

Instabilities in Block Copolymer Films Induced by Compressible Solvents

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We combine a simple lattice-gas model for fluid mixtures along with polymer mean-field theory for block copolymer melts to study the stability of thin films of diblock copolymers in the presence of compressible fluid solvents. Using a free energy analysis, the stable and unstable thicknesses of a copolymer thin film are obtained for given solvent conditions. Our results suggest that the interplay between confinement, the compressibility of the solvent, and its selectivity to polymer component can lead to significant changes on the ordering and stability of the diblock copolymer thin films. Our results are in qualitative agreement with recent experimental results.

Thermodynamics of block copolymer systems has been the subject of extensive studies from both technological as well as fundamental viewpoints.¹ For A-*b*-B diblock copolymers, the self-assembly behavior has been well-characterized and is determined by the fraction of A monomers (f), and by the incompatibility of the different blocks, quantified by $\chi_{AB}N$, where χ_{AB} denotes the Flory–Huggins interaction parameter between A and B blocks and N the degree of polymerization ($\chi_{AB} \propto 1/T$, where T denotes the temperature).¹ Below the temperature corresponding to order–disorder transition (ODT), diblock copolymers phase separate into ordered structures consisting of A-rich and B-rich phases.¹ The influence of a variety of external conditions on the phase morphology of diblock copolymers has also been studied. Addition of good or neutral solvents to block copolymers has been shown to reduce the ODT, an effect rationalized as due to the dilution of the A–B contacts.² The influence of confining surfaces has also been studied, for which the phase morphology of block copolymer melts has been shown to be influenced by both the interactions with the confining surfaces and the thickness of the film.^{3–5,7,8}

Recently, significant attention has been directed toward the use of compressible solvent media such as supercritical CO₂ as an environmentally benign option for polymer synthesis and processing.^{9,10} A unique feature of such fluids is that the solvent density and its “quality” for the polymer can be varied by changes in compressibility resulting from external conditions such as pressure and temperature.¹¹ In diblock copolymer systems which exhibit an upper critical order–disorder temperature (UODT, i.e., order upon cooling), the solvent has been shown to screen the unfavorable enthalpic interactions between dissimilar polymer segments, reducing the ODT and leading to a phase mixing of the system.¹⁰ In the systems which exhibit a lower disorder–order temperature (LDOT, i.e., order upon heating), compressible solvents have been demonstrated to change the ODT significantly due to a differential dilation of the copolymer segments.¹⁰

The present work was motivated by recent experimental observations by Arceo et al.⁴ which demonstrated that in the presence of compressible, supercritical CO₂, the ODT of thin films of the diblock copolymer PS-*b*-PMMA (a UODT system)

is enhanced significantly relative to the bulk ODT. At a given value of $\chi_{AB}N$, for which the bulk system was in the disordered phase, they observed that the thin film broke up into a terraced morphology with a second layer of finite thickness supported on a brush layer on the substrate. They equated the formation of such a terraced topography of islands and holes as a lowering of the ODT of thin films relative to bulk. To understand the mechanisms governing these observations, in this work we examine the hypothesis that under confinement, the compressibility of the solvent can interplay strongly with other influences such as the solvent selectivity leading to nontrivial changes in stability of thin films. With this motivation, in this article we use a numerical mean-field approach to study the onset of instability (dewetting of film into layered phases) in thin (confined) polymer films supported on neutrally selective substrate in the presence of a selective, compressible solvent. We term this instability temperature in block copolymer thin films as the “layered dewetting temperature (LDT)” (to distinguish it from ODT, a term synonymous with a sharp ordering transition). We specifically consider only the case of a symmetric diblock copolymer, and use a one-dimensional calculation to probe the stability in thin film systems and onset of formation of parallel lamellar phases in the bulk systems.

