

Wetting transitions in symmetrical polymer blends

S. M. Engels^{a)} and F. A. M. Leermakers

Laboratory of Physical Chemistry and Colloid Science, Wageningen University, Dreijenplein 6, 6703 HB Wageningen, The Netherlands

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The characteristics of wetting in polymer blends are investigated by a self-consistent-field theory. A symmetrical system is chosen: the interface between two homopolymeric liquids *A* and *B* is wetted by a third homopolymer *C* which is equally insoluble in both liquids. All components have the same molecular weight ($N_A = N_B = N_C = N = 10$ or 100). The emphasis of this study is on the wetting transitions induced by varying the interactions between the components. Cahn's argument, which predicts complete wetting near the critical temperature of two system components, is verified in this context. We show that it is necessary to consider the effective interaction parameters $\chi_{AC}^{\text{eff}} = \chi_{BC}^{\text{eff}}$ to verify Cahn's argument. Since we vary the solubility of *C* (given by $\chi_{AC} = \chi_{BC}$) and the thickness of the *AB* interface (determined by χ_{AB}) independently, we have a two-dimensional parameter space. In this parameter space we can distinguish three regimes representing wetting transitions with different characteristics. One of these regimes indeed shows Cahn-type transitions. A key observation is that the wetting transitions near the simultaneous critical point of mixtures *A/C* and *B/C* are of a second-order type. A second regime in the parameter space represents wetting transitions which are understood from the high surface tension of the *AB* interface. In many cases these wetting transitions are also of a second-order type, but become first order when $N\chi_{AB} > 8$. In the third regime we find what might be called "pseudowetting:" from inspection of the adsorption isotherms it follows that *C* seems to wet the *AB* interface, but with increasing amount of *C* in the system, the wetting layer is suddenly destroyed. The reason for this is clear. Here, the apparent wetting point χ_{AC}^{wet} is close to $\chi_{AC}^{\text{eff,crit}}$, but $\chi_{AB} < \chi_{AC} = \chi_{BC}$, the wetting film is unstable. As a result, while at first Cahn's argument seems to be fulfilled, it eventually fails in this region of the parameter space. © 2001 American Institute of Physics. [DOI: 10.1063/1.1345498]

I. INTRODUCTION

In the field of wetting the subjects of research are related to the development of a new phase at the interface between two other phases. Since wetting occurs in numerous systems and under many conditions, the study of wetting is of great interest for a large variety of applied research topics. One example is the development of new coatings. A coating should, for example, protect a surface against another (wetting) compound. There are also many examples in which two materials should remain in contact with each other, not allowing a third component to intervene. Adhesive tape for instance should not easily be removed by moisture. Recently, it was proposed that wetting also plays an important role in protein organization in cell membranes.¹ Obviously, this is important for the investigation of membranes or protein functions. In the literature there is a special interest for systems which may display second-order-type wetting transitions, alternatively called critical wetting. Systems showing second-order wetting transitions are so attractive from an experimental point of view since uniform layer thicknesses can easily be achieved in such systems. However, in experimental studies, second-order transitions are rarely observed. Recently, the wetting transitions of only three experimental liquid systems have been identified as being critical. Two of

these experimental systems are of interest for petroleum engineering: with increasing temperature both pentane and octane films grow continuously onto the water-vapor interface.^{2,3} The third experimental observation of critical wetting concerned the methanol/nonane system in which methanol wetted the nonane liquid/vapor interface.⁴ In theoretical studies it is possible to investigate wetting characteristics for a large parameter space, for example, for a range of molecular weights, as has been done by Pereira and Wang in Monte Carlo simulations,⁵ by Ragil *et al.* in Cahn-type calculations,⁶ and by Leermakers and Van Eijk in self-consistent-field Scheutjens–Fleer calculations.^{7,8} Ragil's calculations led to the experimental observation of critical wetting by pentane.

The present theoretical study can be viewed as a continuation of the work of Leermakers⁷ and Van Eijk.⁸ In contrast to the previous self-consistent-field wetting studies, our focus is on a mixture of three homopolymers. The solvents are denoted by *A* and *B*, and the wetting component by *C*. The system is chosen as symmetrical as possible: all polymers have the same degree of polymerization ($N_A = N_B = N_C = N$) and the wetting component is equally well soluble in both solvents ($\chi_{AC} = \chi_{BC}$, where χ is the well-known Flory–Huggins parameter). The advantage of using such a symmetrical system is that curvature effects of the macroscopic interface are not present; the interface remains flat. By avoiding curved interfaces many complications like

^{a)}Electronic mail: sonja.engels@fenk.wau.nl

curvature-dependent surface tensions are eliminated, which facilitates the prediction of trends. Moreover, in our self-consistent-field calculations simple flat lattices can be used for noncurved interfaces.

The emphasis is on the wetting transitions occurring in the ternary system by varying the solubility of the wetting component (keeping $\chi_{AC} = \chi_{BC}$) and the mutual miscibility of the solvents χ_{AB} . As a consequence of the variation in the miscibility, the width of the interface which will be wetted changes as well. Our results show that for this simple system there exists a large parameter space for the interaction parameters which give rise to second-order wetting transitions (if the long-range van der Waals contributions are negligible). We also check the occurrence of complete wetting close to the critical point as predicted by Cahn. Cahn's argument takes a special position in the field of wetting as it is the only general statement available to search for wetting transitions. The argument is based on considerations of temperature effects. Here, we study the effect of interaction parameters instead of temperature. We indeed find Cahn wetting, and the associated transitions are of second-order type. If we enter the region where $\chi_{AB} < \chi_{AC} = \chi_{BC}$, Cahn wetting at first instance seems to occur, but real wetting is never found. The *wetting-like* transitions which do occur in the metastable regime of this region can be investigated in small finite systems and are associated with what might be called "pseudowetting," which has unusual behavior. The Cahn wetting argument thus fails for a set of systems. This means that the Cahn argument is not as generally true as claimed in the literature.

In the following, we will first explain which wetting transitions could be expected if the interaction parameters are varied. We, therefore, position Cahn's argument in the context of interaction parameters. We do not review the general aspects of wetting, but refer to Schick,⁹ who introduces wetting transitions in terms of adsorption isotherms and wetting phase diagrams. We then briefly explain those aspects of the self-consistent-field method of Scheutjens and Fleer which are of importance for this study. In the subsequent section the results are presented and discussed, where we distinguish three different regimes in our two-dimensional parameter space spanned by χ_{AB} and $\chi_{AC} = \chi_{BC}$. In the last section the conclusions are summarized.

II. WETTING TRANSITIONS BY χ VARIATION

Cahn's argument states that a wetting transition from partial to complete wetting must take place before the critical temperature T^{crit} is reached.^{10,11} At the critical temperature the phase boundary between two phases ceases to exist and the three-phase system turns into a two-phase system. Cahn's argument is based upon a consideration of the temperature dependence of the surface tensions for systems in which the long-range forces are less important than the short-range forces. Suppose that we have a situation of partial wetting in a solid-liquid-vapor system. According to Young's equation¹² ($\sigma_{sv} = \sigma_{sl} + \sigma_{lv} \cos \alpha$) we then have for the surface tensions: $\sigma_{lv} > \sigma_{sv} - \sigma_{sl}$. The surface tension of the interface which becomes critical (σ_{lv} , in this example system)

decreases more rapidly with $(T^{\text{crit}} - T)$ than the difference between the surface tensions of the noncritical interfaces ($\sigma_{sv} - \sigma_{sl}$) does. Consequently, at a certain moment σ_{lv} will no longer exceed $\sigma_{sv} - \sigma_{sl}$, so that Young's condition for complete wetting by the liquid phase ($\sigma_{sv} = \sigma_{sl} + \sigma_{lv}$) is met. This phenomenological consideration of the temperature dependences does not only apply to the wetting of a solid wall. It is also applicable in the case of three liquids: if the temperature approaches the critical temperature at which phases α and β will become miscible, either α will wet the $\beta\gamma$ interface (if $\sigma_{\alpha\gamma} < \sigma_{\beta\gamma}$) or β will wet the $\alpha\gamma$ interface (if $\sigma_{\alpha\gamma} > \sigma_{\beta\gamma}$).

