Regular Article

No violations of critical-point wetting in ternary three fluid-phase systems with short range interactions

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GRAPHICAL ABSTRACT
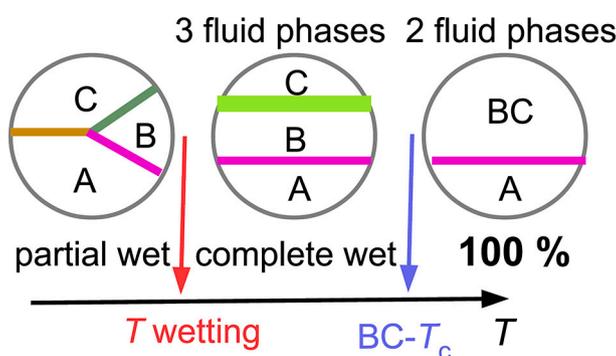
ABSTRACT

Hypothesis: In ternary three-fluid phase systems one can have either three- or just two interfaces. In a wetting transition the system switches from partial to complete wetting, i.e., from having three- to two interfaces. The system can also undergo a bulk phase transition when the number of bulk phases changes from three to two. Upon varying the temperature one will find that first the system switches from having three interfaces to two, before it changes from having three phases to two. This order of events is predicted by Cahn.
SCF computations: We use a quasi-off lattice variant of the Scheutjens Fleer self-consistent field theory, which implements a mean field approximation with short-range interactions parameterised by Flory-Huggins interaction parameters, to generate a set of wetting phase diagrams for this system. There exists special coordinates such that each wetting phase diagrams has a power-law wetting transition line.
Findings: Overlooking the full set of wetting phase diagrams, it is concluded that no exceptions to the Cahn rule exists unless the system is exactly (ideally) molecularly symmetric, sometimes called 'the neutral value' where the contact angle remains 90° up to the bulk critical point. Importantly, all wetting transitions may be induced similarly, that is they all can be classified and understood from Cahn's perspective.

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Introduction

Wetting characteristics, that is the way three equilibrated phases are spatially arranged, are important for many applications: the acceptance of particles in composite materials may depend on the wetting characteristics; formulations in cosmetic products may rely on the wetting of these products on skin or hair; the formulation of active ingredients in crop protection agents should facilitate the spreading of the actives on leaves. In these (and many other) applications the known- or approximate locus of the wetting transition is of key importance and any rational argument to point in the direction from partial to complete wetting is of key importance.

In classical wetting theory we have a solid substrate (S) in contact with a liquid (L) (minority component) and its vapour (V) (majority component). [1] In this system there can be up to three interfaces S-L, S-V and L-V with associated interfacial free energies γ_{SL}, γ_{SV} and γ_{LV}, respectively. To characterise the wetting state of the system it is convenient to define a spreading parameter

$$S \equiv \frac{\gamma_{SV} - (\gamma_{SL} + \gamma_{LV})}{\gamma_{LV}} \tag{1}$$

(Usually our interest is in the sign of S and then only the nominator may be considered as S) When $S > 0$, the liquid wets the surface (complete wetting, and there are only two interfaces S-L and L-V) and when $S < 0$, partial wetting occurs. Then the minority liquid sits as a 'drop' in between the majority phase and the substrate. There exist a famous argument by Cahn which serves as a guide when and where to expect a wetting transition, that is when the system switches from a finite value of the spreading parameter to zero. Cahn noticed [2] that when $(\gamma_{SV} - \gamma_{SL}) < \gamma_{LV}$, the system is in the partial wet state. He further assumed that there exists a suitable control parameter T in the system which can be use to systematically vary both the difference $(\gamma_{SV} - \gamma_{SL})$ and γ_{LV}. Furthermore there exists a value for T, T^{cr}, the critical value of T, for which the L-V interface vanishes, that is, where the difference between the liquid an vapour disappears. In the vicinity of the critical point it is expected that $\Delta\gamma \equiv (\gamma_{SV} - \gamma_{SL}) \propto (T^{cr} - T)^{\tau}$ and $\gamma_{LV} \propto (T^{cr} - T)^{\mu}$. He argued that $\Delta\gamma \sim \rho_L - \rho_V$ where ρ is the density. Then, already known by Van der Waals, the value of the scaling coefficient μ is generally found to be larger than the value of τ (in mean field theory $\mu = 3/2$ and $\tau = 1/2$ [3]) and this implies that at some T going towards T_{cr}, we will find the situation that the spreading parameter $S = 0$, that is, we find a wetting transition before the bulk suffers a critical point. This phenomenon is also known as critical point wetting. Only when $\Delta\gamma = 0$ also known as the 'neutral value', the contact angle remains 90° up to the bulk critical point -the surface is 'neutral' with respect to the two liquid components-. Indeed, the 'neutral value' is a pivoting point for which the system switches from going to either the complete 'wet' state or to the complete 'dry' state when the bulk critical point is approached. In the dry state, the V-phase wets the surface. At the neutral value the roles of L and V switch.

