = \frac{1}{d^2} \{ \Psi \ln \Psi + (1 - \Psi) \ln(1 - \Psi) + \Psi(1 - \Psi) \times [ \gamma d + (1 - \Psi(1 - \Psi)) \gamma_0 ] \} + F_c \quad (1)$$

where the logarithmic terms account for the random mixing entropy [11] and  $F_c$  is the energy of the adsorbate molecules. In the interfacial terms, proportional to  $\Psi(1 - \Psi)$ ,  $\gamma$  is the line tension between **A** and **B** domains, and  $\gamma_0$  is a positive “crossing energy” which accounts for curvature corrections [12] to the line tension description near domains corners. To make the model self-consistent we require that, within the coexistence region of the two phases (i.e.,  $\Psi$  not too large/small), the crossing term overcomes the entropy so that  $F \rightarrow \infty$  for  $d \rightarrow 0$ .

The equilibrium size of the patches is obtained by minimization of  $F$  with respect to  $d$ . In the absence of adsorbate ( $F_c = 0$ ), the free-energy is minimal for  $d \rightarrow \infty$ ; this means, as one would expect, that the coexisting **A**-rich and **B**-rich phases are completely separated into two macroscopic regions in the plane. To understand the role played by the adsorbate layer, we write its energy as

$$F_c = \Psi f_{AC} - \Psi(1 - \Psi) \frac{\eta}{d}, \quad (2)$$

where  $f_{AC}$  is the surface energy of **C** molecules adsorbing on an **A**-rich substrate, and  $\eta$  is the magnitude of reduction in energy (per unit length) across an **A/B** interface due to ordering modification of **C**.  $\eta$  acts to effectively reduce the line tension and can be determined from a more microscopic model which is presented below. The first term is independent of  $d$  and is only relevant for the fine structure below bulk **A** regimes, which has been extensively studied in the context of incommensurate systems and is less important here. Minimizing the free energy we find that for small  $\eta$  the optimum domain size is still infinite, but when  $\eta > \gamma$  there is separation of **A** and **B** with **finite** patches of size

$$d_m(\Psi) = \frac{2}{\eta - \gamma} \left[ \frac{\ln \Psi}{1 - \Psi} + \frac{\ln(1 - \Psi)}{\Psi} + (1 - \Psi + \Psi^2) \gamma_0 \right]. \quad (3)$$

Small  $\gamma_0$  or  $\Psi$  give negative  $d_m$  but this nonphysical situation (where  $F$  is in fact a maximum) is excluded in our model, by requiring large enough  $\gamma_0$ , because it corresponds to volume fractions outside the coexistence region of the mixture. The average extent (coherence length) of an **A** domain is larger than  $d_m$  because it can consist of more than one patch. Since the average number of successive patches is  $\sum_n n \Psi^n / \sum_n \Psi^n = (1 - \Psi)^{-1}$ , the measured domain size  $D$  is predicted to vary with the volume fraction  $\Psi$  as

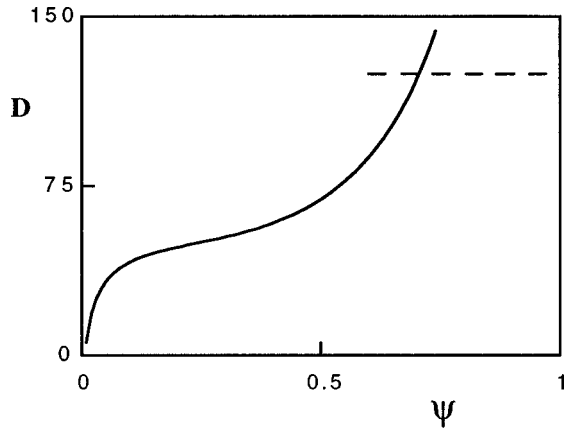


FIG. 3. Average domain size,  $D$ , as a function of the volume fraction of **A** molecules,  $\Psi$ . Equation (4) is plotted as a solid line and the dashed line indicates the value of  $D$  in the high  $\Psi$  regime.  $D$  is measured in units of  $a$  and the values used for the parameters are  $\gamma_0=6$ ;  $\eta-\gamma=0.1a^{-1}$ .

