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Terminally Anchored Chain Interphases: The Effect of Multicomponent, Polydisperse Solvents on Their Equilibrium Properties

John H. van Zanten†

Polymers Division, Materials Science and Engineering Laboratory,
National Institute of Standards and Technology, Gaithersburg, Maryland 20899

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ABSTRACT: A theoretical description of terminally anchored chain interphases is presented for the case of an interphase in contact with a multicomponent solvent composed of species of varying quality and *size*. This work is an extension of a model proposed by Lai and Halperin (*Macromolecules* **1992**, *25*, 6693) to calculate the global properties of a terminally anchored chain interphase, or polymer brush, in contact with a *binary* solvent in which each component is of *monomeric size*. Here it is shown that the solvent size, in addition to the solvent quality and chain surface density, has a profound influence on the equilibrium properties of the terminally anchored chain interphase. At low chain surface densities there are two limiting behaviors for a terminally anchored chain interphase in contact with a pure solvent depending on the solvent quality. Under good solvent conditions the interphase collapses to a constant, solvent-swollen thickness as the solvent becomes much larger than the monomer size of the terminally anchored chain. However, under athermal or bad solvent conditions the interphase essentially collapses upon itself in the limit of large solvent size. At large chain surface densities the interphase collapses with increasing solvent size regardless of solvent quality. The case of binary solvents is even more interesting. Under some conditions instead of a solvent-size-induced collapse of the interphase, an enhanced swelling of the interphase is observed with increasing solvent sizes over some ranges of solvent size, quality, and chain surface densities. The methods presented here are easily extended to ternary and higher order solvent solutions. The phenomena described here may be exploited for various technological applications of terminally anchored chain interphases, such as separations and control of interfacial properties. The approach outlined here yields a simple calculational procedure for qualitatively examining the various global properties of these interphases which are inherent to each potential application as a function of chain surface density and solvent quality and size.

I. Introduction

Terminally anchored chain interphases have received considerable interest, both theoretical and experimental, in the scientific literature of the past several years.[1-20] These systems present an interesting theoretical and experimental challenge due to the complex nature of the situation wherein one has chain molecules in a constrained geometry. Terminally anchored chain interphases are of practical importance due to their occurrence, or potential use, in such areas as colloidal stabilization, liquid chromatographic separation, hybrid ceramic/polymer membranes, surface modification for biocompatibility, drug delivery, selective adsorbents, micellar extraction, biomembrane transport, supported catalysis, and others. The fundamental interest in such systems is due to the interesting conformations that terminally anchored chains adopt when the unperturbed chain dimensions begin to overlap. As one would expect, the equilibrium properties of a terminally anchored chain interphase in contact with a solvent phase are intimately related to the nature of the solvent, or free, molecules in contact with the interphase.

Many theoretical approaches have been utilized to describe terminally anchored chain interphases. Among these are scaling or mean-field theories,[3-7] self-consistent-field methods,[8-11] statistical mechanical models,[12] and numerical simulations.[13,14] The scaling approaches yield, in an elegant way, the correct trends over a variety of conditions. Unfortunately they only allow one to calculate the bulk properties of the interphase. However, they are relatively simple and provide a significant amount of insight into the factors which have the strongest influence on the equilibrium properties. The other methods allow for the detailed (*i.e.*, spatially dependent) prediction of the local interphase properties at different levels of detail. Unfortunately these methods are not as computationally transparent as the scaling approaches. The self-consistent-field methods allow the development of analytical expressions under limiting conditions such as for strongly stretched chain interphases. Statistical mechanical and numerical simulation techniques require somewhat complex numerical calculations. These difficulties led the author to consider an extension of the mean-field approach originally developed by Lai and Halperin[5,6] for terminally anchored chains of finite extensibility. This approach allows one to describe the global conformational properties of the terminally anchored chain interphase in terms of the chain length, solvent quality, and the surface density of the terminally anchored chains. It is also readily amenable to developing closed-form analytical expressions which describe the various interphase properties which can provide insight into the design of terminally anchored chain interphases for given applications.

In this paper the Lai and Halperin[5,6] theory for terminally anchored chain interphases of finite extensibility is extended to include both solvent quality and *size*. Here only the situation wherein the solvent molecules are completely immersed either in the terminally anchored chain interphase or in the bulk solvent solution in contact with the interphase is considered. That is, the situation in which any mobile species (*i.e.*, for the case in which the given mobile species is larger than the terminally anchored chain monomer size) straddle the interface between the terminally anchored chain interphase and the bulk solution is neglected. This assumption limits the applicability of the theory to situations in which the solvent molecules are somewhat smaller than the terminally anchored chains. The relative simplicity of this approach leads to a theory which accounts for the effect of solvent size in a relatively straightforward manner. A more general approach allowing the existence of mobile species which straddle the interface would most likely require one of the techniques

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† E-mail: johnvz@enh.nist.gov.

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which yield a description of the local interphase properties. The general case of a multicomponent solvent in contact with a terminally anchored chain interphase is presented here. The original derivation only considered the case of monomer-sized solvents.[6] Here the size of the solvent molecules is found to have a profound influence on the equilibrium properties of the terminally anchored chain interphase. For the sake of simplicity this report will only consider the equilibrium thicknesses of the terminally anchored interphases for various solvent conditions. The implications of these findings on the partitioning and retention of target solutes in terminally anchored chain interphases, especially as to their potential uses as chromatographic stationary phases and adsorbents, will be considered in a subsequent contribution.[22]

II. Terminally Anchored Chain Interphase in Contact with a Multicomponent Solvent Mixture

The terminally anchored chains are assumed to be flexible, neutral, and monodisperse. The terminally anchored chain interphase is described essentially within the framework of the Alexander model.[3] The polymer volume fraction is assumed to be constant throughout the interphase and the chains are uniformly stretched. The terminally anchored chain interphase is in contact with a multicomponent solvent mixture of differing interactions and sizes which is miscible in all proportions. It is also assumed that the various solvent volume fractions are also constant throughout the interphase. Finally it is assumed that neither the chains nor solvents have any preference for the anchoring surface. If the last assumption is not made, it is impossible to consider the global properties of the interphase and a self-consistent means of calculating the interphase properties would be required in order to account for any local properties such as wetting transitions.[23]

The terminally anchored chains are assumed to be of size N and monomer size a. They are connected to a locally flat interface at a surface density $\sigma = a^2/D^2$, where D is the distance between anchoring sites. Extending the work of Lai and Halperin,[6] the free energy of a terminally anchored chain in contact with such a solvent can be written as

$$F = F_{\mathrm{conf}} + F_{\mathrm{mix}} \tag{1}$$

The first term is due to the configuration of the terminally anchored chain. It is due to the stretched configurations that terminally anchored chains must adopt as their surface density increases. The second term is due to the various interactions between the solvents and terminally anchored chains.