When instead we have no substrate but three fluid phases, one phase rich in component A, a second bulk phase rich in component B and a wetting fluid (relatively) rich in component C, it is generally expected that we have a similar situation. Suppose we start at a partial wet state, that is, the C phase sits as a lens in between the two bulk phases, we should expect a wetting transition due to the change of a control parameter T, before either the A-C or B-C critical point is reached (assuming that A-B remains far from critical). Careful experiments consistent with this are available in the literature, see e.g. ref. [4]. Again, when $\gamma_{AB} = \gamma_{AC}$ for all values of the control parameter, we do not expect the wetting transition until the system looses one of its phases. For such 'neutral value' the contact angle remains 90° up to the bulk critical point. Again, this is not seen as a violation of the Cahn conjecture because such situation can only exist in theory. Indeed, this 'neutral value' is again expected to have a pivoting role, at which there is a switch from the C-rich phase

wetting the A-B interface to the B-rich phase wetting the A-C interface or the A-rich phase wetting the B-C interface.

In a recent report it was argued that for ternary three-fluid phase systems the above argument is apparently not followed and the Cahn argument does not apply in large parts of parameter space. [5]. These authors use their own mean field density functional theory and use two spatially varying densities, the third density can be replaced by a pressure dependence. They argue that their functional is valid near bulk critical points. Importantly they can obtain both analytical and numerical results that agree with each other. So we must accept that for their functional the Cahn argument does not always hold. Possible failures of the Cahn argument are known for systems with long range interactions [6–8], but the recent claim explicitly was made for ternary systems with short range interactions. A few decades ago one of us used the Scheutjens-Fleer variant of the self-consistent field theory to study wetting transitions in ternary three-fluid phase systems and found no such violations. [9] unfortunately, in this work not all possible scenario's were considered and that is why we here revisit these systems using a slightly revised model which produces less artifacts. Below we will present wetting phase diagrams (see below) in special coordinates where the 'neutral value' plays a key role and conclude from these that no exceptions exist because the smallest deviation from this neutral value was shown to behave according to the Cahn conjecture. This must be contrasted to the results of Indekeu and Koga [5], who report that in a wide region of parameter space, specifically around the neutral value, the violation of the Cahn argument was found. It is not the goal of the present paper to specifically pin point to potential weak spots in e.g. the functional used by Indekeu and Koga. [5] or to potential flaws in their analysis; instead we want to contrast their results to ours.

The Self-consistent field approach for chain-like molecular components has been introduced by Scheutjens and Fleer in the late 70's of the previous century. This method can be seen as numerically exact (that is, on the mean field level) as it avoids Taylor series expansion altogether. It is numerically exact for all parameter settings, that is close to the tricritical point but also further away from it. Molecular interactions are parameterized by Flory-Huggins interaction parameters χ_{XY} with XY = {AB, AC, BC} (see Eqn (2) for the definition of χ, which can essentially be seen as the inverse temperature T), wherefore a positive value signals repulsion between unlike contacts driving segregation between components. Unfortunately our earlier work [9] was limited to special cases where $\chi_{BC} = \chi_{AC}$. In the present paper we target all relevant parameter settings for ternary systems and reach the conclusion that there are no exceptions to the Cahn argument. Even though the SCF method used in the current work is of the mean field type, has underlying Flory-Huggins features (short-ranged interactions, as mentioned) and it makes use of a freely jointed chain approximation for the chain statistics, we argue that it implements fundamentally similar approximations as the work that is challenged. As the SF-SCF method is numerical in nature it is nontrivial to prove that there are no critical point wetting exceptions. We pick up the challenge to convincingly prove that there is no (hidden) parameter combination that may falsify our thesis. This is a relevant statement because in ternary systems, there are various intricacies in having three phase equilibria. [10]

In our approach we have for given χ_{AB}, both χ_{BC} and χ_{AC} as control parameters which we can vary independently to force the phase transitions in the system. Formally (cf. eqn (2) below) both parameters are inversely proportional to the temperature T. Alternatively we thus could have opted for just one control parameter T, similarly as Indekeu and Koga. [5] However, in the spirit of Flory-Huggins theory and common practise we treat the two parameter to be independent, that is, we take it that it is possible to, e.g., change one while keeping the other constant. Of course the implementation of this idea in practise may be hard to do.

