the film thickness matches about 1.5 times the characteristic time of the surface spiral wave (Fig. 4d). We can easily model these results by superposing (two damped cosines) originating at the two boundary surfaces of the films with all parameters but the film thickness kept const-
tant (solid lines in Fig. 4c). This is shown in Fig. 4f for the particular film thickness realized in Fig. 4c. The model no longer describes the experimental data, however, when the film thickness is further decreased. This discrepancy can be seen in Fig. 4e and is observed in all samples thinner than about 100 nm. To understand this effect, we may compare the total film thickness to the most probable wave length at early times. As the wave vectors of the spiral surfaces approach the bulk value at r = 0 we may extrapolate the data for Q=360 degrees obtained from light scattering ex-
periments on bulk PEP/PDPE samples [14] to r = 0. We ex-
timate a_0_up=Q = 3.6 x 10^-1 A^-1 for T = 221 K, cor-
dentsponding to A_0 = 0 - 174 nm. Since the substrate sur-
face is covered by a PEP-rich layer in contrast to the poly-
mer/vacuum interface, a minimal film thickness of a_0 = 1.5 x 10^-1 nm - 261 nm is needed in order to realize a composition wave with a_0 < Q < Q. As the film thickness falls below this limit, the system is forced to de-
compose with a larger characteristic wave, which then is determined by the macroscopic dimensions of the film.

Finally, we shall mention that the above results on the thickness dependence are in quantitative agreement with cold-dynamical simulations, mapped on the polymer system under consideration [6, 10]. With a detailed discussion be-
ning beyond the scope of this paper, it is worth mentioning that the results of such (three-dimensional) simulations can be used to investigate the in-plane morphology of samples showing the interference effects described above. It was shown that 'constructive interference' of the spiral wave fronts corresponds to the existence of a region close to the center of the film consisting of a large number of droplets of either of the two phases. This occurs in Fig. 4c and can be understood as the compromising reaction of the system to competing surface fields which tend to enrich the particular layer by one and the other phase at the same time. The resulting disorder disappears as soon as the film thickness approaches a value where both surface fields favor the same phase to be enriched at any point in the film (Fig. 4d). 'Constructive interference' therefore corresponds to an almost perfectly layered structure.

In summary, we have investigated the effects of the boundary surfaces on the spiral wave movement in thin films of a binary polymer mixture. The surface layer formed during the decomposition process was found to follow a growth law in accordance with recent theoretical predictions. For sufficiently thin films, it was shown that the entire phase morphology can be determined by surface effects.

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The local of the g substrates are indicated by the vertical lines. (All substrates were stripped from the substrate prior to film deposition)

Dynamical Formation of Metastable Phases at Interfaces

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A Ginzburg-Landau model of non-coarsened order-parameter dynamics is analyzed. The model involves three different phases: a stable high-temperature phase, a metastable low-temperature phase and a metastable phase. It is shown that a macroscopic portion of metastable phase can be formed by a dynamic instability which splits the front between two stable high and low-temperature phases. The presence of an external field blocks this metastable phase formation and leads to a non-monotonic behaviour of the metastable phase as a function of time.

Usually metastable phases are produced by fast tempera-
ture quenches. The common picture is that due to kinetic obstacles the stable phase does not have enough time to form and a macroscopic portion of metastable phase can be created. There are many concrete examples of metastable phases in physics and metallurgy [1] and for more than a century [2] experimental and technical experience on creating metastable crystaline structures and glasses from the melt has accumulated. It is, however, only recently that theoretcical mechanisms have been studied. Two general mechanisms have been proposed [3]: First, the nucleation rate of metastable gerns may be larger than that of stable gerns. Second, the growth rate of the metastable phase ex-
ceeds that of the stable phase.

It is the purpose of this work to review briefly a third mechanism for the formation of a metastable phase which was proposed recently [4-6]. The corresponding scenario is that upon rapid cooling the metastable phase nucleates at the growing interface between the stable high-temperature phase and the stable low-temperature phase (2) and then grows faster than the stable low-temperature phase. This is directly connected to a splitting instability of the 0-front which splits into two independent 01 and 12 interfaces both of which moving with a different velocity such that a macroscopic portion of the metastable phase can be formed dynamically.