I. Description of Theoretical Framework

A novel theoretical approach is utilized to study the phase and stability behavior of block copolymer thin films in the presence of compressible solvent. Unlike many previous studies considering phase behavior in physically “confined” systems,^{5,7} our framework considers a model of the more realistic “supported film” of diblock copolymers in a bath of compressible fluid environment.¹³ We consider a mixture of diblock copolymers and a compressible solvent in a semi-infinite system, where the solvent is a poor solvent for the copolymer (and hence they phase separate), and the copolymer units have attractive interactions with the substrate (and hence they segregate toward the substrate). These characteristics mimic very closely the experimental situation of Arceo et al.,⁴ where they studied phase behavior of PS-*b*-PMMA diblock copolymer film in the presence of supercritical CO₂, which is a poor solvent for both blocks. In addition, CO₂ has a preferential interaction with one of the blocks (PMMA), an effect incorporated by introducing a relative

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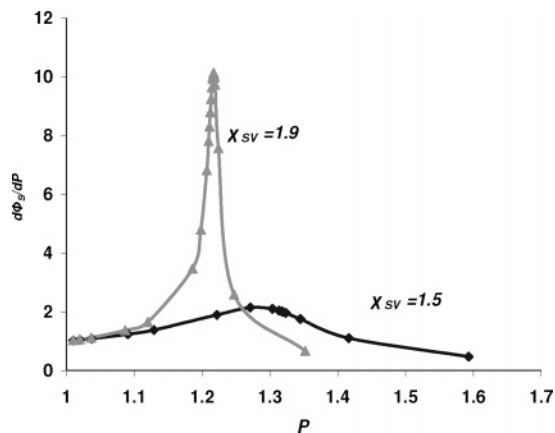


Figure 1. Plot of $d\tilde{\phi}_s/dP$ vs P . The peak is sharper and higher for $\chi_{sv} = 1.9$ than for $\chi_{sv} = 1.5$. $\chi_{sv} = 1.9$ is closer to the critical point.

solvent selectivity for one of the blocks. Our system differs slightly from the experiments of Arceo et al., in that the experimental conditions involved a substrate that had preferential interactions with one of the components. In contrast, to minimize the number of parameters in our model, we limit ourselves to the situation where the substrate is symmetric with respect to its interactions with the blocks.

The solvent phase is assumed to be compressible, and its equation of state is modeled by using an incompressible, binary solvent–void mixture, where the volume fraction of the solvent varies in response to the external pressure. We use a lattice-gas model for the binary solvent (S)–void (V) mixture with the incompatibility between them denoted as χ_{sv} .^{14,15} This model has a simple analytical equation of state that enables us to relate its chemical potential and compressibility to the external conditions such as pressure and temperature (i.e., $1/\chi_{sv}$). Explicitly, if we consider a binary mixture of a solvent and voids with identical monomeric volumes denoted ρ^{-1} , the activity coefficient z of the solvent can be obtained as

$$\ln z = \ln \frac{\tilde{\phi}_s}{1 - \tilde{\phi}_s} + \chi_{sv}(1 - 2\tilde{\phi}_s) \quad (1)$$

where $\tilde{\phi}_s$ denotes the volume fraction of the solvent. The dimensionless pressure (denoted \tilde{P}) and isothermal compressibility ($\tilde{\kappa}_T$) are obtained by using thermodynamic definitions as

$$\tilde{P} = \frac{P}{\rho k_B T} = 1 - \chi_{sv} \tilde{\phi}_s^2 - \ln(1 - \tilde{\phi}_s) \quad (2)$$

$$\tilde{\kappa}_T = \frac{\kappa_T}{1/\rho k_B T} = \frac{1 - \tilde{\phi}_s}{\tilde{\phi}_s [1 - 2\chi_{sv}(1 - \tilde{\phi}_s)\tilde{\phi}_s]} \quad (3)$$

To illustrate the qualitative features of the above model, in Figure 1 we display the quantity $d\tilde{\phi}_s/dP$ (proportional to the compressibility of solvent) as a function of pressure for different values of χ_{sv} . We observe that $d\tilde{\phi}_s/dP$ increases with an increase in the pressure P , reaches a maximum, and then decreases thereafter. This manifestation of an intervening maximum is commonly termed the “density fluctuation ridge” in the literature,^{11,12} and has also been observed in the fluid properties of CO₂. It is evident from Figure 1 that the “ridge” is more pronounced for the case of $\chi_{sv} = 1.9$, which is closer to the critical point as compared to $\chi_{sv} = 1.5$ (for our lattice-gas model, the critical point corresponds to $\chi_{sv} = 2.0$ and $\tilde{P} = 1.193$). This behavior is again qualitatively consistent with previous experimental work involving supercritical CO₂.^{11,16}