Cahn's argument does not predict the order of the wetting transition which has to occur before the critical temperature is reached. It only states that the interface will be completely wetted before $T = T^{\text{crit}}$, and this can occur either after prewetting or after a continuous growth of the layer. It has been shown that Cahn's argument can be violated if long-range forces have to be taken into account and if short-range forces favor wetting, but the long-range forces do not.^{13,14} In that case, the wetting phase γ might form a layer at the interface between phases α and β , but this layer will not grow to an infinite thickness as is the case for complete wetting. Its thickness will be bounded by the long-range forces which attract the $\beta\gamma$ interface to the $\alpha\gamma$ interface. The thickness of the wetting layer will, therefore, be comparable to the bulk correlation length so that only at the critical point the layer can grow to macroscopic thicknesses. Thus, instead of $T^{\text{wet}} < T^{\text{crit}}$, as stated by Cahn, long-range forces could lead to $T^{\text{wet}} = T^{\text{crit}}$.

In this study, we assume that the polymers are long enough to describe their wetting behavior by short-range forces only. Pereira and Wang have shown that it followed from numerical calculations that the van der Waals (long-range) model gives similar results to the short-range model if the effective range of the van der Waals interaction is much smaller than the size of the polymer chains.¹⁵ The wetting temperature in one of the experimental observations of a second-order transition was very close to the critical temperature of the nonane-methanol mixture under consideration.⁴ If long-range forces would be important for this mixture, no second-order transition would be found. (The other second-order transitions observed were not close to the critical point,^{2,3} but also in these cases it was assumed by the analysis of the Hamaker constant that the short-range forces became more important than the long-range forces near the wetting temperature).

Temperature is, of course, not the only parameter influencing the surface tensions. The interactions between the components are other examples of surface tension-determining variables. These variables are also experimentally accessible, for example, by varying the concentration of an additional solute.³ The Flory-Huggins interaction parameters χ are the variables of interest in the present study. The effect of a decreasing value for χ is similar to the effect of an increasing temperature: the interface becomes less sharp and the separate phases cannot exist anymore if χ becomes critical. From the Flory-Huggins free-energy expression, it can easily be derived that for a three-component system the criti-

cal χ for two components P and Q depends on the volume fraction of the other component R as

$$\chi_{PQ}^c = \frac{1}{2(1-\phi_R)} \left(\frac{1}{\sqrt{N_P}} + \frac{1}{\sqrt{N_Q}} \right)^2, \quad (1)$$

which reduces for our system to

$$\chi_{PQ}^c = \frac{2}{N(1-\phi_R)}. \quad (2)$$

While the temperature is the only variable in Cahn's argument, the interaction parameters between each pair of components ($\chi_{AB}/\chi_{AC}/\chi_{BC}$) can, in principle, be chosen independently from each other. However, the resulting (triangular) phase composition diagram depends on the combination of all χ parameters. As the temperature influences the mutual miscibilities of all components at once, the value of each χ parameter also changes all miscibilities at once. Thus, each value of $\chi_{AC} = \chi_{BC}$ will have its own critical χ_{AB} . Cahn's argument can, therefore, easily be translated in terms of interaction parameters instead of temperature. Before χ_{AC} becomes critical either the A -rich phase or the C -rich phase will wet the interface between the two other phases depending on the relative values of σ_{AC} and σ_{BC} . If both χ_{AC} and χ_{BC} become critical, the only possible outcome is that the C -rich phase will wet the solvent-rich phases.

Thus, according to Cahn's argument, decreasing the value of χ_{AC} (keeping χ_{BC} equal to χ_{AC}) should give rise to a wetting transition. However, if we consider the *effective* interaction parameter $\chi_{AC}^{\text{eff}} = \chi_{BC}^{\text{eff}}$, it can be seen that this wetting transition should also be found by decreasing the value of χ_{AB} .⁷ By the effective interaction parameter the wetting component is considered as being in contact with just one solvent which combines the properties of both solvent A and solvent B . In first order we can make the simplification of neglecting the volume fraction of C in the solvent-rich phases. The effective interaction parameter can then be written as

$$\chi_{AC}^{\text{eff}} = \chi_{AC} - \chi_{AB} \phi_A^{(B)} (1 - \phi_A^{(B)}). \quad (3)$$

Obviously $\phi_A^{(B)}$, which is the volume fraction of A in the B -rich phase, is dependent on χ_{AB} : the larger the interactions between A and B , the smaller the volume fraction of A in B . If χ_{AB} is sufficiently close to the critical point of A and B , the quantitative relation between $\phi_A^{(B)}$ and χ_{AB} can be derived from the van der Waals theory for liquid/liquid interfaces:¹⁶

$$\phi_A^{(B)} = \frac{1}{2} - \sqrt{\frac{3}{8}(N\chi_{AB} - 2)}. \quad (4)$$

This can be substituted into Eq. (3) and the resulting χ_{AC}^{eff} as function of χ_{AB} is plotted in Fig. 1. It is seen that $\chi_{AC}^{\text{eff}} < \chi_{AC}$ and that χ_{AC}^{eff} decreases with decreasing χ_{AB} . This means that if we have a certain combination of χ_{AB} and $\chi_{AC} > \chi_{AC}^{\text{crit}}$ giving rise to partial wetting, the effective interactions χ_{AC}^{eff} can become equal to χ_{AC}^{crit} with constant $\chi_{AC} = \chi_{BC}$ and decreasing χ_{AB} , while χ_{AB} remains noncritical. Thus, we can expect the Cahn-type wetting transition to occur also by decreasing the value of χ_{AB} instead of decreasing χ_{AC} . As a consequence, the larger the value for χ_{AC} , the

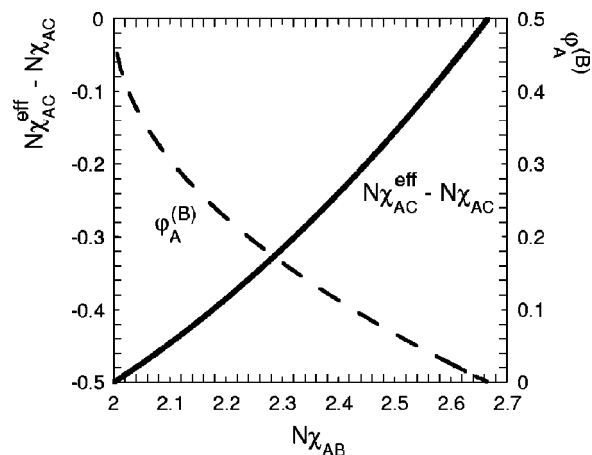


FIG. 1. Effective interaction parameter $N\chi_{AC}^{\text{eff}}$ ($=N\chi_{BC}^{\text{eff}}$) as function of the real $N\chi_{AB}$. For small χ_{AB} the effective interaction between the wetting component and the solvents can already be close to the critical value χ_{AC}^{crit} if the real value of χ_{AC} is still relatively far from χ_{AC}^{crit} . The diagram also shows the volume fraction $\phi_A^{(B)}$ of component A in the B -rich solvent phase as function of $N\chi_{AB}$.

smaller the value for χ_{AB} for which χ_{AC}^{eff} equals χ_{AC}^{crit} . From all of this, it still remains impossible to predict the conditions, i.e., the exact values of the interaction parameters, for Cahn-type wetting transitions. It is only known that their values should be such that χ_{AC}^{eff} is sufficiently close to χ_{AC}^{crit} . It should be emphasized again that Eq. (4) and Fig. 1 can only be used as indications since they are only directly applicable for systems in which $\chi_{AB} \approx \chi_{AB}^{\text{crit}}$ and $\chi_{AC} = \chi_{BC} \gg \chi_{AC}^{\text{crit}} = \chi_{BC}^{\text{crit}}$, so that the volume fractions of C in A and B are negligible. Therefore, we use Eq. (4) only to indicate the trends which could be expected. In the self-consistent-field calculations, performed to create the adsorption isotherms, we do not neglect the amount of C in the solvents.