It is a good habit to collect wetting results into so-called wetting phase diagrams. Below we will present such phase diagrams basically using χ_{BC} vs χ_{AC} coordinates, highlighting that we have two indepen-

dent control parameters. A line in such a phase diagram indicates the combination of the value of the control parameter $\chi_{AC} = \chi_{AC}^{\text{wet}}$ and the corresponding value of $\chi_{BC} = \chi_{BC}^{\text{wet}}$ at which the wetting transition occurs. We find a wetting phase diagram for each specified values of χ_{AB}. A line in the wetting phase diagram splits the parameter space into two: those parameters that corresponding to systems in the partial wet state and those corresponding to the complete wet state. We understand that when $\chi_{AB} = \chi_{AC}$, that is, at the neutral value for the system, the wetting transition occurs **exactly** at the corresponding critical point $\chi_{BC}^{cr'}$ (where the prime indicates the special critical point for systems with equal values for $\chi_{AB} = \chi_{AC}$). This motivates us to use special coordinates for our wetting phase diagram, namely $\chi_{BC} - \chi_{BC}^{cr'}$ versus $\chi_{AB} - \chi BC$ and use a double logarithmic scale. (In these coordinates the 'neutral value' and formally its wetting transition occur at minus infinity. It turns out that in these coordinates the wetting transition lines have a power-law dependence (they show up as straight lines). This implies that all wetting transitions are intricately related to the value of the bulk critical point for the neutral value setting.

The structure of the paper is as follows. First subsection in the methodology section we will review where to find the three-phase regions in systems that contain three fluid-like components. After this we outline the key characteristics of the SF-SCF method that is used. For the full details we refer to earlier literature. We will then mention the strategies that have been used to localise wetting transitions in the system. In the result and discussion section we will focus on the various regions of three-phase coexistence and we will split this up into two parts: (i) the parameter settings relatively far from the tricritical point, notably above the triple point $\chi_{AB} > \chi^{\text{tr}} = (4/N)\ln 2$. In this region of parameter space we find phenomenological power-law scaling relations that connects all wetting transitions to a corresponding critical point. The continuity of the fitting coefficients provide a strong argument that there is no hidden region of partial wetting that might persists until the critical point. The only exception is for the 'neutral value' condition. (ii) The parameter settings in between the tricritical point $\chi_{AB} = 18/7N$ and the triple point $\chi_{AB} = (4/N)\ln 2$. In this range of parameters we will argue and illustrated by giving selected results on worst case scenario's, that there is no case of partial wetting; all parameters give complete wetting and thus there cannot be a Cahn violation in this part of parameter space. As this concludes our scan of parameter space we draw our conclusions (as expressed by our title) in the designated part of the paper.

Methodology

In the introduction we already have outlined the classical wetting theory, discussed the Cahn argument and mentioned that it has recently been challenged. In this section we will first go into details about the phase behaviour in ternary systems, and then elaborate on the SF-SCF method that is used to generate the wetting phase diagrams. At the end of this section we go into details how using the SF-SCF method wetting transitions may be located.

Three fluid-phase coexistence in ternary systems

Within SF-SCF modelling we can take any ternary system A_{N_A}, B_{N_B} and C_{N_C}, where the N_X is the degree of polymerisation of component X may be different for each component $X = A$, B, C. We do not expect that the molar volume of each component is of key importance. Therefor we opt for a simplification, $N_A = N_B = N_C$. This will allow us to cut the search for wetting transitions short by at least a factor of three. The work that is challenged here [5] also focused on the symmetric case with $N_X = 1$ for all X. SCF-like models that deal with $N = 1$ may be referred to as regular solution models (or derived from this approach), those with larger values of N are of the Flory-Huggins type or approaches that are derived from it. [11] Both approaches are lattice based and take the system as incompressible. In these systems there are three Flory-Huggins