The above model for the compressible solvent is combined with mean-field theory for block copolymers^{5,7} to analyze the stability of block copolymer films exposed to a bath of the solvent. For this, we consider an *incompressible* mixture of solvent, voids, and block copolymers in a *semi-grand canonical ensemble*, where the solvent activity coefficient and the total number of block copolymers are constrained to specified values. We consider symmetric A-*b*-B diblock copolymers ($f = 0.5$), and denote by n and ϕ the number of chains and the volume fraction of the block copolymers relative to the total volume of the system. The degree of polymerization of block copolymer is denoted as N . It is assumed that both A and B components have the same statistical length b , and that their segments occupy the same volume $\rho^{-1} = b^3$ as that of the solvent and voids. All lengths are nondimensionalized by the radius of gyration R_g of the copolymer. The polymer–solvent and polymer–void interactions are chosen to be identical and are denoted as χ_{sp}^+ . These interactions are chosen to model a highly incompatible polymer–solvent mixture, which brings about phase separation between polymer-rich and solvent-rich phases.¹⁸ However, the solvent is also assumed to be relatively selective to one of the polymer segments (assumed to be the A segment), with the solvent selectivity quantified by a parameter denoted χ_{sp}^- . Negative values of χ_{sp}^- models the preferential affinity of the solvent toward the A segments. The void is assumed to be nonpreferential to either of the block copolymer components. Both segments of diblock copolymer are assumed to have identical interactions with the substrate, which corresponds to neutrally interacting walls.

In a mean-field approximation, the free energy (expressed on a per diblock chain basis) for the thin film of a block copolymer–compressible solvent mixture can be written as

$$\begin{aligned} F/nk_B T = & -\ln \mathcal{Z}[W_A, W_B] - \frac{zN}{\phi} \mathcal{Z}_S[W_S] + \frac{1}{\phi V} \text{dr} \{ \chi_{AB} N \Phi_A \\ & (\mathbf{r}) \Phi_B(\mathbf{r}) + \chi_{sp}^+ N (\Phi_S(\mathbf{r}) + \Phi_V(\mathbf{r})) (\Phi_A(\mathbf{r}) + \Phi_B(\mathbf{r})) + \\ & \chi_{sp}^- N \Phi_S(\mathbf{r}) (\Phi_A(\mathbf{r}) - \Phi_B(\mathbf{r})) + \chi_{sv} N \Phi_S(\mathbf{r}) (1 - \Phi_A(\mathbf{r}) - \\ & \Phi_B(\mathbf{r}) - \Phi_S(\mathbf{r})) - N (H_A(\mathbf{r}) \Phi_A(\mathbf{r}) + H_B(\mathbf{r}) \Phi_B(\mathbf{r})) - \\ & (W_A(\mathbf{r}) \Phi_A(\mathbf{r}) + W_B(\mathbf{r}) \Phi_B(\mathbf{r}) + W_S(\mathbf{r}) \Phi_S(\mathbf{r})) + N (1 - \\ & \Phi_A(\mathbf{r}) - \Phi_B(\mathbf{r}) - \Phi_S(\mathbf{r})) [\ln(1 - \Phi_A(\mathbf{r}) - \Phi_B(\mathbf{r}) - \\ & \Phi_S(\mathbf{r})) - 1] \} \quad (4) \end{aligned}$$

In the above equation, $\Phi_A(\mathbf{r})$, $\Phi_B(\mathbf{r})$, $\Phi_S(\mathbf{r})$, and $\Phi_V(\mathbf{r})$ represent the local volume fractions of A, B, S, and V, respectively. The potential fields acting on the A, B segments and the S molecules are denoted by $W_A(\mathbf{r})$, $W_B(\mathbf{r})$, and $W_S(\mathbf{r})$, respectively. \mathcal{Z} is the partition function of a single polymer chain in the external fields $W_A(\mathbf{r})$ and $W_B(\mathbf{r})$, and \mathcal{Z}_S is the partition function of a solvent molecule in external potential field $W_S(\mathbf{r})$. The surface potential fields are denoted by $H_i(\mathbf{r})$, where $i = A$ and B . These functionals are chosen to be identical in form to that proposed by Matsen.⁷ The surface potential is applied only on the lower wall (i.e., substrate), so that the block polymer is attracted to the substrate. The final term in the free energy equation is the translational entropy contribution due to the presence of voids.