To allow for high surface densities of terminally anchored chains, an expression for the configurational free energy which accounts for the finite extensibility of the terminally anchored chains is adopted. This configurational energy can be expressed in terms of the inverse Langevin function

$$F_{\mathrm{conf}} = \frac{1}{a}\int_0^{\mathrm{h}} \mathcal{L}^{-1}(z/Na)\,\mathrm{d}z \tag{2}$$

where h is the thickness of the terminally anchored chain interphase and $\mathcal{L}(x) = \coth x - 1/x$ is the Langevin function.[5,6] This form will reduce to the Gaussian stretching expression, $F_{\mathrm{conf}} = (3/2)(h^2/Na^2)$, that many investigators have used when considering stretched terminally anchored chains of very low surface density (*i.e.*, when $h \ll Na$).[3-8,10,11] When one sets $u = z/Na$, this expression can be further simplified as

$$F_{\mathrm{conf}} = N\int_0^{h/Na} \mathcal{L}^{-1}(u)\,\mathrm{d}u \tag{3}$$

Up to this point the derivation has been essentially that of Lai and Halperin.[5,6] The terminally anchored polymer volume fraction in the interphase, ϕ_P (throughout this report $i = P$ will refer only to the terminally anchored chains), is related to the thickness of the terminally anchored chain interphase by the following relation:

$$\frac{h}{Na} = \frac{\sigma}{\phi_P} = \frac{\sigma}{N}\Big(N + \sum_{i\neq P} n_i N_i\Big) = h^*(n_i) \tag{4}$$

where n_i is the number of solvent species i molecules associated with each terminally anchored chain and N_i is their size (since the case of solvent molecules straddling the interphase–solvent interface is neglected this approach is most applicable for $N_i^{1/2} \ll N$). Therefore, with this development (eq 4) the influence of solvent size has been accounted for and the configurational free energy contribution in its final form is

$$F_{\mathrm{conf}} = N\int_0^{h^*(n_i)} \mathcal{L}^{-1}(u)\,\mathrm{d}u \tag{5}$$

The Flory–Huggins mixing energy will be used for F_{mix} of the terminally anchored chain interphase.

$$F_{\mathrm{mix}} = \sum_{i\neq P} n_i \ln \phi_i + \sum_{i\neq j} \chi_{ij} \frac{n_i N_i n_j N_j}{\sum_i n_i N_i} \tag{6}$$

where ϕ_i is the volume fraction of solvent species i in the terminally anchored chain interphase and χ_{ij} is the interaction parameter between species i and j. The translational entropy of the grafted chains is neglected because the chains are assumed to be anchored at the interface of the interphase.[4] The bulk solvent solution will also be modeled as a regular solution in the Flory–Huggins approximation, with its free energy being given by

$$F_{\mathrm{bulk}} = \sum_{i\neq P} n_i \ln \Phi_i + \sum_{i\neq j} \chi_{ij} \frac{n_i N_i n_j N_j}{\sum_i n_i N_i} \tag{7}$$

where Φ_i is the volume fraction of species i in the bulk solvent. Here the terminally anchored chains are ignored since due to their anchoring they are not present in the bulk solvent phase. However, the effect of mobile chains of the same species being present in the bulk solvent phase can still be addressed.

The equilibrium state of a terminally anchored chain interphase is determined by equating the chemical potential of each mobile species i in the two phases, the bulk solvent, and the terminally anchored chain interphase. This condition leads to the following expression:

$$\sigma\mathcal{L}^{-1}(\sigma/\phi_P) + \frac{1}{N_j}\left(\ln\frac{\phi_j}{\Phi_j} + \Phi_j - \phi_j\right) + \sum_{i\neq j,P}\frac{\Phi_i - \phi_i}{N_i} + (1 - \phi_j)$$
$$\sum_{i\neq j}\chi_{ij}\phi_i + (\Phi_j - 1)\sum_{i\neq j}\chi_{ij}\Phi_i + \sum_{\substack{i,k\neq j\\ i\neq k}}\chi_{ik}(\Phi_i\Phi_k - \phi_i\phi_k) = 0 \tag{8}$$

This condition must be satisfied for all of the mobile species present in the system. The most important observation to be made here is that the equilibrium volume fractions depend on the various solvent sizes. However, they are independent of the terminally anchored chain size, as is typically found for scaling or mean-field arguments.[3-6] The first term is the contribution due to the cost of stretching the terminally anchored chains as the interphase is swollen with solvent. The next two terms comprise the entropy of mixing contribution, and it is these two terms which are affected by the solvent sizes. The last three terms, the heat of mixing contribution, are a result of the interactions between the various species which are present. Given the solvent composition, sizes, and interaction parameters, along with the surface density of the terminally anchored chains, the volume fractions of the various species in the terminally anchored chain interphase can be readily calculated since

$$\phi_P = 1 - \sum_{i \neq P} \phi_i \tag{9}$$

Once the volume fractions of the solvent species in the terminally anchored chain interphase are known, the equilibrium layer thickness, h, is given by combining (4) and (9). Therefore, the equilibrium thickness of a terminally anchored chain interphase in contact with a multicomponent solvent of varying quality and size is a linear function of the chain size, N. This linear dependence of the layer thickness with respect to the chain size is the signature of strongly stretched terminally anchored chain interphases.[3]

III. Terminally Anchored Chain Interphases in Contact with a Pure Solvent

The equilibrium composition of a terminally anchored chain interphase in contact with a pure solvent can be determined from the single solvent case of the equilibrium condition given by (8). For a pure solvent A the relevant expression is

$$\sigma\mathcal{L}^{-1}\left(\frac{\sigma}{1-\phi_A}\right) + \frac{1}{N_A}(\ln \phi_A + 1 - \phi_A) + \chi_{AP}(1-\phi_A)^2 = 0 \tag{10}$$