To see the splitting instability in its simplest setting we refer Ref. [4] and consider usual Ginzburg-Landau dy-
namics for a one-component non-conserved dimensionless order parameter q(x,t) (model A without noise). Inter-
facial dynamics is studied in one spatial dimension as a function of time t. In the one-dimensional geometry any roughening effects are neglected. The relaxation equations for the order parameter dynamics read

\[ \frac{\partial q(x,t)}{\partial t} = \frac{\partial}{\partial x} \left[ D \frac{\partial q(x,t)}{\partial x} - \beta \frac{\partial \delta(F(q))}{\partial q(x,t)} \right] \]

with the free energy functional

\[ \delta(F(q)) = \int \frac{1}{2} \left( \frac{\partial q}{\partial x} \right)^2 - \frac{1}{2} \frac{D}{\beta} \frac{\partial^2 q}{\partial x^2} + \frac{1}{4} \frac{\beta}{\lambda} q^2 - \frac{1}{2} \lambda q^4 \]

where \( \lambda > 0 \).

\[ F(q) = \int \frac{1}{2} \left( \frac{\partial q}{\partial x} \right)^2 - \frac{1}{2} \frac{D}{\beta} \frac{\partial^2 q}{\partial x^2} + \frac{1}{4} \frac{\beta}{\lambda} q^2 - \frac{1}{2} \lambda q^4 \]

with a control parameter \( \beta(T, T - 7) \). For \( T > T_g \) the coexistence temperature between two stable phases (0) and (2) is greater than \( T = T_g \). We briefly discuss how the explicit form of \( F(q) \) influences the splitting instability. As can be clearly seen in Fig. 1, where \( -\delta F(q) \) is shown for different control parameters \( \beta \), three phases are involved: a) the stable high-temperature phase (0) (e.g. liquid) chosen to be \( q = 0 \); b) the stable low-temperature phase (2) (e.g. crystal) chosen to be \( q = 2 \); c) a metastable phase (1) lying on \( q = 1 \) in between the two stable phases.

We are now looking for dynamical solutions \( q(x,t) \) of (1) with an arbitrary initial profile and boundary conditions

\[ q(x,0) = \begin{cases} 0 & \text{for } x < 0 \\ 1 & \text{for } x = 0 \\ 2 & \text{for } x > 0 \end{cases} \]

(4)

\[ \lim_{t \to \infty} q(x,t) = \begin{cases} 0 & \text{for } x < 0 \\ 1 & \text{for } x = 0 \\ 2 & \text{for } x > 0 \end{cases} \]

(5)

for all \( x \geq 0 \). In order to get an insight into the splitting insta-
stability let us discuss the existence of steady state solutions between the phases 01, 12 and 02. These are profiles moving with a constant interface velocity, \( c_{12} \), \( c_{02} \), c_0, c_2. In terms of steady state velocities the scenario of the splitting instability can be understood as follows [4]: If \( c_{12} > c_{02} \) then steady state motion of the 0 interface is possible with a velocity \( c_{02} \) between \( c_{12} \) and \( c_0 \). On the other hand, for \( c_{02} > c_{12} > c_0 \) there is no steady state solution for the 02 interface. The 02 interface splits into two independent 01 and 12 interfaces which move asymptotically for large times

\[ \frac{d}{dt} \left( \frac{\partial q(x,t)}{\partial x} \right) = \frac{1}{2} \left( \frac{\partial q(x,t)}{\partial x} \right)^2 + \frac{1}{2} \frac{D}{\beta} \frac{\partial^2 q(x,t)}{\partial x^2} + \frac{1}{4} \frac{\beta}{\lambda} q^2 - \frac{1}{2} \lambda q^4 \]

(2)

\[ \frac{d}{dt} \left( \frac{\partial q(x,t)}{\partial x} \right) = \frac{1}{2} \left( \frac{\partial q(x,t)}{\partial x} \right)^2 + \frac{1}{2} \frac{D}{\beta} \frac{\partial^2 q(x,t)}{\partial x^2} + \frac{1}{4} \frac{\beta}{\lambda} q^2 - \frac{1}{2} \lambda q^4 \]

(3)
with their corresponding steady state velocities $v_{10}, v_{20}$. Since $v_{10} > v_{20}$ the metastable phase from the unstable phase (0) than the stable phase grows into the metastable phase and a macroscopic portion of metastable phase is created dynamically. This portion grows linear in time $w_2(t) = v_2 t$. For $v_{20} = v_0$ the splitting transition occurs. The actual value of the steady state velocities depends on the detailed shape of $f(q)$. This implies that there is a critical control parameter $b_{c}$ corresponding to $v_{20} = v_0$. For the concrete choice (3), the value of $b_{c}$ is 0.15419. For $b > b_{c}$ the width of the 02 steady state front diverges indicating a dynamical previewing by the metastable phase.

In the first case the interface motion is first steady state type and then slows down due to the presence of the external field. For very large times, it approaches its equilibrium profile where the 02-interface position is at a fixed $x_0$, $x_0$ decreases for increasing $a$. For large times, the interface position approaches $x_0$ exponentially in time, i.e. $x_0(t) \sim A e^{-t/\tau}$ with a characteristic decay time $\tau$. In the second case the width of the metastable phase first grows up to a maximal width $w_{max}$, $w_{max}$ decreases with decreasing coupling $a$ and can even reach macroscopic values. Then the width shrinks back again to a microscopic layer exponentially in time. This interesting non-monotonic behaviour of the width $w(t)$ is shown in Fig. 3 for three different parameter combinations, two of them are in the regime where the splitting instability occurs for $a = 0$.