In mean-field approximation, the above free energy is minimized over the local volume fraction fields Φ 's and the potential fields W . This leads to a set of equations for the Φ_i 's and W_i 's ($i = A, B, S$, and V) which are then solved in a self-consistent manner.^{5,7,24} To model the influence of the substrate boundary upon the polymer conformations, the Dirichlet boundary condition is applied for the end-segment distribution function

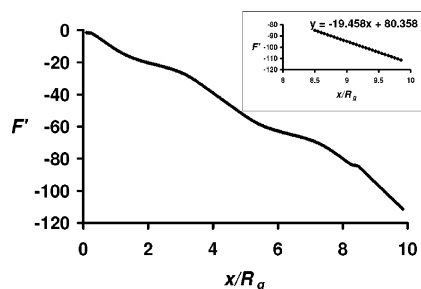


Figure 2. Free energy per unit area of the film as a function of x distance from the substrate. The value of the Flory–Huggins interaction parameter is $\chi_{AB}N = 12$ and the volume fraction of copolymer is $\phi = 0.35$. The solvent condition is fixed corresponding to $\chi_{SV} = 1.9$, $z = 1.2118$, $\bar{P} = 1.35$, $\chi_{SP}N = -25$.

of the polymer conformations. The semi-infinite nature of film is modeled by a Neumann condition on the other boundary.¹⁸ To model bulk phase behavior of the block copolymer–solvent mixture, periodic boundary conditions are applied. Details of the self-consistent equations and the resulting framework are quite similar to those detailed in prior works^{5,7} and we refer the interested reader to the Appendix.

II. Free Energy Analysis

In our semi-grand canonical framework, the thickness (Δ) of the copolymer film is not a specified quantity, but is rather determined by the equilibrium conditions corresponding to the solvent–polymer phase equilibrium. To extract the free energy per unit area corresponding to the block copolymer film, we follow the following procedure: For given solvent conditions and A–B interactions ($\chi_{AB}N$), the free energy per unit area of the film is dependent on the thickness x of the slab of the block copolymer film considered. In Figure 2, we display a representative plot for this dependence of the free energy per unit area (denoted by F') as a function of x . It is observed that when the slab of material considered falls wholly within the diblock copolymer film, F' is an oscillatory function of x (mimicking the composition profile within the film), whereas for the situation where the slab considered falls in the solvent-rich phase F' varies linearly with x . The latter embodies the contributions arising from the free energy per unit area of the block copolymer film (a x independent quantity), and the free energy contribution arising from the solvent–void interactions (which is extensive and scales linearly with x). A linear fitting was used to extract these independent contributions to F' . This is shown in the inset of Figure 2, which displays the “linear” region of the F' . Explicitly, we represent

$$F' = F + F_S x \quad (5)$$

where F_S represents the free energy of the solvent–void phase per unit volume and F represents the surface energy of the film per unit area. We used this (intercept) F as the surface free energy for our subsequent analysis.

We now briefly review the manner in which F determines the onset of instabilities in block copolymer thin films. It is well-known that for solvent-free block copolymer melts, the presence of a substrate that exhibits preferential selectivity to one of the segments induces exponentially decaying composition oscillations even when the temperature is above the bulk ODT.^{8,19,20} When the block copolymer is confined between two such substrates, interference of such concentration oscillations induced by the surfaces leads to a thickness dependence of the overall free energy of the film,^{3,4,8} and can lead to macroscopic

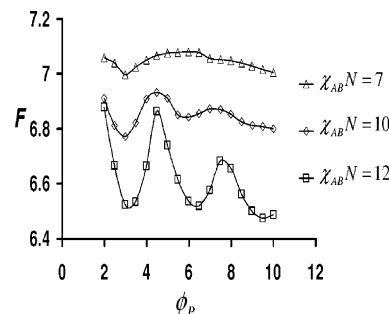


Figure 3. Free energy as a function of total polymer concentration Φ_P for three different values of $\chi_{AB}N$. The solvent condition is fixed corresponding to $\chi_{SV} = 1.0$, $z = 0.814$, $\bar{P} = 1.35$, $\chi_{SP}N = -25$. These values of F are corrected with the bulk value of free energy

dewetting instabilities where the film breaks up into a discontinuous layer forming “islands” and “holes”.^{3,4,21–23} The criteria for instability to develop in a thin film of thickness (Δ) is expressed in terms of the second derivative of free energy with respect to thickness:⁸

$$\frac{\partial^2 F}{\partial \Delta^2} < 0 \quad (6)$$

In contrast, for temperatures below the bulk ODT, the free energy of the thin film system exhibits periodic oscillations as a function of the film thickness. The minima of the free energy–thickness dependencies correspond to the stable thicknesses while the maxima correspond to the unstable thicknesses.