For the case of $N_A = 1$ this expression reduces to that previously found for the case of a pure monomer-sized solvent by Lai and Halperin.[5] Upon inspection it is apparent that for the case of a pure solvent in contact with a terminally anchored chain interphase, the solvent volume fraction, and therefore the interphase layer thickness, will decrease to a limiting value with increasing solvent size for solvent of any quality, with the layer essentially collapsing for large solvents when $\chi_{AP} \geq 0$. That is, a terminally anchored chain interphase will essentially collapse when in contact with any polymer melt where $\chi_{AP} \geq 0$. When $\chi_{AP} < 0$, the interphase thickness collapses to a value which may not be that of the completely collapsed interphase depending on the surface density of the terminally anchored chains. For situations in which the surface density does not lead to collapse of the interphase, this limiting thickness increases with increasing solvent quality. This is a size-exclusion mechanism which will prove interesting when the chromatographic behavior of terminally anchored chain interphases is considered in a subsequent contribution.[22]

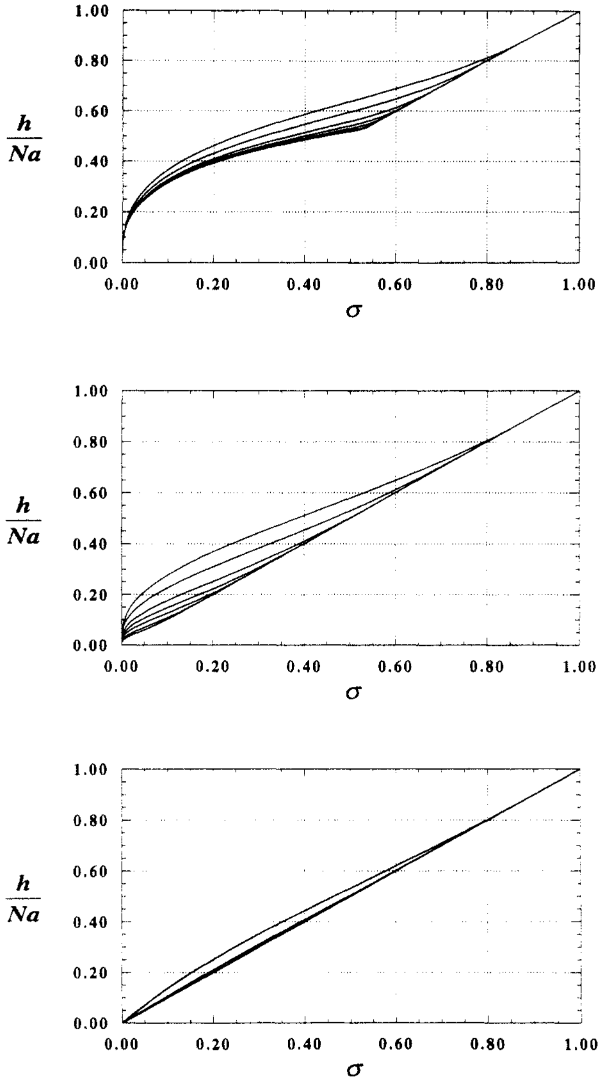

Figure 1. Terminally anchored chain interphases in contact with a pure solvent at equilibrium: the effect of chain surface density. The equilibrium dimensionless interphase thickness, h/Na, is shown as a function of chain surface density, σ, for three solvent conditions: $\chi_{AP} = -1$, top; $\chi_{AP} = 0$, middle; $\chi_{AP} = 1$, bottom. The seven solvent sizes considered here are $N_A = 1$, 2, 5, 10, 20, 50, and 100, which correspond to the upper to lower curves, respectively, in each plot.

In Figure 1 the dimensionless layer thickness, h/Na, of a terminally anchored chain interphase in contact with a pure solvent is displayed as a function of the terminally anchored chain surface density for fixed solvent size and quality. Here good ($\chi_{AP} = -1$), athermal ($\chi_{AP} = 0$), and bad ($\chi_{AP} = 1.0$) solvents, from top to bottom in Figure 1, respectively, and solvent sizes $N_A = 1, 2, 5, 10, 20, 50$, and 100 are considered. The interaction parameters and solvent sizes are selected simply for convenience. As previously noted, the interphase thickness decreases to a limiting value with increasing solvent size irrespective of the solvent quality or terminally anchored chain surface density. When $\chi_{AP} \geq 0$, the interphase layer essentially collapses upon itself for the case of a very large solvent at all nonzero chain surface densities. This is due to the equilibrium condition only being satisfied by complete expulsion of the solvent, greatly reducing the mixing entropy contribution to expression (10), as the solvent size increases. Also, there is a limiting terminally anchored chain surface density at which essentially complete collapse occurs, which is dependent on the solvent quality and *size*. This limiting chain surface density decreases with decreasing solvent quality and increasing solvent size, which is consistent with the difficulties inherent with mixing a large species solvent of bad quality with a terminally anchored chain interphase. The athermal solvent case, $\chi_{AP} = 0$, clearly displays the size-exclusion effect present here, since there is no heat of mixing in this situation. The largest spread in equilibrium thicknesses appears to occur