An additional type of wetting transitions can be expected to occur. The Cahn-type wetting transition from partial to complete wetting occurs for decreasing χ_{AB} . If, however, χ_{AB} is increased, the polymeric solvent A -solvent B interactions become more and more unfavorable. (Note that an increasing χ_{AB} is not accompanied by a proportional increase in σ_{AB} , since χ_{AB} only concerns the enthalpic effects and σ_{AB} also has entropic contributions). A polymer film between the solvents can help to avoid these unfavorable contacts. Indeed, this type of wetting transitions has been found for a system of two monomeric solvents wetted by a polymer.⁷

Consequently, it is possible to have at a fixed value for $\chi_{AC} = \chi_{BC}$ a window of partial wetting in terms of χ_{AB} . Both with increasing and decreasing χ_{AB} a wetting transition occurs.

III. SF SCF IN WETTING STUDY

To study the wetting characteristics of the homopolymers, the lattice mean-field method developed by Scheutjens and Fler¹⁷⁻¹⁹ is applied. The Scheutjens-Fler self-consistent-field (SF SCF) method provides an easy way to calculate volume fraction profiles for (multicomponent) systems at equilibrium and their corresponding partition func-

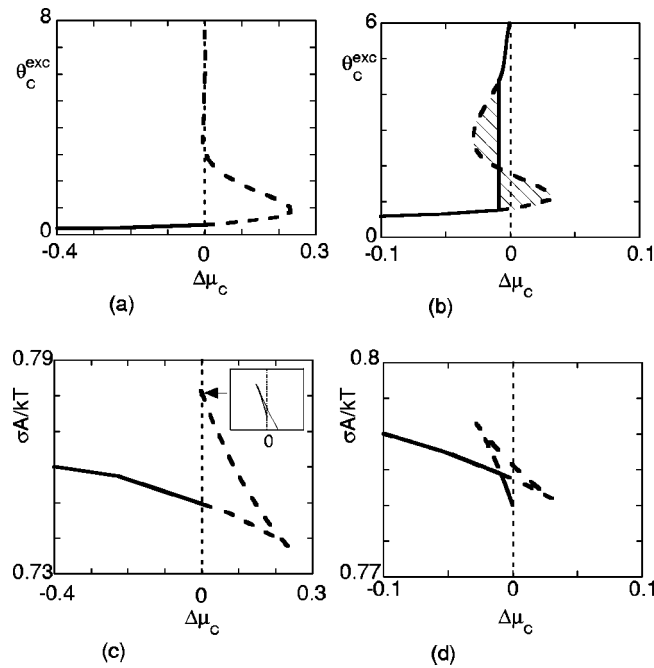


FIG. 2. Typical examples of adsorption isotherms following from mean-field calculations. The dashed lines represent the metastable states, not found in experiments. Mean-field isotherms for partial wetting are like the isotherm in (a). They can simply be cut off at the coexistence line ($\Delta\mu_C = 0$). The corresponding surface tension, plotted in (c), decreases continuously until coexistence is reached from $\Delta\mu_C < 0$. Mean-field isotherms with prewetting steps are similar to the isotherm in (b). One way to find the $\Delta\mu_C$ corresponding with the prewetting step is to apply the equal-area method. Another way is to use the corresponding plot of the surface tension as in (d), where $\Delta\mu_C(\text{kink}) = \Delta\mu_C$ (prewetting step).

tions. For our noncurved interfaces we can use a simple one-dimensional lattice. Partial and complete wetting are distinguished by constructing adsorption isotherms: the excess amount of C at the AB interface is plotted versus the chemical potential of the wetting component. Both quantities can be calculated from the volume fraction profiles:

$$\theta_C^{\text{exc}} = \sum_{z=1}^M [\phi_C(z) - \phi_C^{\text{bulk}}], \quad (5)$$

$$\frac{\mu_C - \mu_C^{\text{bulk}}}{kT} = \ln \phi_C^{\text{bulk}} - \frac{N}{2} \sum_{XY} (\phi_X^{\text{bulk}} - \delta_{CX}) \chi_{XY} \times (\phi_Y^{\text{bulk}} - \delta_{CY}). \quad (6)$$

δ_{CX} is the Kronecker delta which equals one for $X=C$ and zero otherwise. In the following we denote the total amount of C in the system by θ_C .

As a result of the mean-field method, the adsorption isotherms show van der Waals loops indicating metastable states. For example, Fig. 2(a) shows a typical isotherm for partial wetting as calculated by the SF method. This isotherm could simply be cut off at the coexistence line ($\Delta\mu_C = 0$, where $\Delta\mu_C$ is the difference between the actual chemical potential of the wetting component and its value at coexistence). Isotherms which represent prewetting steps have loops already before coexistence is reached, see Fig. 2(b). The prewetting step can be located by an equal-area method as indicated in Fig. 2(b), but it is more convenient to use the

surface free energy σ as a function of $\Delta\mu_C$, see, for example, Fig. 2(d). For our system σ can be calculated by the equilibrium volume fraction profiles as

$$\frac{\sigma A}{kT} = \sum_{z,X} \phi_X(z) \ln G_X(z) + \frac{1}{2} \sum_{z,X,Y} \chi_{XY} [\phi_X(z) \langle \phi_Y(z) \rangle - 2\phi_X(z)\phi_Y^{\text{bulk}} + \phi_X^{\text{bulk}}\phi_Y^{\text{bulk}}]. \quad (7)$$

In this equation $G_X(z) = \exp\{-u_X(z)/kT\}$, where $u_X(z)$ is the potential felt by segments of type X ; the angular brackets represent a three-layer average.

σ is higher for the metastable state than for the equilibrium state. Figures 2(c) and 2(d) show examples of curves for σ as function of $\Delta\mu_C$. In the partial wetting regime, there is no intersection for $\Delta\mu_C \leq 0$. The surface tension decreases continuously until coexistence is reached as in Fig. 2(c). In case of prewetting, there is a discontinuity in the first derivative of the surface tension as a function of $\Delta\mu_C$. This discontinuity occurs if the curve for the stable state intersects with that of the metastable state (for $\Delta\mu_C \leq 0$), as in Fig. 2(d). It means that there is a transition from one stable state (microscopically thick film) to another stable state (mesoscopically thick film). Thus, the prewetting step occurs at $\Delta\mu_C$ corresponding with this intersection point. The critical prewetting point is that T or χ for which the kink disappears because the loop in Fig. 2(d) shrinks to a point.

IV. RESULTS AND DISCUSSION

The calculations are performed for two different chain lengths: either all polymers in the system have length $N=10$, or they all have $N=100$. Since the results for both values of N are nearly identical if the values for the interaction parameters were changed as to keep $N\chi$ constant, we can generally write the results in terms of $N\chi_{AC} = N\chi_{BC}$ and $N\chi_{AB}$. However, the analyses around critical points are carried out for systems in which $N=10$ only, since the calculations were very time consuming and $N=100$ would even require much larger systems. Therefore, the results for systems near critical points are presented in terms of χ and it has to be remembered that for these results N equals 10.