In our study, we consider neutrally selective surfaces and probe the effect of the selective solvent upon instability and ordering in thin films. In contrast to the above-discussed situation (for selective surfaces), for solvent-free block copolymer melts in the presence of neutrally selective surfaces, there are no free energy oscillations induced in the film at temperatures above the bulk ODT. However, for temperatures below the ODT, the free energy of the thin film system does exhibit periodic oscillations as a function of the film thickness, with the minima corresponding to the stable thicknesses while the maxima correspond to the unstable thicknesses. To compare with this expectation, Figure 3 displays the dependence of the free energy per unit area (F) of our solvent + block copolymer film as a function of the amount of copolymer present inside the film (denoted Φ_P , determined in a manner similar to F , and taken as a measure of the thickness of the film) for three different values of Flory–Huggins parameter $\chi_{AB}N$. The solvent conditions are fixed such that the parameters $\chi_{SV} = 1.0$, $z = 0.814$, $\bar{P} = 1.35$, and $\chi_{SP}N = -25$.

Overall, the trends evident in Figure 3 are similar to the behavior expected for a pure block copolymer melt near a selective substrate. In Figure 3, for $\chi_{AB}N = 7$, we observe only one minimum (Δ_{\min}) in the free energy profile, corresponding to the stable thickness. For thicknesses smaller than Δ_{\min} , holes appear on the surface coexisting with regions of thickness $\Delta = \Delta_{\min}$.³ For thickness larger than Δ_{\min} , the film would prefer breaking into a region of minimum stable thickness and a region of infinite thickness, corresponding to macroscopic dewetting. The second case ($\chi_{AB}N = 10$) corresponds to a diblock copolymer film near its layered dewetting temperature (LDT, defined below), where the second minimum in the free energy–thickness dependence gets more pronounced. For the case of $\chi_{AB}N = 12$, the free energy dependence on film thickness exhibits periodic oscillations, indicative of ordering in thin films. The minima in this curve correspond to stable thicknesses

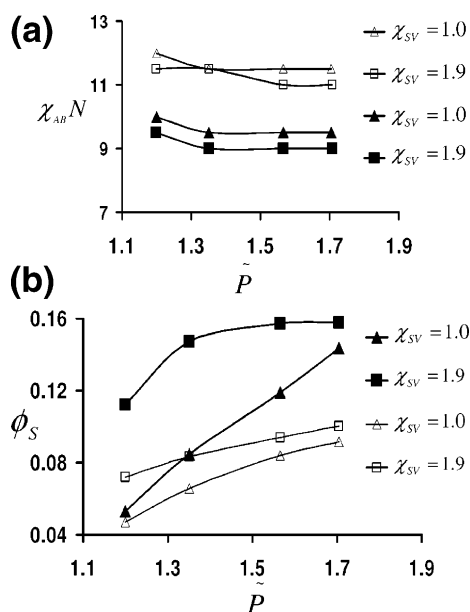


Figure 4. (a) The LDT (thin film systems, closed symbols) and ODT (bulk systems, open symbols) $\chi_{AB}N$ versus pressure (\tilde{P}) for two values of χ_{SV} . (b) The solvent volume fraction Φ_S vs pressure for the cases shown in part a. The volume fraction of the block copolymer relative to the total volume of the system is fixed at $\phi = 0.15$.

involving different numbers of A–B layers, while the interspersed maxima correspond to unstable thicknesses. For thickness intermediate between two minima, common tangent construction can be used to determine the breakup of a film into regions of stable thicknesses. Such a framework ensures the equality of chemical potential of both the block copolymer and the solvent in the coexisting thicknesses.