parameters χ_{XY} which essentially are dimensionless nearest-neighbour exchange interaction parameters:

$$\chi_{XY} = \frac{Z}{2k_BT}\left(2U_{XY} - U_{XX} - U_{YY}\right) \qquad (2)$$

where Z is the lattice coordination number and U_{XY} is the interaction energy when two neighbouring sites are occupied by a X and a Y component, respectively. A setting for the parameters χ in regular solution has the same effect as the parameter setting $N\chi$ in Flory-Huggins (provided all molecules are of same length). Hence characteristic χ in regular solution translate to $N\chi$ in Flory-Huggins. Stated otherwise, in Flory-Huggins models the relevant values of χ are N times smaller than in regular solution. The structure of the interfaces will slightly depend on N, but we believe that this difference is not fundamental. Working with lattice models has its limitations. For large values of N it is expected that the mean field models become more accurate. Here and below we focus on $N = 4$ for simplicity. As compared to regular solution, the increase of N from 1 to 4 reduces the need to have large interaction parameters which give rise to so-called lattice artifacts (more about this below).

Let's first set all interaction parameters to the same value $\chi \equiv \chi_{AB} = \chi_{BC} = \chi_{AC}$. The advantage of using a regular-solution-like (or Flory-Huggins-like) system is that we know all relevant regions in the phase diagrams. [10] In the symmetric situation the phase diagram has several one-phase regions, various two-phase regions, (surprisingly) more than 1 three-phase regions and one (triple) point for which four phases coexist. In slightly more detail, it is known that when $N\chi < 18/7$ there can be no three-phase coexistence. [10] This point is known as the tricritical point as at this point two lines of critical points terminate. In the region $18/7 < N\chi < 4\ln 2$ we have (two separate regions of) three phase coexistence. Characteristic for these regions, the compositions of the three phases are not similar: two phases have a similar composition and the third phase is markedly different (you may find an example in Fig. 6). This must be distinguished from systems for which $N\chi > 4\ln 2$. [10] In this exact point (we refer to it as the triple point) there are three phases having a similar composition built-up (the majority component has volume fraction 2/3 and the other two components have volume fraction 1/6), which coexist with a fourth phase which has equal volume fractions of each component, 1/3) for an example see Fig. 5d below). When $\chi > (4/N)\ln 2$ there is a single region of three-phase coexistence. Of course, as soon as the three χ-values are not equal to each other, the three phases will all have their own composition. Examples of such situation are given below in Fig. 1c,d.

When there are three phases in the system, we should be on the outlook of wetting phenomena. [1] To theoretically study wetting transitions in the system, it is not enough to be able to compute the compositions of the three coexisting phases, but one also needs to evaluate the structure and thermodynamics of the interfaces. We use the self-consistent field theoretical framework of Scheutjens and Fleer (SF-SCF) for this task. SF-SCF can be seen as an extension of the Flory-Huggins theory accounting for inhomogeneous systems. That is, the approach is targeted to compute the structure and thermodynamics of interfacial systems. In the following section we present the basic ingredients of this modelling technique. This includes the discussion of the premises and it provides the SCF rules for computing the potentials and volume fraction profiles of the molecules. For full details we refer to the literature. [12–15,9]

SF-SCF protocol

Similarly as the Flory Huggins theory, the SF-SCF is lattice based. Classically, the molecules occupy lattice sites such that each segment fills a particular site. Below we employ a grit-refinement strategy which deviates from the classical approach, but first we outline the classical Ansatz. We use the variable N to denote to the number of lattice sites occupied by a given molecule, that is the number of segments per chain.

Here we have three components and thus we take A_N, B_N and C_N. Also following Flory-Huggins theory the system is filled to capacity, that is another way to say that the system is incompressible. The incompressibility relation is reasonable for liquid systems and has a few not so elegant side-effects: (i) the volume is not an independent thermodynamic variable and the intensive parameter p (pressure) is not operational. (ii) there is no vapour phase. Interactions in this model are accounted for using a mean field approximation (Bragg-Williams approximations) and as mentioned already the interactions are parameterised by Flory-Huggins interaction parameters. As there are three components in the system, we also have three independent interaction parameters χ_{AB}, χ_{BC} and χ_{AC}. To select the $A|C|B$ scenario (that is the C-phase is in between the A and B phase) we insist the following rules according to the values of the three interaction parameters. As A is the substitute for the substrate we want χ_{AB} to be the largest of the three. As C should go preferentially in between the A-B interface, we need $\chi_{BC} \leq \chi_{AC}$. Hence we have $\chi_{AB} \geq \chi_{AC} \geq \chi_{BC}$, and obviously all values should be above some threshold value to allow for three coexisting phases. As known for a long time the lowest possible interaction parameter to have three-phase coexistence is in the molecularly symmetric system given by $\chi^{\text{tc}} N = 18/7$. [10] We note that wetting transitions in other parts of the phase triangle can be found by cyclic iterative renaming of the components.