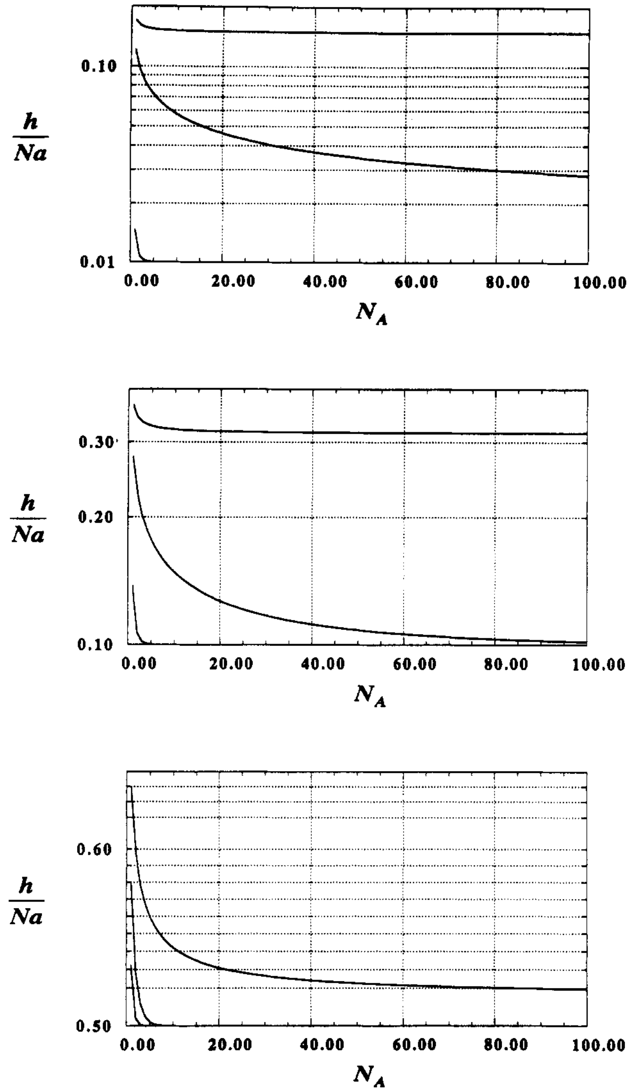

Figure 2. Terminally anchored chain interphases in contact with a pure solvent at equilibrium: the effect of solvent size. The equilibrium dimensionless interphase thickness, h/Na, is shown as a function of solvent size, N_A, for three chain surface densities: $\sigma = 0.01$, top; $\sigma = 0.10$, middle; $\sigma = 0.50$, bottom. The three solvent qualities considered here are $\chi_{AP} = -1$, $\chi_{AP} = 0$, and $\chi_{AP} = 1$, which correspond to the top, middle, and bottom curves, respectively, in each plot.

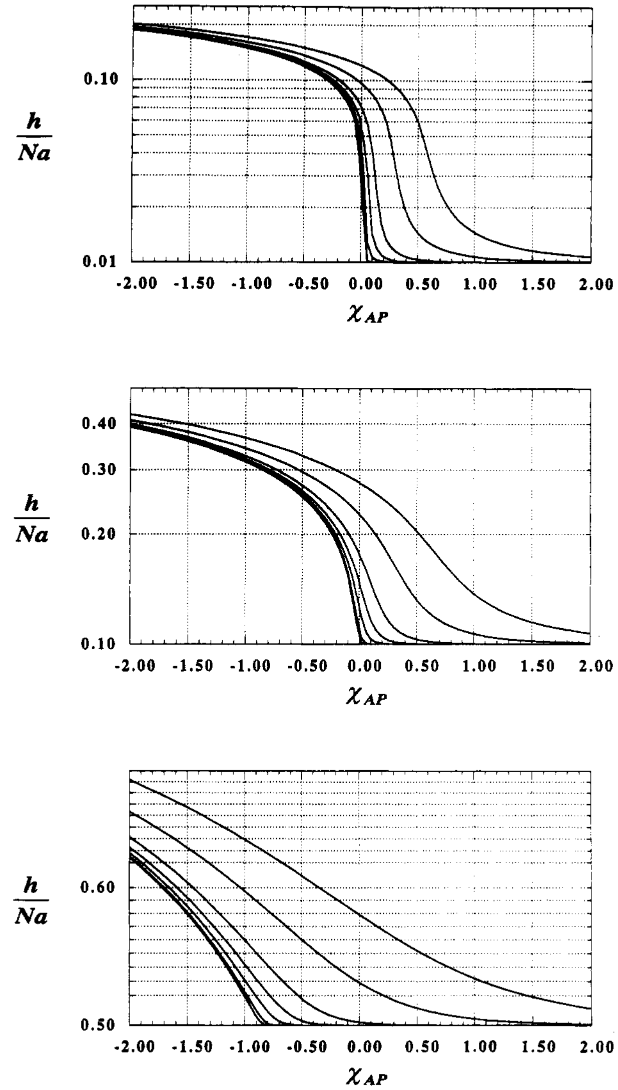

Figure 3. Terminally anchored chain interphases in contact with a pure solvent at equilibrium: the effect of solvent quality. The equilibrium dimensionless interphase thickness, h/Na, is shown as a function of solvent quality, χ_{AP}, for three chain surface densities: $\sigma = 0.01$, top; $\sigma = 0.10$, middle; $\sigma = 0.50$, bottom. The seven solvent sizes considered here are $N_A = 1$, 2, 5, 10, 20, 50, and 100, which correspond to the upper to lower curves, respectively, in each plot.

at $\sigma \approx 0.05$, which is a relatively low chain surface density. The bad solvent case, $\chi_{AP} = 1$, however, is another story. Under these conditions the interphase is essentially collapsed for $N_A \geq 5$, and there is very little difference between the equilibrium heights.

The good solvent case, $\chi_{AP} = -1$, displays somewhat more complex behavior. It is apparent in Figure 1 (top) for surface densities below some limiting value; the interphase thickness collapses to a limiting state which is still swollen with solvent as the solvent size increases (see Figure 2). This phenomenon occurs under these conditions because, as the solvent size increases, the entropy of mixing term becomes negligible, with the equilibrium condition being satisfied by balancing the configurational energy of the terminally anchored chains and the solvent–chain interactions. The limiting interphase thickness and surface density both increase with increasing solvent quality as might be expected (see Figure 3). In addition, under these solvent conditions it is apparent that the interphase thickness also displays an inflection point near the limiting surface density, which is dependent on the solvent size. This limiting surface density at which the interphase essentially collapses decreases with increasing solvent size. In contrast with the athermal solvent case, the largest spread in equilibrium thicknesses appears to occur at $\sigma \approx 0.52$, which is a very high chain surface density. This variation in behavior has interesting implications which can be exploited for different applications.

As noted previously, the equilibrium interphase thickness is strongly coupled to the solvent size. This is demonstrated in Figure 2 where the influence of solvent size on the thickness of the interphase is explicitly considered. Three chain surface densities, $\sigma = 0.01$, 0.10, and 0.50 from top to bottom, respectively, are considered. At each chain surface density three solvent qualities, $\chi_{AP} = -1$, 0, and 1 (from top to bottom, respectively), are displayed. For all three chain surface densities considered here, the chain interphase rapidly collapses with increasing solvent size under bad solvent conditions. This is essentially due to the unfavorable heat of mixing effects. This is what was also shown in the lowermost plot of Figure 1. The good solvent case also displays a rapid collapse to a limiting layer thickness when $\sigma = 0.01$ and 0.10, and the magnitude of the collapse increases with the increasing chain surface density. Under these conditions, which lead to swelling of the interphase since the heat of mixing is favorable and the sterically induced chain stretching contribution to the energy is very small, the collapse is due to the diminishing of the entropy of mixing with increasing solvent size. However, at $\sigma = 0.50$ the collapse is much more gradual, as is also apparent in the uppermost plot of Figure 1, with much of the collapse occurring when $1 \leq N_A \leq 20$. After this point the collapse of the layer is much more gradual. The different behavior under these conditions is essentially a result of the sterically induced chain stretching which of itself will reduce the degree of swelling. The athermal solvent case is most interesting. At $\sigma = 0.01$ the collapse of the layer is very gradual, with significant swelling present at $N_A = 100$ because of the negligible contribution of the sterically induced chain stretching. When $\sigma = 0.10$, however, the layer still collapses gradually, with essentially complete collapse for $N_A \geq 100$ since there is a larger degree of sterically induced chain stretching. At the highest chain surface density, $\sigma = 0.50$, the collapse, while not as rapid as in the bad solvent case, is essentially complete for $N_A \geq 8$ due to the large magnitude of the steric interactions between the terminally anchored chains.