In the results presented below, we interpret LDT as the $\chi_{AB}N$ at which a periodic double-well minimum appears in the free energy–thickness dependence plot. This criterion identifies the $\chi_{AB}N$ for which films intermediate in thickness to the minima break up into coexisting thicknesses corresponding to the minima. In the experimental results corresponding to our study, the breaking up of the unstable film into such layers of periodic thicknesses was construed as an indication of self-organization within the film, and was identified as the ODT of the thin film by Arceo et al.⁴ On the basis of such an identification, we study the effect of solvent properties on the LDT. Due to the number of components and their interactions, the above model has a vast parameter space with potentially rich behavior. To render the parameter space manageable, we fix the degree of polymerization at $N = 100$. The size of the overall system is fixed at $\Delta' = 20R_g$, where R_g is the radius of gyration of the copolymer. The value of the following polymer–void and polymer–solvent repulsive interaction parameter is kept fixed: $\chi_{SP}^+ = 2.0$. In this work, we focus on the interplay between compressibility, density fluctuation effects of the solvent, and other physical conditions such as solvent selectivity (χ_{SV}) upon the thin film phase behavior.

III. Results

In Figure 4a we compare the differences in phase behavior between the thin film and bulk systems in the presence of compressible solvent. For a specified value of relative solvent selectivity $\chi_{SV}N$ and the solvent–void interaction parameter χ_{SV} , it is observed that the LDT in thin films occurs at a lower value of $\chi_{AB}N$ compared to the corresponding bulk system ODT. Moreover, with increasing pressure, this layered dewetting

transition is also seen to be shifted to lower values of $\chi_{AB}N$. In Figure 4a, the comparison between thin film and bulk systems is presented for two different values of χ_{SV} , from which it is observed that increasing χ_{SV} also lowers the value of $\chi_{AB}N$ for onset of instability. It is pertinent to note our results suggest that the layered dewetting transition for thin films can occur at $\chi_{AB}N$ values lower than both the conditions at which the block copolymer solvent mixture orders in bulk as well as the ordering temperature of a thin film of pure block copolymer orders in vacuum ($\chi_{AB}N = 10.5$). This result is qualitatively consistent with experimental observations of Arceo et al. that the ordering transition temperature of block copolymer thin film increases relative to bulk in the presence of slightly selective supercritical CO₂ solvent.⁴

To rationalize the above results, we note that in contrast to the situation for neutral (nonselective) solvents discussed earlier,² a selective solvent can lead to a preferential swelling of one of the components relative to the other, leading to an effectively enhanced repulsion between the blocks. Indeed, it has been found that a highly selective solvent can lead to ordering in block copolymer at lower values of $\chi_{AB}N$ than even the pure block copolymer.² Our results are rationalized by noting that for a specified solvent condition, the amount of solvent inside the copolymer thin film is higher than that of the corresponding bulk system. For thin films, the polymer density vanishes at the substrate, and there is an increase in solvent density both near the substrate and at the polymer–vapor interface due to entropic considerations.¹³ This is clearly demonstrated in Figure 4b, where the total solvent volume fraction (Φ_S) in the film is plotted as a function of pressure for the cases considered in Figure 4a. For a given χ_{SV} , it is seen that the solvent volume fraction is always higher in the thin film ($\phi = 0.15$) as compared to its bulk analogue. Since in our study the solvent is relatively preferential to A segments, the A block is “pulled” toward both the substrate and the free surface. So even in the absence of a preferential surface potential, the presence of a selective solvent creates effectively an enhanced pseudorepulsion between the A and B copolymer segments. We implicate the solvent sorption and selectivity induced enhanced repulsion to be responsible for earlier observation of instability in thin films.

The effects of χ_{SV} and external pressure on the phase behavior in thin films can now be explained. We note that χ_{SV} reflects the distance of supercritical fluid from critical conditions, with the critical temperature corresponding to a value of $\chi_{SV} = 2.0$. The amount of solvent intake into the film is directly related to the value of solvent activity coefficient (z), which in turn is directly proportional to the volume fraction of solvent in the solvent–void phase. At a given value of solvent pressure, increasing χ_{SV} increases the repulsive interactions between solvent and voids, and hence, the volume fraction of solvent in the supercritical solvent phase increases. This correspondingly enhances the amount of solvent sorption in the film. This effect is shown in Figure 4b, where at a given pressure, the amount of solvent sorption is higher for $\chi_{SV} = 1.9$ than for $\chi_{SV} = 1.0$ for both bulk and the thin film system. Since the value of $\chi_{AB}N$ for which ordering occurs in thin film is a function of the amount of solvent inside the film, it is clear that increasing χ_{SV} shifts the layered dewetting temperature to lower values of $\chi_{AB}N$ (Figure 4). Along similar lines, at a given χ_{SV} , higher pressure implies lower compressibility, and hence the volume fraction of solvent in the supercritical phase (and the amount of solvent absorbed in the film) is higher. Therefore, increasing pressure leads to lowering of the layered dewetting temperature, albeit this shift is not substantial.