As has been outlined in the discussion of the effective interaction parameter, it is not possible to predict *a priori* the exact values of the interaction parameters for which Cahn-type wetting transitions occur. What we can predict from the effective interaction parameter is that Cahn-type transitions occur for decreasing $N\chi_{AB}$. Detailed numerical analysis around critical points must be done carefully and a large number of lattice layers (i.e., a large system) is needed, leading to time-consuming trials to find the wetting transitions.

If we consider the two-dimensional parameter space given by the interaction parameters χ_{AB} and $\chi_{AC} = \chi_{BC}$, we find three different regimes, each with their own characteristics for the wetting transitions. In one of these regimes (where $\chi^{\text{wet}} \approx \chi^{\text{crit}}$ and $\chi_{AB}^{\text{wet}} > \chi_{AC}^{\text{wet}} = \chi_{BC}^{\text{wet}}$) Cahn-type wetting transitions are found. Another regime ($\chi^{\text{wet}} \gg \chi^{\text{crit}}$ and $\chi_{AB}^{\text{wet}} > \chi_{AC}^{\text{wet}} = \chi_{BC}^{\text{wet}}$) shows wetting transitions which are not associated with any critical state and which must, therefore, be *additional* to Cahn transitions. In the third regime (χ^{wet}

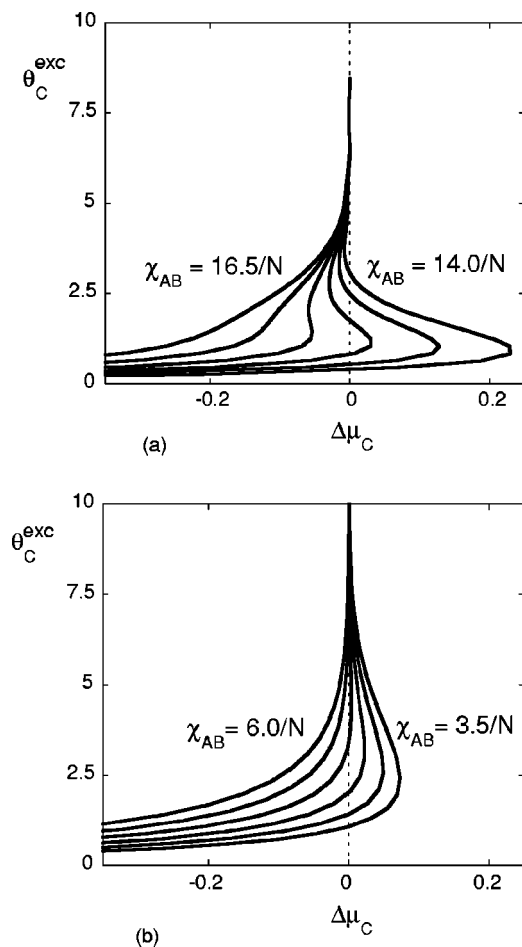


FIG. 3. Examples of the adsorption isotherms obtained for $\chi_{AC} = \chi_{BC} = 7/N$ and $\chi_{AB} = \chi_{BC} = 3/N$, respectively. Diagram (a) is a typical example of a first-order wetting transition. Diagram (b) presents a second-order wetting transition. The wetting transitions for these polymer-solvent interactions are induced by increasing the value for χ_{AB} . (In these pictures, the isotherms are given for χ_{AB} incremented by $0.5/N$.)

$\approx \chi^{\text{crit}}$ and $\chi_{AB}^{\text{wet}} < \chi_{AC}^{\text{wet}} = \chi_{BC}^{\text{wet}}$) unusual “hidden pseudowetting transitions” occur instead of Cahn’s transitions and these transitions are thus violating Cahn’s argument. We will discuss these three regimes separately.

A. First regime: Additional to Cahn

These results concern a type of wetting transition which is additional to Cahn’s wetting transition. In Fig. 3, two collections of adsorption isotherms are presented as calculated by SF SCF; for two values of $N\chi_{AC} = N\chi_{BC}$ the isotherms were calculated for a range of $N\chi_{AB}$ values. Cahn’s wetting transition is expected to occur if the interface between the solvents *A* and *B* becomes less sharp, i.e., if χ_{AB} is decreased. However, Fig. 3 shows that we find wetting transitions by increasing χ_{AB} (at constant χ_{AC}). This kind of wetting transitions has also been found for a monomer/monomer interface wetted by a polymer.⁷ Wetting for increasing χ_{AB} can be explained by the fact that the developing layer of *C* at the interface between *A* and *B* screens the *A/B* interactions, which become more and more unfavorable with increasing χ_{AB} . From Fig. 3 it can also be seen that it is possible to find either first- or second-order wetting transitions. Figure 3(a)

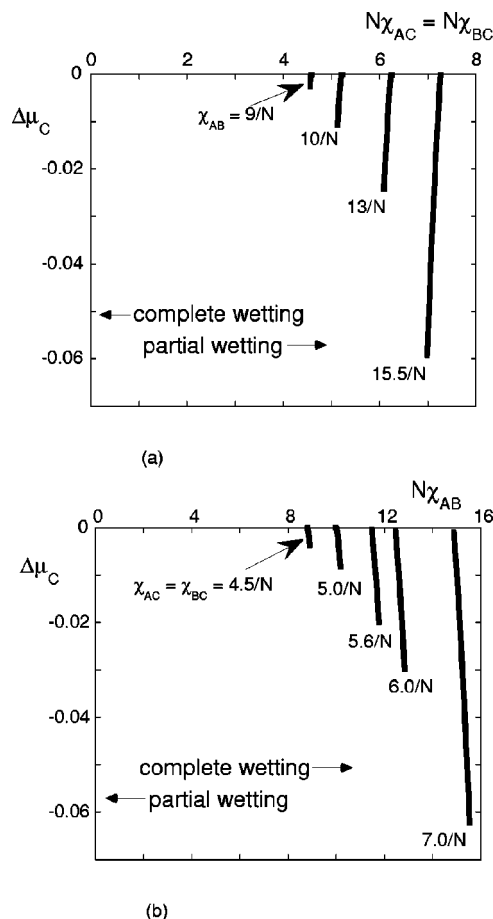


FIG. 4. Phase diagrams showing the prewetting lines as a function of χ_{AC} (a) and as a function of χ_{AB} (b). Extrapolating the line connecting the critical prewetting points predicts a tricritical point for $\chi_{AC} = \chi_{BC} \approx 4.3/N$ and $\chi_{AB} \approx 8/N$. For smaller values of interaction parameters, second-order wetting transitions occur.