As noted previously, the equilibrium interphase thickness is also strongly coupled to the solvent quality. This is demonstrated in Figure 3 where the influence of solvent quality on the thickness of the interphase is explicitly considered. In Figure 3 the dimensionless equilibrium layer thickness is shown as a function of solvent quality. Once again the three chain surface densities, $\sigma = 0.01$, 0.10, and 0.50 (from top to bottom, respectively), are considered. At each of these chain surface densities seven representative solvent sizes, $N_A = 1$, 2, 5, 10, 20, 50, and 100, are displayed. At the lowest chain surface density, $\sigma = 0.01$ (Figure 3, top), the chain interphase is substantially swollen ($h/h_{\text{collapsed}} \geq 2$) for all chain lengths considered here when $\chi_{AP} \leq 0$. This is a result of the favorable heat of mixing and small degree of sterically induced stretching. As the interaction parameter approaches zero, the collapse of the interphase becomes very rapid for $N_A \geq 5$. Under these conditions the contribution of the mixing entropy becomes important; however, its effectiveness is reduced with increasing solvent size, thereby leading to the collapse of the interphase. When $\chi_{AP} \geq 0.5$, the interphase is essentially collapsed for $N_A \geq 5$ since the mixing entropy contribution is strongly influenced by the solvent size. Sufficiently small solutes, $N_A = 1$ or 2, still display some degree of swelling for fairly bad solvents at this low chain surface density since the mixing entropy is much more favorable for smaller solvents. Also at this surface density it is apparent that the greatest separation of the interphase thicknesses occurs at $\chi_{AP} \approx 0.05$. When the chain surface density is increased 10-fold to $\sigma = 0.10$ (Figure 3, middle), the observed thickness collapse with decreasing solvent quality is more gradual. At this surface density $h/h_{\text{collapsed}} \geq 2$ occurs when $\chi_{AP} \leq -0.25$ for all of the solvent sizes considered here. Also under these conditions the greatest spread in equilibrium thicknesses occurs at a slightly reduced χ_{AP} value from the previously considered chain surface density. This slight reduction in the χ_{AP} value, along with attenuation of the interphase collapse rate, is due to the increased contribution of the steric terminally anchored chain interactions at this 10-fold higher surface coverage. This effect becomes more obvious as the chain surface density is further increased to $\sigma = 0.50$ (Figure 3, bottom). Here the rate of interphase collapse is much more gradual, and the interphase is even collapsed under very good solvent conditions for the larger solutes, $N_A \geq 5$. The χ_{AP} values at which collapse occurs for the various solvent sizes are also much broader at this chain surface density which may prove interesting when the chromatographic potential of these interphases is considered. The collapse of the interphase with decreasing solvent quality is a smooth and continuous process as was first noted by Zhulina *et al.*[24]

IV. Terminally Anchored Chain Interphases in Contact with a Binary Solvent

The equilibrium composition of a terminally anchored chain interphase in contact with a binary solvent can be determined from the binary solvent case of the equilibrium condition given by (8). Here it is assumed that the bulk solvent phase contains two species, A and B, with the relevant equilibrium criteria being

$$\sigma\mathcal{L}^{-1}\left(\frac{\sigma}{1-\phi_A-\phi_B}\right)+\frac{1}{N_A}\left(\ln\frac{\phi_A}{\Phi_A}+\Phi_A-\phi_A\right)+ \frac{1-\Phi_A-\phi_B}{N_B}+\chi_{AP}(1-\phi_A)(1-\phi_A-\phi_B)+ \chi_{AB}(\phi_B(1-\phi_A)-(1-\Phi_A)^2)-\chi_{BP}\phi_B(1-\phi_A-\phi_B)=0 \quad (11)$$

and

$$\sigma\mathcal{L}^{-1}\left(\frac{\sigma}{1-\phi_A-\phi_B}\right)+\frac{1}{N_B}\left(\ln\frac{\phi_B}{1-\Phi_A}+1-\Phi_A-\phi_B\right)+ \frac{\Phi_A-\phi_A}{N_A}+\chi_{BP}(1-\phi_B)(1-\phi_A-\phi_B)+ \chi_{AB}(\phi_A(1-\phi_B)-\Phi_A^{\,2})-\chi_{AP}\phi_A(1-\phi_A-\phi_B)=0 \quad (12)$$

In contrast with the pure solvent situation, it is much more difficult to quickly deduce the limiting behavior of the binary solvent case for given scenarios. The interplay between solvent size and quality, along with the effects of chain surface density, lead to many interesting phenomena.

The influence of solvent size is most easily examined for the case of no heat of mixing or all athermal interactions between the various species, $\chi_{AB} = \chi_{AP} = \chi_{BP} = 0$. Under athermal conditions it is easily shown that within the model described herein

$$\phi_A = \Phi_A\left(\frac{\phi_B}{1-\Phi_A}\right)^{N_A/N_B} \quad (13)$$

Since athermal mixing is assumed, $\phi_B < 1 - \Phi_A$; therefore, ϕ_A will become much smaller than Φ_A as N_A/N_B increases for any chain surface density of significance (*i.e.*, $\sigma \geq 0.001$). In Figures 4 and 5 this very situation is considered. The dimensionless interphase thickness, h/Na, is displayed as a function of Φ_A for the representative chain surface densities, $\sigma = 0.01$, 0.10, and 0.50, and solvent sizes, $N_A = 1$, 2, 5, 10, 20, 50, and 100, considered in the pure solvent case. Here solvent B is taken to be monomeric in size, $N_B = 1$, in order to focus on the effect of increasing the size of only one of the solvent species. The equilibrium expression of interest for this situation is