Some final remarks concern a possible experimental verification in real growth experiments. One possibility is to study dynamics of surface melting which was in a similar framework discussed by the author and Lipowsky [7]. Liquid crystalline systems often provide a number of metastable phases upon undercooling and many crystalline solids are ideal candidates for an experimental verification of the splitting instability [8].

In the steady state regime, it converges to a finite microscopic value; for $b > b_{c}$, it diverges logarithmically as $\ln(b_{c} - b)$, and for $b < b_{c}$, it diverges to even macroscopic values. Also, in the inset of Fig. 2, the time evolution of a typical order parameter profile is shown clearly showing the buildup of the metastable phase.

The same splitting effect is also possible for several order parameters. The case of two non-conserved order parameters was explicitly examined by Tuckerman and Bechhoefer [5].

The splitting instability is non-generic. Whether it occurs or not does not depend on the detailed form of the free energy density $f(q)$. In our chosen form (3), it does occur but in other choices it does not. We simply mention that the choice (3) represents a typical one with realistic free energy differences and typical undercoolings. Thus in certain systems one should see the splitting instability and in other ones one should not.

There are a number of possible mechanisms that limit the growths of the metastable phase in reality. One of them is an external field which is coupled to the order parameter. If the order parameter is simply a scaled particle number density, a gravitational field can be regarded as such a disturbing external field but other examples are also conceivable. The Ginzburg-Landau model is readily generalized to the case of a constant external field by adding the term $a q \partial q / \partial x$ to the free energy density $f(q)$ which thus becomes position dependent. $a$ plays the role of a coupling parameter. Furthermore we now take a semi-infinite geometry $x \geq 0$. For different shapes of $f(q)$, Bocquet and the author have solved numerically the time evolution of the order parameter profile in an external field [6]. The results depend on the fact whether for $a = 0$ the interface motion is in the steady state regime or in the regime where the splitting instability occurs.

In the first case the interface motion is first steady state like and then slows down due to the presence of the external field. For very large times, it approaches its equilibrium profile where the 02-interface position is at a fixed $x_0$, $x_0$ decreases for increasing $a$. For large times, the interface position approaches $x_0$ exponentially in time, i.e. $x_0(t) \sim A e^{-t/\tau}$ with a characteristic decay time $\tau$. In the second case the width of the metastable phase first grows up to a maximal width $w_{max}$, $w_{max}$ decreases with decreasing coupling $a$ and can even reach macroscopic values. Then the width shrinks back again to a microscopic layer exponentially in time. This interesting non-monotonic behaviour of the width $w(t)$ is shown in Fig. 3 for three different parameter combinations, two of them are in the regime where the splitting instability occurs for $a = 0$.

Some final remarks concern a possible experimental verification in real growth experiments. One possibility is to study dynamics of surface melting which was in a similar framework discussed by the author and Lipowsky [7]. Liquid crystalline systems often provide a number of metastable phases upon undercooling and many crystalline solids are ideal candidates for an experimental verification of the splitting instability [8]. Some unusual large layer-thicknesses were observed at growing liquid-solid interfaces of atomic materials by Bilgram and coworkers [9] which may be ascribed to the splitting instability. However, the latter experiments may also be explained by diffusing gas microbubbles, see e.g. [10]. Another promising system is colloidal suspensions where dynamics happens on a much larger time scale than for atomic systems. Here effects of an external field on a growing metastable phase may also be detectable (for a possible experiment with different metastable phases see [11]).

References

Irreversible Multilayer Adsorption
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Random sequential adsorption (RSA) models have been studied [1] due to their relevance to deposition processes on surfaces. The depositing particles are represented by hard-core extended objects; they are not allowed to overlap. Numerical Monte Carlo studies and analytical considerations are reported for 1D and 2D models of multilayer adsorption processes. Deposition without screening is investigated; in certain models the density may actually increase away from the substrate. Analytical and numerical studies of the late stage coverage behavior show the crossover from exponential time dependence for the lattice case to the power law behavior in the continuum description. 2D lattice and continuum simulations rule out some "exact" conjectures for the jamming coverage. For the deposition of dimers on a 1D lattice with diffusional interaction we find that the limiting coverage (100%) is approached according to the 1/4 power-law prefaced, for fast diffusion, by the mean-field coverage regime with the intermediate 1/2 behavior. In case of a dimer deposition it > 3 with diffusion the solids fraction decreases according to the power-law 1/3-0.5. In the case of RSA of lattice hard squares (2D with diffusional relaxation the approach to the bulk coverage is 1/2). In case of RSA-deposition with diffusion by two square models on a 2D lattice the coverage also approaches according to the power law 1/3, while in a dense periodic lattice the final state is a frozen random regular grid of domain walls connecting single site defects.