presents a family of adsorption isotherms for $\chi_{AC} = \chi_{BC} = 7.0/N$, which proves the presence of first-order wetting transitions. In Fig. 3(b) another set of adsorption isotherms for $\chi_{AC} = \chi_{BC} = 3.0/N$ clearly shows a second-order character of the wetting transition. For several combinations of interaction parameters the prewetting lines have been localized by the μ dependence of the surface free energy. The prewetting lines are shown in the wetting phase diagrams collected in Fig. 4. Usually, the temperature T or $T - T^{\text{crit}}$ is used as control parameter instead of χ . Since $\chi \propto 1/T$, the relative positions of wetting point, critical prewetting point, and critical point are reversed with respect to standard wetting phase diagrams,^{9,20} where $T^{\text{wet}} < T^{\text{pr}} < T^{\text{crit}}$. In Fig. 4(a) the control parameter is $N\chi_{AC} = N\chi_{BC}$. The wetting transition from partial to complete wetting occurs with decreasing control parameter; component *C* will wet the *A/B* interface if the repulsive interactions between the wetting component and the solvents is sufficiently low. In Fig. 4(b) the control parameter is $N\chi_{AB}$, which (as already shown in Fig. 3) has to be increased to find a wetting transition. From the steepness of the prewetting lines it can be concluded that small variations in the value of the interaction parameters have relatively large effects. Focusing on the region near coexistence (not shown), it appears that the prewetting lines approach the coexistence

line tangentially, as should be expected.²⁰ It is seen that the prewetting lines will disappear if both $\chi_{AC} = \chi_{BC}$ and χ_{AB} are sufficiently low, namely, for $\chi_{AC} = \chi_{BC} \approx 4/N$ and $\chi_{AB} \approx 8/N$. This combination of χ -values marks the tricritical point, at which the wetting transitions change from first order to second order. Note that for binary systems the critical χ equals $2/N$, which is far from our tricritical point. Thus, in our system second-order transitions occur for a relatively large range of χ values. Replacing our polymeric solvents by monomeric solvents would result in a system showing the same kind of wetting transitions additional to Cahn wetting, but they are mainly of first order.⁷

If one would not consider the effective interaction χ_{AC}^{eff} , but only the interaction χ_{AC} itself, one could incorrectly conclude from the results above, especially from the upper diagram in Fig. 4, that Cahn's argument has been verified: complete wetting occurs for smaller χ_{AC} , partial wetting for larger χ_{AC} . However, from the consideration of the effective interaction, it is expected that complete wetting would also occur for smaller χ_{AB} and partial for larger χ_{AB} . The lower diagram in Fig. 4 shows the contrary. Thus, these wetting transitions found for sharp interfaces between the solvents (i.e., large χ_{AB}) must be additional to Cahn-type transitions.

B. Second regime: Cahn-type transitions

We now discuss the wetting transitions found in our system near the critical points. As said before, each value of χ_{AB} will give rise to its own value for χ_{AC}^{crit} . The easiest way to find an indication for a combination of critical interaction parameters is to calculate the binodals of a system in which $\chi = \chi_{AB} = \chi_{AC} = \chi_{BC}$. We then have only one parameter which controls the existence of three-phase coexistence. The three-phase region in ternary phase diagrams arises from overlap of the binodals. The critical χ is that χ for which the three-phase region just disappears, thus for which the binodals do not overlap any more but where they are just tangent to each other. Because of the symmetry in a system with $\chi_{AB} = \chi_{AC} = \chi_{BC} = \chi$ and $N_A = N_B = N_C = N$, the binodals are then also tangent to the equimolar lines $\phi_A = \phi_B$, $\phi_B = \phi_C$, and $\phi_A = \phi_C$ in the ternary phase diagram. If we know that the three-phase region just disappears for χ^{crit} , we can expect that in a system with $\chi_{AC} = \chi_{BC} = \chi^{\text{crit}}$ and $\chi_{AB} > \chi^{\text{crit}}$, the mixtures A/C and B/C will become critical if χ_{AB} is decreased, but according to Cahn, C will first wet the A/B interface.

The binodals are calculated numerically by the generalized Flory–Huggins free-energy density expression, which coincides with the Scheutjens–Fleer result for homogeneous systems and which for $\chi = \chi_{AB} = \chi_{AC} = \chi_{BC}$ reads

$$f_{FH} = \frac{\phi_A}{N} \ln \phi_A + \frac{1 - \phi_A - \phi_C}{N} \ln (1 - \phi_A - \phi_C) + \frac{\phi_C}{N} \ln \phi_C + \chi \phi_A (1 - \phi_A - \phi_C) + \chi \phi_C (1 - \phi_A - \phi_C) + \chi \phi_A \phi_C. \quad (8)$$

Figure 5(a) shows the results for different values of χ . (Only binodals of the mixture A/B are shown, but Fig. 5(a) applies

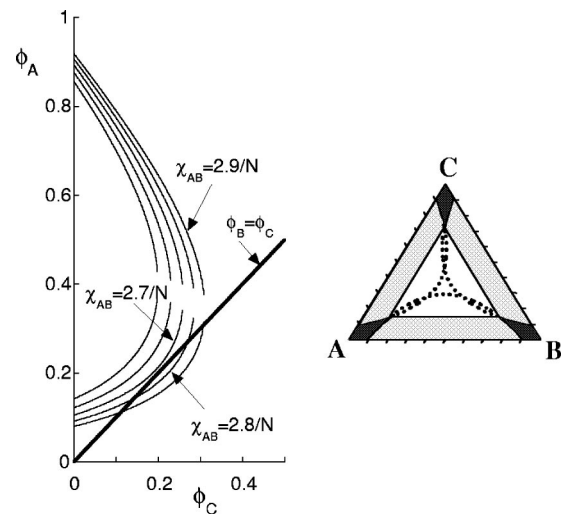


FIG. 5. Binodals for a system with $N_A = N_B = N_C = N$ and $\chi_{AB} = \chi_{AC} = \chi_{BC} = \chi$, calculated by minimization of the Flory–Huggins free energy. If χ_{AB} is close to $2.7/N$, the binodal will be tangent to the line $\phi_B = \phi_C$. The ternary phase composition diagram for $\chi = 2.8/N$ shows that the three-phase region (white triangle) results from overlap of the (dotted) binodals. The dark areas in this diagram are the one-phase regions, the light-gray areas are two-phase regions.

for mixtures A/C and B/C if all subscripts in Fig. 5(a) are changed accordingly). If χ exceeds the value of about $2.7/N$, the binodals overlap and three phases can coexist. If χ is smaller than about $2.7/N$, the ternary phase diagram has only one- and two-phase regions bounded by three separate binodals. Choosing for the interaction parameters $\chi_{AC} = \chi_{BC} \approx 2.7/N$ should give rise to a wetting transition according to Cahn's argument with complete wetting for $\chi_{AB} < \chi_{AB}^{\text{wet}}$. Indeed, this is found, as shown in Fig. 6. Note that for a clearer picture, the isotherms are not plotted versus $\Delta\mu_C$ but versus μ_C . In Fig. 6 a set of adsorption isotherms is given for

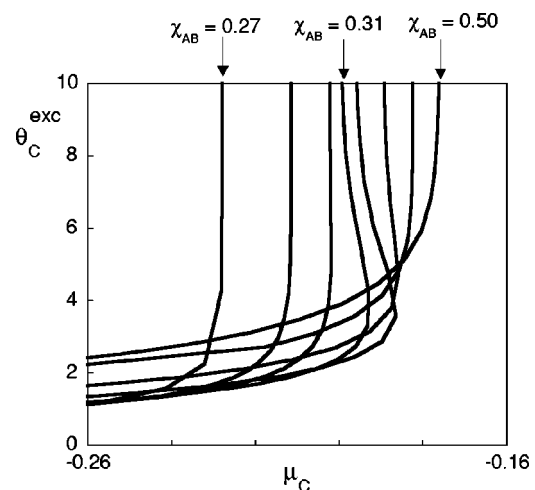


FIG. 6. Adsorption isotherms for $N_A = N_B = N_C = 10$ and $\chi_{AC} = \chi_{BC} = 0.27$. From left to right the adsorption isotherms have χ_{AB} values of 0.27, 0.28, 0.29, 0.31, 0.35, 0.40, 0.45, and 0.50. Note that θ_C^{exc} is plotted vs μ_C instead of $\Delta\mu$. It is easy to see that the system is in the partial wetting regime for $\chi_{AB} = 0.35$, whereas it is in the complete wetting regime both for $\chi_{AB} = 0.27$ and $\chi_{AB} = 0.50$. Both wetting transitions are of a second-order type.