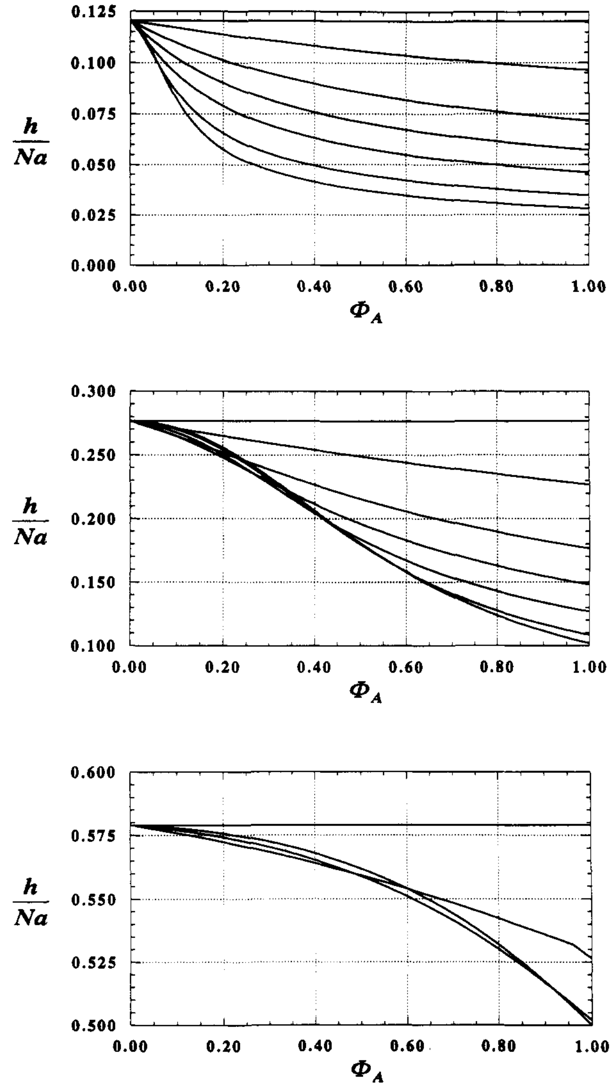

Figure 4. Terminally anchored chain interphases in contact with a binary solvent at equilibrium: the effect of solvent size and composition under athermal solvent conditions. The equilibrium dimensionless interphase thickness, h/Na, is shown as a function of solvent composition, Φ_A, under athermal conditions, $\chi_{AB} = \chi_{AP} = \chi_{BP} = 0$, for three chain surface densities: $\sigma = 0.01$, top; $\sigma = 0.10$, middle; $\sigma = 0.50$, bottom. In all three plots the size of solvent B is $N_B = 1$. The seven solvent A sizes considered here are $N_A = 1, 2, 5, 10, 20, 50$, and 100, which correspond to the upper to lower curves at the far right, respectively, in each plot. One should note that these curves do cross over one another.

$$\sigma\mathcal{L}^{-1}\left(\frac{\sigma}{1-\Phi_A(\phi_B/(1-\Phi_A))^{N_A/N_B}-\phi_B}\right)+\ln\frac{\phi_B}{1-\Phi_A}+1-\Phi_A-\phi_B+\frac{\Phi_A(1-(\phi_B/(1-\Phi_A))^{N_A/N_B})}{N_A}=0 \quad (14)$$

At all three surface densities interesting solvent-size-induced mixing phenomena are apparent. As N_A increases, the volume fraction of species B, ϕ_B, in the terminally anchored chain interphase increases to a limiting value (which never exceeds the value for pure solvent B in contact with the interphase and decreases with increasing Φ_A) for all surface densities and binary athermal solvent compositions. This increase is due to mixing entropy effects, since the contribution of solvent A to the equilibrium expression is rapidly diminished as N_A becomes large, thereby causing a concomitant decrease in ϕ_A and an increase in ϕ_B. At low chain surface coverages the overall degree of swelling (*i.e.*, $\phi_A + \phi_B$) will usually decrease with increasing N_A.

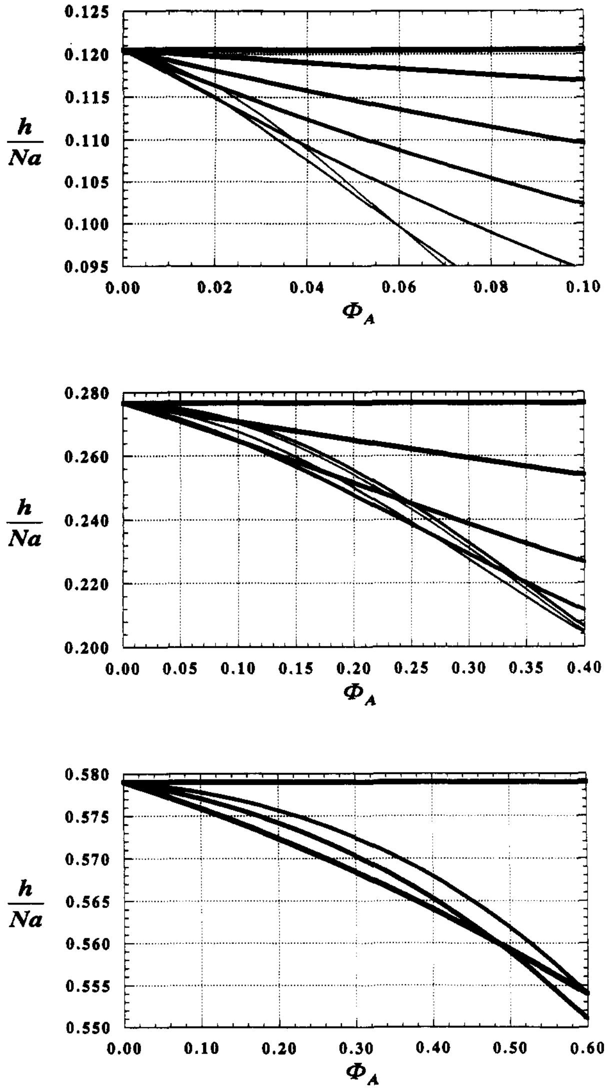

Figure 5. Terminally anchored chain interphases in contact with a binary solvent at equilibrium: the effect of solvent size and composition under athermal solvent conditions—the swelling crossover. The plots of Figure 4 are expanded in the region of the interphase thickness crossovers to highlight this phenomena with more clarity. The plots are the same as those in Figure 4 with the exception of the fact that the seven solvent A sizes considered here, $N_A = 1, 2, 5, 10, 20, 50$, and 100, correspond to lines of various thickness, with the thickness decreasing with increasing solvent size.