The SF-SCF machinery is targeted to compute interfacial characteristics of the system. To do so for polymeric components, we need a suitable chain model to estimate the conformational entropy of the molecular components in the interfaces. In SF-SCF the so-called freely jointed chain (FJC) model is adopted for this basically because in this model there exists a computationally inexpensive way to evaluate chain partition functions. In the FJC model two neighbouring segments along the chain occupy neighbouring sites on the lattice. However, longer ranged correlations are ignored: segments have ranking numbers $s = 1, 2, \cdots, N$ and segments $s - 1$ and $s + 1$ may occupy the same site. This might occurs when the chain performs so-called back folding steps. This excluded volume problem is counteracted by the incompressibility condition which states that each site (on average) must be filled exactly once. We note in passing that in the limit of $N \to 1$, the SF-SCF method is identical to the regular solution model, which for homogeneous systems the (dimensionless) free energy G of mixing per unit area, which features spatially varying densities (volume fractions) φ_X, $X =$A, B, C:

$$G = \sum_z \left[\varphi_A(z) \ln \varphi_A(z) + \varphi_B(z) \ln \varphi_B(z) + \varphi_C(z) \ln \varphi_C(z) + \right.$$

$$\left. \chi_{AB} \varphi_A(z) \langle \varphi_B(z) \rangle + \chi_{AC} \varphi_A(z) \langle \varphi_C(z) \rangle + \chi_{BC} \varphi_B(z) \langle \varphi_C(z) \rangle \right] \quad (3)$$

As outlined by Safran [3] the angular brackets, which should accurately account for the interactions when there are density gradients, have a continuous approximation $\langle X(z) \rangle \approx X(z) + \lambda \frac{\partial^2 X(z)}{\partial z^2}$, where λ is a lattice parameter. This second derivative can, after partial integration be transformed in Cahn-Hilliard square gradient terms. Taylor series expansion of the logarithmic terms (using the tricritical densities), basically leads to the two-density functional of Indekeu and Koga. [5] However, it must be noted that Indekeu and Koga have only two square gradient terms (i.e. accounting for gradients for A-C and B-C interactions but those for the A-B ones is missing) where in our approach we have all three. At this point we can not oversee all consequences of this. The fact that Indekeu and Koga used Taylor series expansion makes their method work as long as there are no large density differences in the system, and it becomes progressively less accurate when the density differences between the phases grow. Below we will see that there easily large density differences exist in three-fluid phase systems. Indekeu and Koga [5] have realised this and specified that their analysis should be strictly used near the tricritical point.

At the basis of the SF-SCF theory there is an equivalent mean field free energy functional which also can be used for chain-like molecules. This SF-SCF free energy expression is given in terms of three types of functions: (i) volume fractions $\varphi_X(z)$, where $X = A$, B, C and $z = 1, 2, \cdots, M$ is a spatial coordinate with M sets the system size. Volume fractions are dimensionless segment concentrations. (ii) $u_X(z)$, so-called segment potentials; the value of the segment potential is given by the work needed to bring a segment from the bulk (where the potential is zero) to the coordinate z, and thus the potential is dependent on the spatial coordinate. (iii) a so-called Lagrange field $\alpha(z)$; this field is independent of the segment type. It's value is tuned such that the system obeys to the incompressibility relation locally, that is $\sum_X \varphi_X(z) = 1$. As a unique value for α is needed for each coordinate z, we again see that this quantity is a function of the spatial coordinate.

The best mean field free energy is found by optimising the free energy function with respect to its variables. This extremisation procedure leads to the self-consistent field rules. Without going into too much details we mention that the optimisation with respect to the volume fractions give a rule which insist on the way the potentials are computed:

$$u_X(z) = \alpha(z) + \sum_Y \chi_{XY} \left(\langle \varphi_y(z) \rangle - \varphi_Y^b \right) \quad (4)$$

where it is understood that the potential is typically expressed in units of the thermal energy $k_B T$.