TABLE I. If $\chi_{AC}=\chi_{BC}$ is increased, Cahn's (second-order) wetting transitions are found for decreasing χ_{AB} .

$\chi_{AC}=\chi_{BC}$	χ_{AB}^{wet}
0.270	0.287
0.274	0.282
0.277	0.279

$\chi_{AC}=\chi_{BC}=0.27$ and different values of χ_{AB} (note that $N=10$). If χ_{AB} equals 0.35, component C will partially wet the A/B interface. Increasing χ_{AB} up to $\chi_{AB}^{wet}\approx 0.40$ results in a second-order wetting transition which is similar to the wetting transitions in the first regime presented above and in Fig. 4(b). But another wetting transition is found in agreement with Cahn's argument by decreasing χ_{AB} from 0.35. This wetting transition occurred for $\chi_{AB}^{wet}\approx 0.287$. It is also seen that Cahn's wetting transition is of second order. Summarizing: a window of partial wetting exists for $0.287 < \chi_{AB} < 0.40$.

If now the value of χ_{AC} is increased, the critical value for χ_{AB} can be expected to decrease. This can be understood by Fig. 1: the larger $\chi_{AC}=\chi_{BC}$, the larger the difference between $\chi_{AC}=\chi_{BC}$ and $\chi_{AC}^{crit}=\chi_{BC}^{crit}$. Therefore, if $\chi_{AC}=\chi_{BC}$ is increased, the difference between $\chi_{AC}=\chi_{BC}$ and $\chi_{AC}^{eff}=\chi_{BC}^{eff}$ must also be increased to achieve $\chi_{AC}^{eff}=\chi_{BC}^{eff}$ ($=\chi_{AC}^{crit}=\chi_{BC}^{crit}$). According to Fig. 1, χ_{AB} must then be smaller. Indeed, as shown in Table I, we find decreasing values for χ_{AB}^{wet} if $\chi_{AC}=\chi_{BC}$ is increased.

C. Third regime: Instead of Cahn transitions (pseudowetting)

From Table I it is seen that Cahn's wetting transitions are found for situations in which all interaction parameters have almost the same values, but still $\chi_{AB}^{wet} > \chi_{AC}^{wet} = \chi_{BC}^{wet}$. As mentioned before, if we increase $\chi_{AC}=\chi_{BC}$, Cahn's wetting transition is expected to be found for decreasing χ_{AB} . This means that at some point the value of χ_{AB}^{wet} would equal that of $\chi_{AC}^{wet}=\chi_{BC}^{wet}$. If we imagine a system in which $\chi_{AB}=\chi_{AC}=\chi_{BC}$, all components may act as the wetting component, because all interfaces have the same surface tensions (see Fig. 7). However, due to the way in which we perform our calculations, we always pre-assume C as the wetting compo-

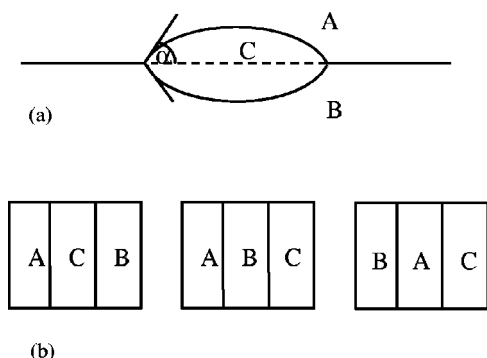


FIG. 7. If $\chi_{AB}=\chi_{AC}=\chi_{BC}$ and $\theta_A=\theta_B=\theta_C$ the system can choose between different equilibrium states which will have the same energy: the contact angle α must equal 60° (a), or $\sigma_{AB}=\sigma_{AC}=\sigma_{BC}=0$: α can take every value, each of the components may act as wetting component (b).

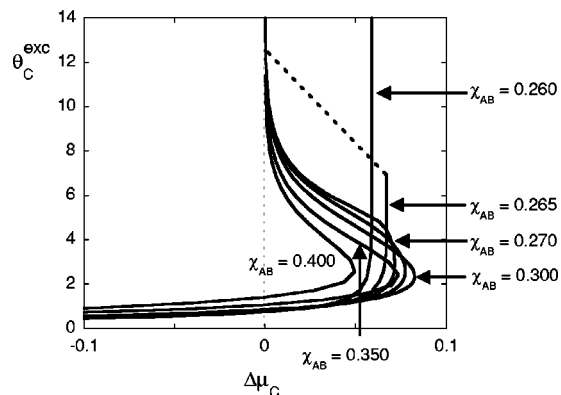


FIG. 8. Adsorption isotherms for $N_A=N_B=N_C=10$ and $\chi_{AC}=\chi_{BC}=0.30$. As long as χ_{AB} is larger than $\chi_{AC}=\chi_{BC}$, the isotherms show regular partial wetting behavior. If χ_{AB} becomes smaller, no Cahn wetting, but pseudowetting, is found. Component C seems to wet the interface in the metastable region ($\Delta\mu_C > 0$), but suddenly the system finds its state of coexistence. The smaller χ_{AB} , the longer the pseudowetting persists. Also, the isotherm $\chi_{AB}=0.260$ will jump to $\Delta\mu_C=0$, but this occurs for values of $\theta_C^{exc} > 14$. The transition from pseudopartial to pseudowetting is of a second-order type.

nent. We start with an "empty" AB interface and use this as an initial guess for the self-consistent-field calculation for a system in which C is the minority component. With this initial guess, C will accumulate at the interface. Then, the total amount of C in the system is incremented by small steps, each time using the previous step as the initial guess.

If we cross the line $\chi_{AB}=\chi_{AC}=\chi_{BC}$ in the two-dimensional parameter space, we arrive in the third regime where $\chi_{AB} < \chi_{AC}=\chi_{BC}$. Here, unexpected wetting-like transitions are observed. In this regime the surface energy of the AB interface is lower than that of either the AC or the BC interface. Complete wetting by component C can, therefore, not be expected although the critical point is approached. Thus, for macroscopic systems, it is obvious that Cahn's argument is violated in this regime. As long as C would not wet the AB interface completely, it is energetically more favorable to have a droplet of C at the interface than to have a droplet of C either in the A or the B -rich phases. However, in our numerical calculations we have access to the metastable states, due to the fact that we (only) do calculations on finite-sized systems. It turns out that we are able to see what could happen if wetting experiments are carefully performed in microscopically small and closed systems: at first instance the systems seem to act in agreement with Cahn's argument, but eventually the argument also fails in these microscopic systems.