However, under some circumstances the overall degree of swelling will actually increase as N_A increases, leading to an increase in the thickness of the interphase. This is apparent in the plots of Figure 4. The onset of the increase in interphase swelling is a subtle function of the chain surface density, solvent composition, and solvent size. This is clearly demonstrated in Figure 5 where the plots of Figure 4 have been expanded to highlight the crossover in swelling behavior due to increases in the size of solvent species A. It is apparent that this solvent-size-induced enhancement of the interphase swelling becomes more prevalent with increasing chain surface density. This is an indication that this phenomena is strongly coupled with the configurational chain energy. Indeed, as the chain surface density increases the configurational energy approaches and surpasses the magnitude of the mixing entropy contributions over a wider range of solvent size and composition, thereby making this effect even more evident. Zhulina, Borisov, and Brombacher[21] have utilized self-consistent-field methods to analyze this situation and have observed a monotonic decrease in the interphase thickness with increasing Φ_A and N_A. The occurrence of any crossover behavior was not reported in their study.

Gast and Leibler[25] have also examined the case of terminally anchored and free polymer chains of the same composition in an athermal solvent. These authors, for reasons unknown to this investigator, have neglected the contribution of the solvent molecules to the free energy in their derivation, and they have also only considered Gaussian chain stretching. They describe three regimes of behavior found within their modeling approach: (I) σ-dominated, (II) Φ_A-dominated, and (III) penetration-dominated. The interphase properties in the σ-dominated region or regime I are essentially the same properties as the interphase in the presence of pure solvent. According to Gast and Leibler,[25] the boundary of this region scales as $\Phi_A \sim \sigma^{2/3}$, while in the model considered here (*i.e.*, finite chain extensibility and Flory–Huggins mixing, including the small solvent contribution) this boundary appears to scale as $\Phi_A \sim \sigma$, and therefore the extent of this regime is somewhat diminished in comparison with the results found by Gast and Leibler. In the present model the Φ_A-dominated regime is most prevalent, with the interpenetration regime essentially only occurring at somewhat small surface coverages. This is apparent in Figures 4 and 5 where the essentially monotonic decrease in interphase thickness with increasing Φ_A is observed. This different behavior is probably due to the consideration of small solvent mixing effects in the model described here.

As mentioned previously, it is much more difficult to quickly deduce the limiting behavior of the binary solvent case for a given scenario. The interplay between solvent size and quality, along with the effects of chain surface density, leads to many interesting phenomena. To examine the effect of varying solvent quality and size, a system which was previously investigated by Lai and Halperin[6] for the case of an interphase in contact with a binary solvent composed of monomer-sized species will be considered. The system is similar to that which was studied by Auroy and Auvray.[16] Here it is assumed that $\sigma = 0.00325$ and $\chi_{AB} = 0$, $\chi_{AP} = -3$, and $\chi_{BP} = 1$. This is a situation in which the bulk solvent mixture is athermal, yet the solvent–chain interactions are very favorable in the case of solvent A and very unfavorable in the case of solvent B.

Two situations are considered here. The first is shown in Figure 6 where the situations in which $N_B = 1$ and $N_A = 1, 2, 5, 10, 20, 50$, and 100 are considered. The uppermost plot in Figure 6 displays the dimensionless equilibrium thickness for all seven solvent sizes over the entire range of solvent composition. The situation in which both solvent A and B are monomer-sized yields the highly nonlinear result first observed by Lai and Halperin[6] within the framework described here and a similar observation made by Marko[10] using the self-consistent-field approach. Here very little change in the slightly swollen interphase with increasing solvent A (good solvent) fraction is observed until $\Phi_A \approx 0.50$, at which point the interphase thickness rapidly grows to the value expected for the case of pure solvent A as $\Phi_A \rightarrow 1$. This highly nonlinear behavior holds for all solvent sizes and makes it abundantly clear that "average" solvent properties cannot be used when one considers these mixed-solvent systems of varying quality and size. This observed behavior has important consequences for partitioning and retention of target species in the interphase.[22] As the size of solvent A is increased, the effects are subtle, yet important, especially for potential applications. The lack of sensitivity to the good solvent size is a result of the low surface coverage considered here, wherein the interphase thickness will reach a limiting value which is still swollen with solvent (see the previous discussion for the pure solvent case). At low Φ_A the interphase thickness *increases* with increasing N_A due to a concomitant increase of ϕ_A under these conditions (see Figure 6, middle plot). This phenomenon is commonly encountered when large molecules partition between two phases of differing chemical composition. This observation will be of great importance when the chromatographic behavior of these interphases is considered in a future contribution.[22] The good solvent size has very little effect again until $\Phi_A \geq 0.90$ where the limiting behavior for the case of pure solvent A becomes relevant (see Figure 6, bottom plot), with this behavior being the same as that previously discussed for the case of a good pure solvent in contact with a terminally anchored chain interphase.