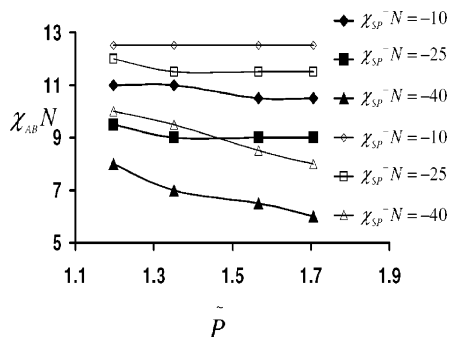


Figure 5. The LDT (thin film systems, closed symbols) and ODT (bulk systems, open symbols) $\chi_{AB}N$ as a function of pressure \tilde{P} for different values of $\chi_{SP}N$ in thin film (closed symbols) and bulk systems (open symbols). The value of χ_{SV} is fixed at 1.5.

The above results indicate that the relative selectivity of a solvent can also play an important role in this instability of block copolymer thin films. These effects are clearly displayed in Figure 5, where it is seen that increasing the selectivity of solvent can shift the ordering transition to much lower values of $\chi_{AB}N$. While a similar trend is also observed for bulk systems, the shift in ordering transitions is more significant for thin films as compared to bulk (Figure 5). These trends are again consistent with our earlier discussion on the interplay between larger sorption of solvent and relative selectivity to one block. Increasing the solvent selectivity renders this effect more pronounced, leading to larger shifts in ordering transitions in thin films.

IV. Conclusions

In summary, we employed self-consistent mean field theory in combination with a lattice gas model for a compressible solvent to examine the phase behavior and stability of thin films and bulk systems in the presence of a compressible fluid. Our formalism considers a supported film rather than that of a confined one as considered in many prior researches. This framework allows for a more realistic approach to study the stability in thin film morphologies. A free-energy analysis was used to analyze the stability and layered dewetting transitions occurring in diblock copolymer thin films. Our results are in qualitative agreement with experimental results⁴ which demonstrated that there is an upward shift of the thin film layered dewetting temperature relative to the bulk ODT in a compressible solvent environment. These experiments were rationalized by suggesting that compressible solvent enhances the disparity in interactions between different diblock segments in thin films more than bulk, leading to significant differences in phase transitions. This reasoning is consistent with our results that the relative selectivity has a very important effect on the phase behavior of the block copolymers. These effects suggest that the interplay of solvent properties and confinement can lead to a richer phase behavior for block copolymer systems, thereby opening up the possibility for another parametric control of the self-assembly morphologies in such systems.

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Appendix

In this section, we describe the details of obtaining self-consistent mean field equations for the block copolymer–

solvent–void system. We explain the various terms in the free energy equation of Section I. \mathcal{Q} stands for the partition function of a single diblock chain in the external fields $W_A(\mathbf{r})$ and $W_B(\mathbf{r})$, and is given as

$$\mathcal{Q} = \int d\mathbf{r} q(\mathbf{r}, 1) \quad (7)$$

where, $q(\mathbf{r}, s)$ is the end-segment distribution function that gives the probability that a section of a polymer chain, of length “ s ” and containing a free chain end has its connected end at \mathbf{r} . This distribution function satisfies the modified diffusion function.^{5,7,24}

$$\frac{\partial}{\partial s} q(\mathbf{r}, s) = \begin{cases} \nabla^2 q(\mathbf{r}, s) - W_A(\mathbf{r})q(\mathbf{r}, s) & \text{if } 0 \leq s \leq f \\ \nabla^2 q(\mathbf{r}, s) - W_B(\mathbf{r})q(\mathbf{r}, s) & \text{if } f \leq s \leq 1 \end{cases} \quad (8)$$