Figure 8 shows a collection of isotherms for the case $\chi_{AB}^{wet} < \chi_{AC}^{wet} = \chi_{BC}^{wet}$. In this example $\chi_{AC}=\chi_{BC}=0.30$ (and still $N=10$). Decreasing the value for χ_{AB} down to 0.30 results in regular isotherms for partial wetting. The excess amount θ_C^{exc} at coexistence is still decreasing: the system does not show any approach to complete wetting. If we decrease χ_{AB} further as to become smaller than $\chi_{AC}=\chi_{BC}$, the characteristics of the isotherms change. θ_C^{exc} at coexistence ($\Delta\mu_C=0$) still decreases, but unexpectedly a vertical part in the isotherm is growing in the metastable region, i.e., where

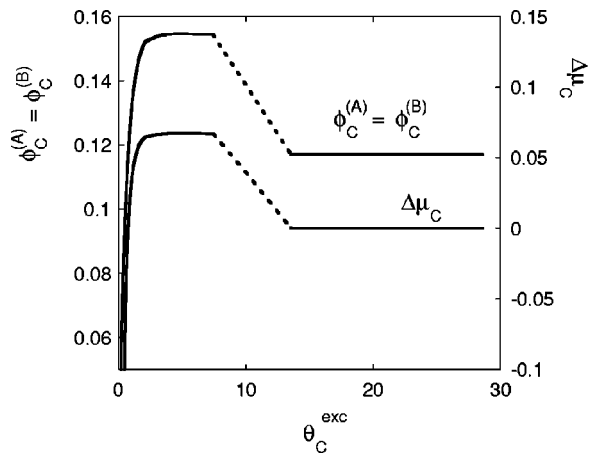


FIG. 9. Volume fractions of C in solvents A and B as a function of the excess amount of C at the interface and the (rotated) adsorption isotherm for $\chi_{AC}=\chi_{BC}=0.30$, $\chi_{AB}=0.265$, and $N=10$. During pseudowetting, $\phi_C^{(A)}$ and $\phi_C^{(B)}$ are constant, but the solvents are supersaturated with C , since at coexistence $\phi_C^{(A)}=\phi_C^{(B)}\approx 0.12$.

$\Delta\mu_C > 0$. Consider, for example, the isotherm for $\chi_{AB}=0.265$ in Fig. 8. With increasing θ_C , the isotherm first resembles isotherms of complete wetting: θ_C^{exc} increases without changing the chemical potential. However, we should call this ‘‘pseudowetting’’ instead of complete wetting, since if θ_C in the system has sufficiently increased, the volume fractions of C in the A - and B -rich phases suddenly decrease, and θ_C^{exc} increases discontinuously. This is reflected, of course, by a sudden decrease in the chemical potential μ_C and $\Delta\mu_C \rightarrow 0$. Associated with this, there is a very pronounced change in the volume fraction profile of the C component at the AB interface (not shown). The jump from pseudowetting back to the coexistence line is presented by the dashed line in Fig. 8. (It is a special task to find the exact shape of this part of the isotherm.) For the isotherm with $\chi_{AB}=0.265$, the value of χ_{AB} is smaller than that of $\chi_{AC}=\chi_{BC}$, thus the pseudowetting must be metastable. The smaller the value of χ_{AB} , the longer the vertical part in the isotherm, i.e., the more pronounced the pseudowetting: compare the isotherms for $\chi_{AB}=0.265$ and $\chi_{AB}=0.260$. Before the system changes from regular partial wetting to pseudowetting, we see ‘‘pseudopartial wetting’’ as presented by the isotherm for $\chi_{AB}=0.27$ in Fig. 8. This isotherm differs from the regular partial wetting isotherms, since it is less curved at maximum μ_C .

This wetting-like behavior can be explained by the fact that our microscopic systems can maintain a situation of supersaturation as long as the amount of C is not sufficient to form a third (C -rich) phase in coexistence with the A - and B -rich phases. In Fig. 9 it is shown how the volume fraction of C in the solvents A and B ($\phi_C^{(A)}=\phi_C^{(B)}$) develops with increasing θ_C^{exc} . At coexistence ($\Delta\mu_C=0$), the solvents A and B are saturated with C . If $\Delta\mu_C > 0$, the solvents are supersaturated. If we enter the region where $\Delta\mu_C > 0$ by increasing the total amount of C in the system, first the volume fractions of C in the supersaturated solvents ($\phi_C^{(A)}=\phi_C^{(B)}$) continue to increase, but at a certain point of supersaturation, $\phi_C^{(A)}$ and $\phi_C^{(B)}$ do not change any more and $\Delta\mu_C$ has a con-

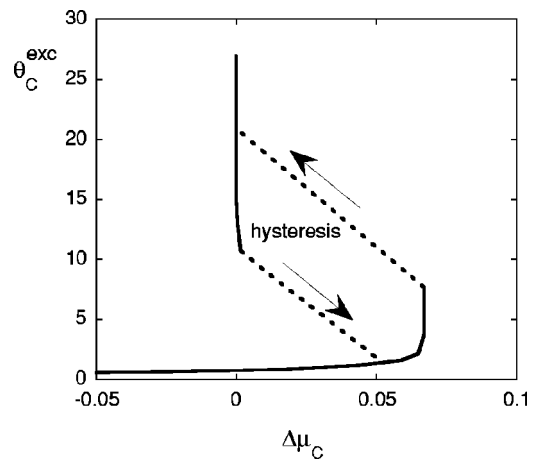


FIG. 10. Pseudowetting is related to supersaturation. No pseudowetting is found if the adsorption isotherm is obtained by decreasing the total amount of C in the system ($\chi_{AC}=\chi_{BC}=0.30$, $\chi_{AB}=0.265$, $N=10$).

stant (positive) value. From that moment, the excess amount of C at the AB interface (θ_C^{exc}) still increases if more C is added to the system. This is the moment where the isotherms behave as if wetting occurs. Suddenly, sufficient C has been added to the system to form three phases at coexistence, and the wetting-like behavior turns out to be pseudowetting. Since the supersaturated system is in a metastable state, it can be expected that hysteresis will occur if now the amount of C in the system is decreased. This has indeed been found, as shown in Fig. 10.

We can conclude that we have hidden (second-order) wetting-like transitions for systems in which C is the wetting component while $\chi_{AB} < \chi_{AC}=\chi_{BC}$. At these hidden transitions the system changes from pseudopartial to pseudowetting. These wetting transitions can only be found if one is able to keep the solvents supersaturated with wetting component C . This could happen in microscopic closed systems. However, since we are very close to the critical point, where molecular fluctuations have relatively large effects, this regime is difficult to explore.

If χ_{AC} is chosen too large, no hidden wetting transition is found anymore. For large χ_{AC} , the interaction parameter χ_{AB} approaches its critical value faster than its value for which χ_{AC}^{eff} equals $\chi_{AC}^{\text{crit}}=2/N$. We find, for example, if $\chi_{AC}=0.50$ that (pseudo) partial wetting occurs for $0.23 < \chi_{AB} < 1.0$. The wetting transition for $\chi_{AB}=1.0$ has already been presented in Fig. 4(b). If χ_{AB} equals 0.23, the wetting component accumulates at the A/B interface for small amounts of C , but before the amount of C is large enough to reach three-phase coexistence, the A/B interface disappears. This occurs if ϕ_C obeys Eq. (2) for $\chi_{AB}=0.23$.

D. Combination of results

Since we had two control parameters in this study ($N\chi_{AB}$ and $N\chi_{AC}=N\chi_{BC}$), we can combine all wetting characteristics of our system in a two-dimensional plot with each of the control parameters along the axes, as shown in Fig. 11. The solid line in this picture represents the combinations of interaction parameters which give rise to first- or