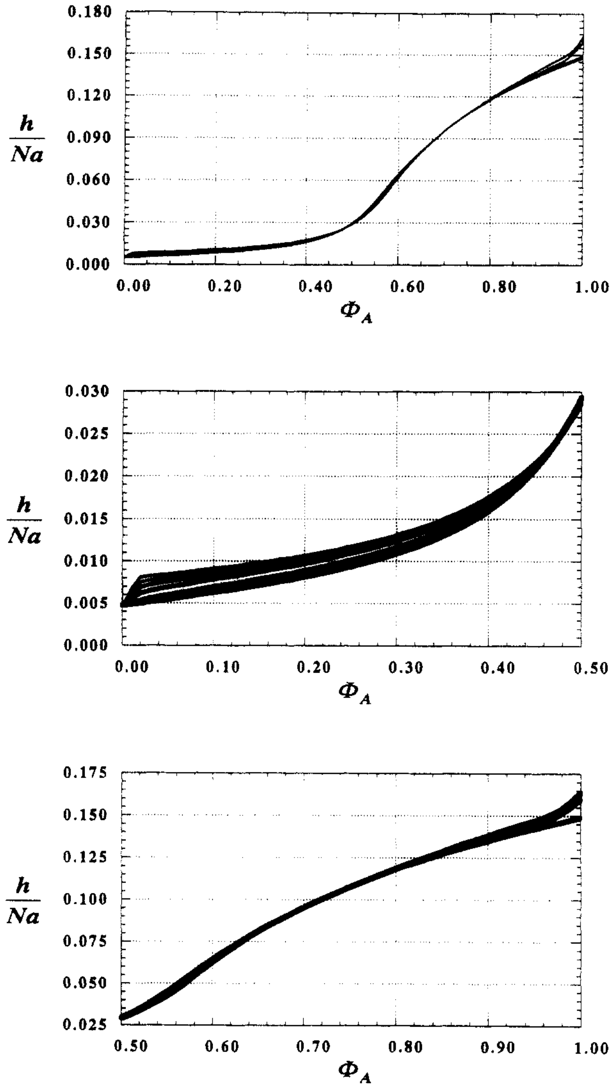

Figure 6. Terminally anchored chain interphases in contact with a binary solvent at equilibrium: the effect of solvent size, quality, and composition. The equilibrium dimensionless interphase thickness, h/Na, is shown as a function of solvent composition, Φ_A, at the solvent conditions $\chi_{AB} = 0$, $\chi_{AP} = -3$, and $\chi_{BP} = 1$ at a chain surface density $\sigma = 0.00325$ as per Lai and Halperin.[6] In all three plots the size of solvent B is $N_B = 1$. The seven solvent A sizes considered here are $N_A = 1, 2, 5, 10, 20, 50$, and 100, which correspond to the upper to lower curves at the far right, respectively, in the top plot. In the middle and lower plots, which are expanded views of the top plot, however, the line thickness corresponds to the solvent size, with the line thickness decreasing with increasing solvent A size. One should note that these curves do cross over one another.

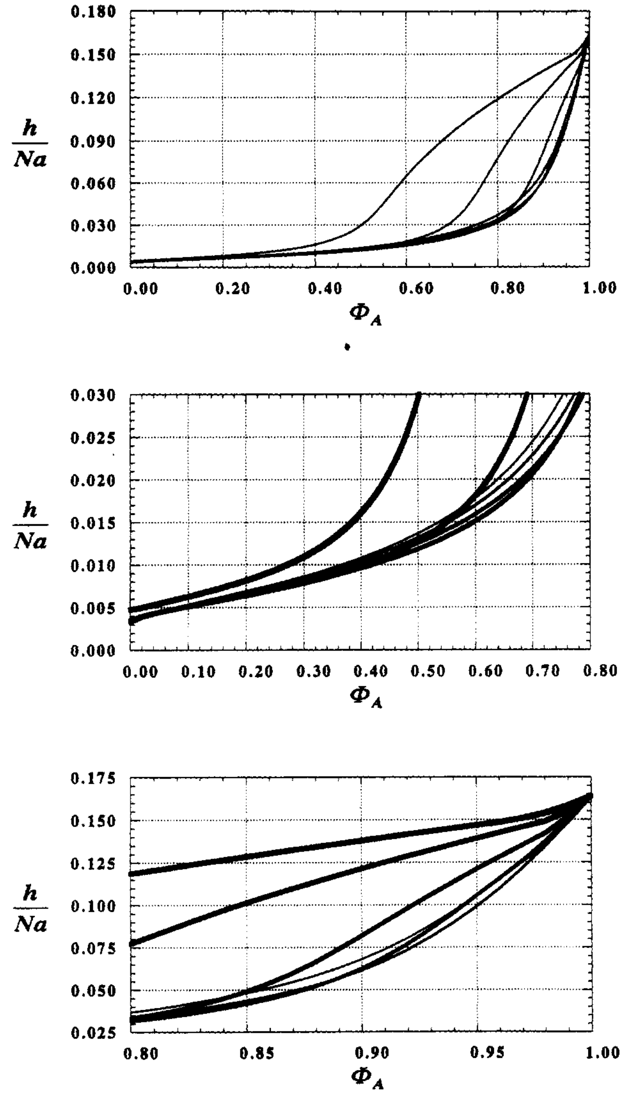

Figure 7. Terminally anchored chain interphases in contact with a binary solvent at equilibrium: the effect of solvent size, quality, and composition. The equilibrium dimensionless interphase thickness, h/Na, is shown as a function of solvent composition, Φ_A, at the solvent conditions $\chi_{AB} = 0$, $\chi_{AP} = -3$, and $\chi_{BP} = 1$ at a chain surface density $\sigma = 0.00325$. In all three plots the size of solvent A is $N_A = 1$. The seven solvent B sizes considered here are N_B = 1, 2, 5, 10, 20, 50, and 100, which correspond to the upper to lower curves at the far right, respectively, in the top plot. In the middle and lower plots, which are expanded views of the top plot, however, the line thickness corresponds to the solvent size, with the line thickness decreasing with increasing solvent B size. One should note that these curves do cross over one another.

The opposite situation where $N_A = 1$ and N_B = 1, 2, 5, 10, 20, 50, and 100 yields yet more interesting behavior. This is presented in Figure 7. The uppermost plot in Figure 7 displays the dimensionless equilibrium thickness for all seven solvent sizes over the entire range of solvent composition. Once again the situation in which both solvent A and B are monomer-sized yields the result first observed by Lai and Halperin.[6] Unlike the previously considered situation, however, the interphase thickness is a strong function of solvent size for $\Phi_A \geq 0.40$. Below this solvent A fraction, the interphase is essentially collapsed for $N_B \geq 2$ due to the presence of the bad solvent. The interphase begins to swell as the fraction of solvent A is increased in the bulk. The swelling behavior is complex, with the existence of size-induced enhancement as was observed in the previous cases, the degree of which increases and then decreases as Φ_A increases (see Figure 7, middle and bottom plots). As $\Phi_A \rightarrow 1$ the interphase thickness collapses as N_B increases due to the exclusion of species B from the interphase, thus exhibiting a size-exclusion mechanism which may be exploited for various separation applications (see Figure 7, bottom plot).

V. Summary

The model of Lai and Halperin for a polymer brush, or terminally anchored chain interphase, in contact with a binary solvent of monomer-sized species of varying quality was extended to the case of a multicomponent solvent of varying quality and *size*. The approach yields simple expressions to determine the qualitative behavior of these systems. The influence of the species size was found to be just as important as the chain surface density and the interactions between the solvent species and the terminally anchored chains. For the sake of brevity only the cases of pure and binary solvents in contact with an interphase were considered here and even these simple systems displayed a wide range of interesting behaviors which may have important technological consequences. However, the calculations are easily extended to more complex solvent mixtures. One should note that ternary and higher order systems will prove to be of importance when the chromatographic properties of these interphases are considered, especially in the context of gradient chromatography and competitive adsorption.[22]

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