In this equation (eq. (4)) we choose φ_Y^b to be the bulk concentration in the phase rich in component B (below we will outline the way these bulk concentrations are found). The angular brackets are needed to correctly count the interactions in regions where the density is not homogeneous. It is specified by a three-layer average $\langle X(z) \rangle = \frac{1}{4} (X(z-1) + 2X(z) + X(z+1))$, which implies a hexagonal configuration of lattice sites. The non-local counting (as mentioned equivalent to the square gradient terms in Cahn Hilliard) of the interactions is important in interfacial systems where the volume fractions are not homogeneous.

The extremisation of the free energy with respect to the segment potential leads to the rules how to compute the volume fraction profiles and the chain partition functions. Consistent with this step we implement these evaluations using a propagator formalism (implying the FJC chain model). In this formalism we define end-point distribution functions G_i for chain number i. In its most general form $G_i(z, s|z', s')$ it represents the statistical weight for chain walks that start at segment s' and at coordinate z' and end at with segment s at position z. We use these distribution functions for s' either $s = 1$ (forward case) or $s = N$ (backward case) and we integrate over the starting coordinate, and find $G_i(z, s|1)$ or $G_i(z, s|N)$. These once integrated end point distribution function generated recursively:

$$G_i(z, s|1) = G_i(z, s) \langle G_i(z, s - 1|1) \rangle$$

$$G_i(z, s|N) = G_i(z, s) \langle G \rangle_i (z, s + 1|N) \rangle \quad (5)$$

where $G_i(z, s)$ is known as a free segment distribution function. When segment s of molecule i is of type X we find $G_i(z, s) = G_X(z) \equiv \exp -u_X(z)$. These propagators, which are discrete variants of the Edwards diffusion equation [16], need initial conditions, that is they are started by $G_i(z, 1|1) = G_i(z, 1)$ and $G_i(z, N|N) = G_i(z, N)$. The first propagator (cf eqn (5)) thus starts at $s = 1$ and runs towards $s = N$, while the second one goes in the reversed direction, it starts at $s = N$ and runs backward to $s = 1$. After $N - 1$ propagator steps we arrive at $G_i(z, N|1)$ or $G_i(z, 1|N)$. These quantities can be integrated over the z-coordinate to find the chain partition function $q_i = \sum_z G_i(z, N|1) = \sum_z G_i(z, 1|N)$.

The end-point distribution functions generated by eqn (5) are used to compute the volume fraction with an equation known as the composition law:

$$\varphi_i(z, s) = C_i \frac{G_i(z, s|1) G_i(z, s|N)}{G_i(z, s)} \quad (6)$$

Here the division by $G_i(z, s)$ is needed because the statistical weight for segment s should be accounted for just once. In the limit of $N \to$

1 the composition law reduces to the Boltzmann equation. Next, the normalisation constant C_i can be shown to obey

$$C_i = \frac{n_i}{q_i} \qquad (7)$$

$$C_i = \frac{\varphi_i^b}{N} \qquad (8)$$

the first of these eqns is used when the number of molecule n_i is specified in the system (canonical calculations). The second one is used when the bulk concentration is given (grand canonical calculations). In the current setting the number of molecules is typically known from the input. In this case we compute the partition function and predict the bulk concentration: $\varphi_i^b = \frac{N n_i}{q_i}$. These bulk concentrations are needed to normalise the segment potentials (cf. eqn. (4)). Obviously we can find the overall volume fraction of component i by summing over the segments, that is, $\varphi_i(z) = \sum_s \varphi_i(z,s)$ where the sum runs over all segments of molecule i. In a typical calculation we compute the bulk volume fractions for component A and C from the values of n_A and n_B using the computed partition functions. For the B-component, however, the volume fraction of the bulk phase is set by $\varphi_B^b = 1 - \varphi_A^b - \varphi_C^b$. This setting makes sure that the reference bulk phase obeys the incompressibility relation.