Q_S is the partition function of a single solvent molecule in the external potential field $W_S(\mathbf{r})$.

$$Q_S = \int d\mathbf{r} \exp\left(-\frac{W_S(\mathbf{r})}{N}\right) \quad (9)$$

The surface potentials of A segments and B segments ($H_A(\mathbf{r})$ and $H_B(\mathbf{r})$) are applied only on the substrate wall. The functional form of surface field $H_i(\mathbf{r})$ ($i = A$ or B) is chosen as⁷

$$H_i(\mathbf{r}) = \begin{cases} \Lambda_i(1 + \cos(\pi x/\epsilon))/\epsilon & \text{if } 0 \leq x \leq \epsilon \\ 0 & \text{if } \epsilon \leq x \end{cases} \quad (10)$$

In the above equation, Λ_A and Λ_B control the strength of surface potential fields for A segments and B segments respectively. ϵ is the width of “surface layer”—the region over which the surface potential field acts. For a positive value of Λ_i , the surface has affinity for the polymer.

In the mean-field approximation, the segment densities and potential fields are determined by a set of self-consistent equations. The densities and potential fields are replaced by their saddle points for which the value of free energy functional is minimum. These equations are obtained by taking the functional derivative of free energy with respect to each of the density and potential fields and equating them to zero. These resulting self-consistent equations are laid out below:

$$\Phi_A(\mathbf{r}) = -\phi V \frac{\mathcal{Q}}{\mathcal{Q} W_A} \quad (11)$$

$$\Phi_B(\mathbf{r}) = -\phi V \frac{\mathcal{Q}}{\mathcal{Q} W_B} \quad (12)$$

$$\Phi_S(\mathbf{r}) = z \exp\left(-\frac{W_S(\mathbf{r})}{N}\right) \quad (13)$$

$$W_A(\mathbf{r}) = \chi_{AB}N\Phi_B(\mathbf{r}) + (\chi_{SP}^+N + \chi_{SP}^-N)\Phi_S(\mathbf{r}) - \chi_{SV}N\Phi_S(\mathbf{r}) - NH_A(\mathbf{r}) - N \ln(1 - \Phi_A(\mathbf{r}) - \Phi_B(\mathbf{r}) - \Phi_S(\mathbf{r})) \quad (14)$$

$$W_B(\mathbf{r}) = \chi_{AB}N\Phi_A(\mathbf{r}) + (\chi_{SP}^+N - \chi_{SP}^-N)\Phi_S(\mathbf{r}) - \chi_{SV}N\Phi_S(\mathbf{r}) - NH_B(\mathbf{r}) - N \ln(1 - \Phi_A(\mathbf{r}) - \Phi_B(\mathbf{r}) - \Phi_S(\mathbf{r})) \quad (15)$$

$$W_S(\mathbf{r}) = \chi_{SP}^+ N(\Phi_A(\mathbf{r}) + \Phi_B(\mathbf{r})) + \chi_{SP}^- N(\Phi_A(\mathbf{r}) - \Phi_B(\mathbf{r})) + \chi_{SV} N(1 - 2\Phi_S(\mathbf{r}) - \Phi_A(\mathbf{r}) - \Phi_B(\mathbf{r})) - N \ln(1 - \Phi_A(\mathbf{r}) - \Phi_B(\mathbf{r}) - \Phi_S(\mathbf{r})) \quad (16)$$

To numerically implement SCFT, the system is divided into a 1-D lattice. Starting with a set of random values for potential fields $W_i(\mathbf{r})$, the segment densities and potential fields are evolved by using the above self-consistent equations. At equilibrium, the value of free energy is minimum. The partition function for diblock copolymer, \mathcal{Z} , and the segment densities are calculated by solving the modified diffusion equation. A fourth order accurate Adams–Bashford algorithm is utilized to solve this partial differential equation.²⁵ For the case of bulk systems, the periodic boundary condition is applied, while for thin films, $q(\mathbf{r}, s) = 0$ is applied on the substrate and $dq/dr = 0$ at the other end. We utilized the following values for discretization in space $\Delta x = 0.05R_g$ and a step size of $\Delta s = 0.0025$. Each run took approximately 2 h of computer time to achieve convergence of 10^{-5} in the value of free energy per chain.

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