$$D(\Psi) = \frac{d_m(\Psi)}{1-\Psi} \quad (4)$$

In Fig. 3 we plot the resulting domain size as a function of  $\Psi$  for a typical choice of the parameters. At large volume fractions the random mixing picture is less reliable because the equivalent role of **A** and **B** patches, assumed in the model, is inadequate in that regime. Instead, we expect the **B** molecules to form thin films surrounding large **A** domains, similar to surfactants bilayers in an  $L_3$  phase of dilute surfactant solutions [13]. Arguments and calculations similar to those of Ref. [13] lead to the conclusion that in this regime the domain size is independent of  $\Psi$ : adding more **B** molecules to the system only increases the width of the **B** films between **A** domains. The value calculated for  $D$  in the large  $\Psi$  regime [14] is indicated by a dashed line in Fig. 3. We note that when  $\Psi \rightarrow 1$  it is insufficient to describe the interactions by  $\gamma$  and  $\eta$  because the **B** regions shrink to a molecular size and a full microscopic treatment is required.

To motivate our phenomenological theory more microscopically and to allow us to estimate the reduction in energy across an **A-B** interface,  $\eta$ , we use an elastic model and consider an array of beads (the adsorbate, **C**-molecules), connected by harmonic springs, which interact with a periodic potential induced by the **A** component of the substrate [Fig. 1(b)]. We define  $\psi(x)$  as the local volume fraction of **A** in the **A/B** mixture and  $\phi(x)$  as the relative change in the beads' position from the minima of the periodic potential. It is sufficient to consider a one-dimensional array of **A/B** stripe domains whose free-energy can be represented, in the continuum approach, by

$$F = \int dx \left[ f(\psi) + \frac{1}{2} \xi^2 (\nabla \psi)^2 + V \psi (1 - \cos \phi) + \frac{1}{2} K (\nabla \phi - \delta)^2 \right], \quad (5)$$

where  $V$ ,  $K$ , and  $\xi$  are constants and  $\delta$  is the mismatch parameter. The first and second terms are the free-energy per

unit area of a uniform **A/B** mixture [11] and an energy penalty for spatial variations of the local composition (which is the origin of interfacial tension). The third term is the substrate-adsorbate coupling, which favors commensurate ordering of beads ( $\phi=0$ ) above **A**, and the last term is the "spring" energy of interaction between the adsorbate molecules [2].

While a formal treatment of the problem requires a functional minimization of  $F$  (or its two-dimensional generalization [3]) with respect to both  $\psi$  and  $\phi$ , here we focus only on the effect of the adsorbate molecules near the **A-B** interfaces. Consider such an interface (Fig. 1), located at  $x=0$ , between **A**-rich phase on the left and **B**-rich phase on the right. At low enough temperatures, the **B** fraction in the **A**-rich phase can be ignored and we take the coexisting phases to be either pure **A** or **B**. For  $\delta$  not much larger than  $\delta_c = 4/\pi\sqrt{V/K}$  there are large regions of commensurately ordered adsorbate molecules below the **A** regions, i.e.,  $\phi$  vanishes as  $x$  decreases from zero. However, for  $x>0$  the **C** molecules, which are not coupled to the **B** domain periodicity, are free to minimize their elastic energy, with  $\phi \sim \delta x$ . The energy change in this transition region can be approximated variationally by defining [see Fig. 1(c)]

$$\psi = \begin{cases} 1 & \text{for } x < 0 \\ 0 & \text{for } x > 0 \end{cases} \quad (6)$$

and choosing

$$\phi = \begin{cases} 0 & \text{for } x < 0 \\ \delta(x-x_0) & \text{for } x > 0, \end{cases} \quad (7)$$

where  $x_0$  is a variational parameter that denotes the boundary of the commensurate region. Substituting these functions in  $F$  and minimizing with respect to  $x_0$  we obtain

$$x_0 = -\frac{2}{\delta} \arcsin\left(\frac{2\delta}{\pi\delta_c}\right). \quad (8)$$