As potentials and densities mutually depend on each other, a fixed point -the so called scf solution- is found by numerical iterative searches. In such procedure, the implemented values of $\alpha(z)$-values are modified until the system obeys to the incompressibility conditions. A possible strategy for this update is to simply use $\alpha^{k+1}(z) = \alpha^k(z) + (\sum_X \varphi_X(z) - 1)$, where k is the kth estimate for the Lagrange field during the iterative search. In practise, however, we solve the SCF equations using a numerical method presented by Evers and coworkers. [15] Routinely a precision of at least 7 significant digits is reached in order 100 iterations and this accuracy is sufficient to accurately evaluation the grand potential $\Omega = F - \sum_i n_i \mu_i$, where μ_i is the chemical potential of component i and F is the Helmholtz energy. Because of its importance we specify how the grand potential is computed and refer to the literature for the free energy and chemical potentials. The grand potential $\Omega = \sum_z \omega(z)$, where $\omega(z)$ is the grand potential density which can be written as [15]

$$\omega(z) = - \sum_i \left(\frac{\varphi_i(z) - \varphi_i^b}{N_i} \right) - \alpha(z)$$
$$- \frac{1}{2} \sum_X \sum_Y \chi_{XY} \left(\varphi_X(z) \langle \varphi_Y(z) \rangle - \varphi_X^b \varphi_Y^b \right) \qquad (9)$$

when there is just one interface in the system, we identify the grand potential with this interfacial tension. However when multiple interfaces are present in the system, the grand potential will obviously collect the sum of the interfacial tensions of all these interfaces.

With the presented SCF-protocol we can study many features of interfaces that exist between coexisting phases. However the classical approach has its problems as soon as the width of the interface is of the same size of the segments (equivalent to the lattice site length -called grit size-). Then the discretisation (use of the lattice) becomes noticeable (typically referred to lattice artifacts) and this complicates for example the identification whether or not a system is wet. To effectively solve for this issue we use the quasi-off lattice implementation of de Lange and coworkers [17]. Their strategy has many similarities with the quasi off lattice method of Romeis and coworkers. [18] These authors use a protocol wherein the segments are twice or three (etc) times larger than the grit size. There are various implementation details; one of these is that the propagator formalism is modified. Formally this means that the chain model depends systematically (chain become progressively more flexible) on the grit-refinement. This poses potential challenges related to the mapping of particular molecular components to theoretical (Kuhn-segment) models, but there are no fundamental issues with respect to the phase diagrams and the location of wetting transitions.

Of course the computation time increases upon increasing the ratio between the segment and grit sizes. This is not so much of an issue as these times are well within the sub-minute time scale. Typically, the refinement level is adjusted until the result becomes sufficiently invariant with respect to the grit-size. Below we have implemented this approach to avoid lattice artifact problems which present themselves in systems far from the tricritical point. In the current work the segment size was set to twice the grit size."

Wetting transitions

There are several ways to study the wetting characteristics and to accurately probe wetting transitions in a system. The first and most natural route is to focus on the interfacial tension of the interfaces and how these change when the wetting control parameter is varied in the system. These quantities feature in Young's law and this naturally leads to the spreading parameter S, cf. eqn (1).

$$S = \cos \theta - 1 = \frac{\gamma_{SV} - (\gamma_{SL} + \gamma_{LV})}{\gamma_{LV}} = \frac{\gamma_{\text{thin}} - \gamma_{\text{thick}}}{\gamma_{LV}} \qquad (10)$$

which relates the three-phase contact angle θ to the spreading parameter S and it defined both γ_{thin} and γ_{thick}. These latter two interfacial free energies are computationally available when adsorption isotherms are generated as discussed below. The γ_{LV} is usually computed in a separate calculation. When the interest is in finding the locus of a wetting transition it suffices to know γ_{thin} and γ_{thick}. Also in ternary systems without a solid substrate it is possible to locate the wetting transition by searching for the condition $\gamma_{\text{thin}} = \gamma_{\text{thick}}$.