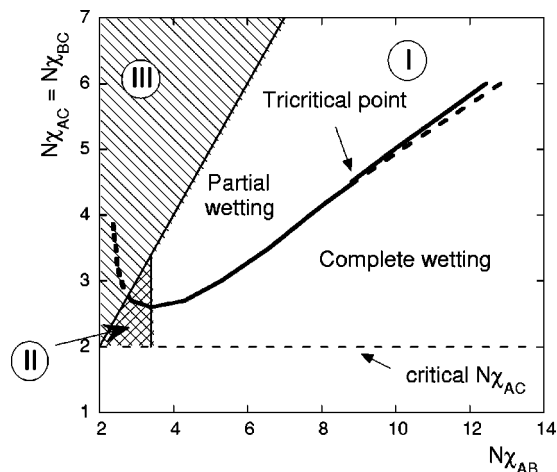


FIG. 11. The wetting behavior for all combinations of χ_{AB} and χ_{AC} ($=\chi_{BC}$) collected in one figure. Three regimes can be distinguished in this parameter space. Region I ($\chi_{AC}^{\text{wet}} \gg \chi_{AC}^{\text{eff,crit}}$ and $\chi_{AB} > \chi_{AC} = \chi_{BC}$) contains wetting transitions which are not associated with any critical point. The dashed line in region I indicates the critical prewetting points, which are associated with first-order wetting transitions. The critical prewetting points are absent for smaller values of interaction parameters, which means that for these values second-order transitions are found. Region II ($\chi_{AC}^{\text{wet}} \approx \chi_{AC}^{\text{eff,crit}}$ and $\chi_{AB} > \chi_{AC} = \chi_{BC}$) includes Cahn-type wetting transitions which occur since $\chi_{AC}^{\text{eff}} \approx \chi_{AC}^{\text{crit}}$. In region III ($\chi_{AC}^{\text{wet}} \approx \chi_{AC}^{\text{eff,crit}}$ and $\chi_{AB} < \chi_{AC} = \chi_{BC}$) pseudowetting transitions are found. Second-order transitions are found for a large parameter space. All Cahn-type wetting transitions and pseudowetting transitions are of a second-order type.

second-order wetting transitions. The critical prewetting points, which are associated with the first-order wetting transitions, are represented by the dashed line. It is seen that for first-order transitions both $N\chi_{AB}$ and $N\chi_{AC} = N\chi_{BC}$ must be very large. For smaller values of the control parameters second-order transitions occur. For points above the wetting line, in Fig. 11 partial wetting is found, for points under the lines complete wetting or a phase transition to a one-phase system is found. The picture clearly indicates that indeed a transition to complete wetting can be found both for decreasing and increasing $N\chi_{AB}$. The wetting transitions at the right-hand side of the diagram (region I) are transitions to avoid unfavorable contacts between the *A*- and the *B*-rich phases. This type of transition is also found in a system with monomer solvents.⁷ The lower part of the left-hand side of the diagram (region II) is associated with Cahn-type wetting transitions, because they occur close to the critical point of the mixtures *A/C* and *B/C*. Cahn-type transitions must exist for all three-phase systems. (The wetting transitions in the left part of region I may also be due to Cahn wetting, since the wetting occurs not too far before the value of $\chi_{AC} = \chi_{BC}$ has diminished to its critical value. Therefore, the boundary between regions I and II should not be considered sharp.) Region III contains the hidden wetting transitions from pseudopartial wetting to pseudowetting which occur instead of the Cahn-type transitions. Interestingly, this means a failure of the Cahn argument for parameters corresponding to region III. Note that in our systems the long-ranged van der Waals interactions are not included. Therefore, the failure of the Cahn argument is of special interest. Our results show that the Cahn argument can not be as general as

TABLE II. Effects of the relative size of interaction parameters on the contact angle.

$\chi_{AB} > \chi_{AC} = \chi_{BC}$	$0^\circ \leq \alpha < 60^\circ$
$\chi_{AB} = \chi_{AC} = \chi_{BC}$	$\alpha = 60^\circ$ or $\sigma_{AB} = \sigma_{AC} = \sigma_{BC} = 0$
$\chi_{AB} < \chi_{AC} = \chi_{BC}$	$60^\circ < \alpha \leq 90^\circ$

claimed in the literature. The pseudowetting transitions lie on a line that smoothly continues the line representing the Cahn transitions. These hidden wetting transitions can, in principle, occur in other systems as well, but it is more difficult to predict when they occur if the system is less symmetrical. The fact that they are not found before, for example, by Leermakers, Dorrepaal, and Besseling in their study of interfaces between two monomeric components,⁷ might be due to the part of parameter space which had been investigated.

These results are in agreement with simple considerations which we collect for convenience in Table II, concerning the relative size of the interaction parameters. As long as $\chi_{AB} > \chi_{AC} = \chi_{BC}$, it may be favorable to form a macroscopic layer of *C* to avoid the existence of an energetically unfavorable *AB* interface, and complete wetting may occur. If $\chi_{AB} < \chi_{AC} = \chi_{BC}$, it is always unfavorable to create new *AC* and *BC* interfaces. Complete wetting will not occur. Still, component *C* will adsorb at the *AB* interface (as long as three phases may coexist) to compensate the newly formed interfaces by eliminating *AB* contacts. The contact angle will not exceed 90° , otherwise less *AB* contacts are eliminated than possible. If all interaction parameters are equal ($\chi_{AB} = \chi_{AC} = \chi_{BC}$), none of the components *A*, *B*, or *C* is preferred as the wetting component: all interfaces *AB*, *AC*, and *BC* have the same surface energies. As a consequence of Young's equation, either the contact angle α will be equal to 60° or all surface tensions will equal zero. The first possibility means that partial wetting will occur, but the second possibility allows every possible behavior between complete wetting ($\alpha = 0^\circ$) and complete drying ($\alpha = 180^\circ$) (see Fig. 7). Because of our choice of system, it is still component *C* which adsorbs at the *AB* interface ($0 \leq \alpha \leq 90^\circ$). Indeed, we find complete wetting for $\chi_{AB} = \chi_{AC} = \chi_{BC} = 0.278$ in combination with $\sigma A/kT$ approaching zero. Physically, this indicates the formation of a microemulsion without the presence of a classical amphiphilic surfactant.

V. CONCLUSION

The Scheutjens–Fleer method is a powerful tool to study systematically the wetting characteristics of a variety of systems. In the present study a system of three homopolymers was investigated, but we could also have chosen a system containing monomeric components or copolymers. Although we had a very simple system with $N_A = N_B = N_C$ and $\chi_{AC} = \chi_{BC}$, we still found a rich wetting behavior. Close to the critical points of the *AC* and *BC* mixtures, approached by decreasing the effective interaction parameters, the *AB* interface is completely wetted by *C* as long as $\chi_{AB} > \chi_{AC} = \chi_{BC}$. This is in agreement with Cahn's argument which was based on considerations of the temperature dependence of surface tensions. In our homopolymer blends Cahn's wet-

ting transitions are found to be of second-order type. However, Cahn's transitions occur only for a very small part of our two-dimensional parameter space. We see two characteristics of Cahn's transitions in our system. First, if starting in a Cahn wetting transition point the value of $\chi_{AC}=\chi_{BC}$ is increased, the next wetting transition point according to Cahn will be found by decreasing χ_{AB} . Second, in our system with three polymers of the same length these transitions are found if all interaction parameters are almost equal. As a result of these two facts, very soon the value of $\chi_{AC}=\chi_{BC}$ exceeds the value of χ_{AB} for which Cahn's transition would be expected. In that case, it is energetically unfavorable for component C to wet the interface between A and B and, indeed, Cahn's argument fails. We then find hidden wetting transitions occurring in the metastable regime. In those situations, C seems to wet the AB interface, but suddenly the volume fraction of C in the solvents decreases and the system jumps to another state. We call this pseudowetting. It is emphasized again that these transitions are not found in real macroscopic systems, but may only exist in finite systems. For macroscopic systems there is no wetting transition available in this region of parameter space, even though the system is close to a critical point.

In addition to Cahn's wetting transition and pseudowetting transitions another wetting transition was found by increasing χ_{AB} . This wetting transition could be explained by the screening effect of the developing C layer. If the effective interactions are not taken into account, these wetting transitions could incorrectly be considered as Cahn-type wetting transitions, since complete wetting is found for

$\chi_{AC} < \chi_{AC}^{\text{wet}}$. This type of transitions is not violating Cahn's argument. Second-order wetting transitions are found for a large parameter space. Only for relatively large χ_{AC} first-order wetting transitions occur.

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