The negative sign of  $x_0$  indicates that, even for  $\delta < \delta_c$ , the adsorbate molecules begin to lose their commensurate ordering *before* they reach the **A-B** interface [15]. The reason for this is that, in contrast to ordinary domain walls between commensurate regions where the insertion of an additional molecule involves a jump of  $2\pi$  in  $\phi$ , here the molecules on the **A** side ( $x < 0$ ) need to only rearrange, with a relatively small jump in phase, which costs less potential energy than the gain in elastic energy. Consequently, the energy **decreases** near the interface for any  $\delta$  and the reduction in energy is

$$\eta = \frac{V}{K} \left[ x_0 \cos(\delta x_0) - \frac{\sin(\delta x_0)}{\delta} \right] \quad (9)$$

With Eq. (8) for  $x_0$ , Eq. (9) predicts that  $\eta$  increases with the mismatch and the elastic constant,  $K$ , and decreases with the potential amplitude  $V$ . Large enough  $\eta$  can drive the total interfacial tension negative even if one is far from the critical temperature of the mixture, so that the **A-B** interface remains sharp, as assumed in Eq. (6). A more rigorous calculation,

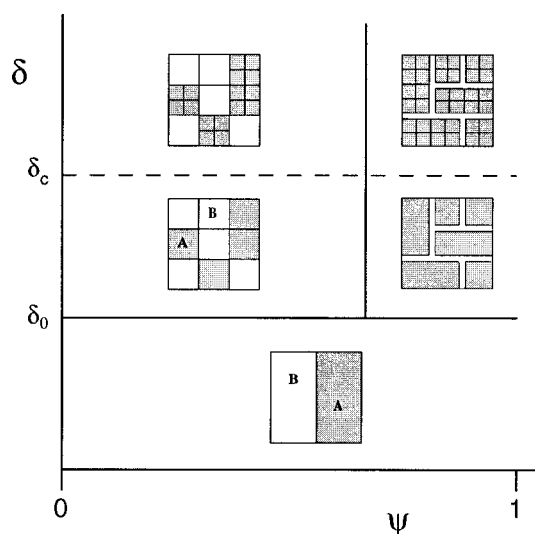


FIG. 4. Schematic phase diagram as a function of the mismatch between the **A** and **C** lattice spacings,  $\delta$ , and the fraction of **A** molecules,  $\Psi$ . At small values of  $\delta$ , the bare interfacial energy dictates macroscopic phase separation of the **A** and **B** monolayer molecules. At larger values of  $\delta$ , this phase separation can be incomplete, with equilibrium finite domains arranged in either random mixing (at small to moderate values of  $\Psi$ ) or in films of **B** (at large values of  $\Psi$ ). When the misfit exceeds the critical misfit for incommensurate domains, an additional fine structure of the domains is superimposed on the incomplete **A/B** phase separation.

with the interfacial width treated as a variational parameter, indeed shows that the reduction of the interfacial tension does not involve an increase in the width [14].

A schematic phase diagram of the system in the  $\Psi$ - $\delta$  plane is presented in Fig. 4. Below the transition misfit  $\delta_0$ , defined by  $\eta(\delta_0) = \gamma$ , phase separation of **A** and **B** is macroscopic. For  $\delta > \delta_0$  the coexisting **A/B** regions are of finite

size, forming a mixture of mesoscopic domains for small or medium  $\Psi$ , and a structure of **A** domains separated by thin films of **B** when the volume fraction is large [16]. The ordering of **C** molecules below **A** regimes is commensurate with the substrate for small misfits, but as  $\delta$  exceeds  $\delta_c$ , incommensurate regions of **C** evolve.

A detailed application of our theory to experiment is not yet available, although the composition dependence of the domain size,  $D(\Psi)$ , which we obtain (Fig. 3) is in qualitative agreement with the experimental results [4,5]. In order to check the validity of the theory more closely one should systematically control the parameters of the system (e.g., by varying the chain length of the molecules which control the misfit  $\delta$ ) and look for the transition line (Fig. 4) between the regime of macroscopic phase separation and that of finite sized **A/B** domains [17]. Many combinations of components which tend to phase separate may provide possible realizations of our model, allowing a large variation of the parameters  $\delta$ ,  $V$ ,  $K$ , and  $\gamma$ . However, the condition  $\eta > \gamma$  may be satisfied only when **A** and **B** are similar molecules, as in the case of a diol-alkane mixture. We note that even if  $\eta < \gamma$  but the difference is small, the dynamics can still be very slow so that, experimentally, finite domains will be measured. In the more practical case, where both molecules are ice nucleators but with different lattice mismatches, the water molecules under the monolayer will order in a more complex way but the main mechanism behind the ‘‘mismatch effect’’ is expected to hold and a finite domain structure should still be observed.

We wish to acknowledge useful discussions with M. Lahav, L. Leiserowitz, R. Popovitz-Biro, and M. Arbel-Haddad. We also acknowledge the donors of the Petroleum Research Fund, administrated by the ACS, and the Minerva Foundation for partial support of this research.

- [1] F. C. Frank and J. H. Van der Merwe, Proc. R. Soc. London, Ser. A **198**, 205, (1949); **198** 216 (1949).
- [2] P. Bak, Rep. Prog. Phys. **45**, 587 (1982), and references therein.
- [3] P. Bak, D. Mukamel, J. Villain and K. Wentowska, Phys. Rev. B **19**, 1610 (1979).
- [4] J. Majewski *et al.*, J. Phys. Chem. B **101**, 8874 (1997).
- [5] Arbel-Haddad *et al.*, J. Phys. Chem. C (to be published).
- [6] M. Gavish, R. Popovitz-Biro, M. Lahav and L. Leiserowitz, Science **250**, 973 (1990).
- [7] J. Majewski, R. Popovitz-Biro, W. G. Bouwman, K. Kjaer, J. Als-Nielsen, L. Leiserowitz, and M. Lahav, Chem. Eur. J. **1**, 304 (1995).
- [8] A. Weinstein and S. A. Safran, Phys. Rev. E **49**, 4306 (1994).
- [9] R. Bar-Ziv and S. A. Safran, Europhys. Lett. **22**, 251 (1993); Phys. Rev. E **49**, 4306 (1994).
- [10] See, for example, D. Andelman *et al.*, in *Micells, Membranes, Microemulsions and Monolayers* (Springer-Verlag, Berlin, 1994).
- [11] S. A. Safran, *Statistical Thermodynamics of Surfaces, Interfaces and Membranes* (Addison-Wesley, Reading, MA, 1994).
- [12] E. M. Blokhuis and D. Bedeaux, Physica A **193**, 201 (1993).
- [13] M. E. Cates, D. Roux, D. Andelman, S. T. Milner, and S. A. Safran, Europhys. Lett. **5**, 733 (1988), and references therein.
- [14] A. Weinstein and S. A. Safran (unpublished).
- [15] For values of  $\delta > \pi \delta_c/2$  Eq. (8) is undefined, indicating that at large misfits the picture of large commensurate regions near an **A-B** interface is inadequate.
- [16] At the level of mean field theory presented here, the topological transformation between these structures cannot be determined.
- [17] Of course, it is always possible that the domain size is limited by dynamics and does not reach its equilibrium value. In that case the measurement is actually related to the average distance between nucleation centers of **A** regions. However, since the equilibrium size decreases with  $\Psi$  (Fig. 3) we expect our predictions to hold for small enough  $\Psi$ .