Another intuitive route to study wetting is to consider so-called adsorption isotherms. In an adsorption isotherm one computes the adsorbed amount (of the C-component) at the A-B interface. To quantify the adsorbed amount we need to choose a Gibbs plane. This is chosen with respect to the solvent (that is, the profile of the B-component). For the specified Gibbs plane the excess adsorption of the solvent is per definition zero. (cf eqn (11) below) Adsorption isotherms present the excess amount of C (with respect to this Gibbs plane, which is minus the excess amount of A) is presented as a function of the volume fraction of C in the B-rich phase. When the adsorption isotherm is a monotonically increasing function and diverges at the bulk binodal (of C in B-rich phase), we know the system (the A-B interface) is wet (by C). Alternatively, when the isotherm features a 'loop' in the super-saturated region, such that the equal area construction is impossible, we find that the system (A-B-interface) is partial wetted by C. Then the isotherm crosses the bulk binodal in a region of the isotherm that there is only a little C at the A-B interface. The interfacial tension at this first crossing of the binodal is called γ_{thin}. Invariable the isotherms return to the bulk binodal at high C loading of the interface. The interfacial tension in this region is referred to as γ_{thick} (for obvious reasons). (See Fig. 2a for an illustration) Again, when upon the change of a control parameters the system suffers a wetting transition, this is found as the condition $\gamma_{\text{thin}} = \gamma_{\text{thick}}$. Wetting transitions can be found to be first-order or second order. [1] In a first-order wetting transition the isotherms merge toward the binodal at high C-coverage from the sub-saturated side, whereas in the second order case the wetting isotherm merge toward the binodal at the super-saturated side. In practise the first-order wetting transitions are identified by the presence of a pre-wetting transition. Then a loop in the isotherm is found before the system reaches the bulk binodal. In this paper we are not *per se* interested in the order of the wetting transition, but in passing we mention that we found first-order wetting only when χ_{AB} is sufficiently large. Wetting transitions near $\chi N = \ln 2$ are found to be of the second order type (critical wetting).

We found that it is laborious to compute a full isotherm before we can know whether or not the system is wet. That is why in practise we implemented a time saving short-cut. To understand this alternative criterion for wetting we must know about the interaction between interfaces. Two 'surfaces' or interfaces that are far apart can be seen as

independent. At fixed chemical potentials, upon bringing the interfaces closer and closer to each other, we can either find that the grand potential goes up (then the surfaces repel each other), or the grand potential goes down (then the surfaces attract each other). For obvious reasons these two scenarios correspond to the wet and the partial wet case, respectively. In other words, we need a switch from attraction between the A-C interface and the C-B interfaces to repulsion to witness a wetting transition from partial wet to wet.

We follow ideas forwarded by Marçelja and Radic, who based their approach on the Landau expansion of the local Gibbs energy density and the symmetry behaviour of the order parameter in the system. [19] Implementing their approach for the location of wetting transitions, we understand that the profile of the C-component (order parameter) is of interest. At the B-C interface, the density of C invariably goes from a value characteristic of the C-rich phase and falls monotonically off to the density of C in the B-rich phase. When the same happens at the C-A interface, that is when the density of C in the C-rich phase monotonically decreases towards the density of C in the A-rich phase, we have the situation that the density behaves 'symmetrically' on both sides of the C-rich domain. In this case the A-C and C-B interfaces attract each other (partial wetting). When C has 'enough' (relative) affinity for the A-rich phase, it may happen that the profile of C has a non-monotonous behaviour at the A-C interface. More specifically, going from the C-rich phase to the A-rich phase the C density goes through a local maximum before it falls off to the low density of C in the A-rich phase. This asymmetric behaviour of the C-profile at the A-C and C-B interfaces signals repulsion between these interfaces. Then this signals the complete wet scenario. We can study the C-profile best when the C-phase is large, that is when the A-C and B-C interfaces are far apart, more specifically when the distance between the interfaces exceed by far the widths of the B-C and A-C interfaces. The non-monotonic C-profile can trivially be picked up as a function of the wetting control parameter and this is the quickest way to find the wetting transitions in the system. We carefully checked that this method gives identical results to the more laborious approaches sketched above.

Results and discussion

As explained in the introduction we focus on the case that the three molecular components have segments A, B and C, respectively, and that all molecular components have the same chain length N. The value of N appears not so important as χN appears the effective interaction parameter. A small value of N needs large χ-values and these in turn give occasionally problems with convergence of the SCF equations. Computation times, however, scale with N and thus we are not keen to take vary large values for N. Here we use the rather low value of $N = 4$ throughout the calculations. In a previous study of three-phase coexistence systems studied by SF-SCF we presented results with larger values of N, [9]. All trend do not depend on the specific choice of N (universal behaviour).

In Fig. 1 we show some typical three-phase density profiles. As an example we show in panel a a typical plot for the density profiles $\varphi_A(z)$, $\varphi_B(z)$ and $\varphi_C(z)$, for the symmetric choice of the interaction parameters $\chi_{AB} = \chi_{AC} = \chi_{BC} = 1$, which is a relatively strong segregation case. By way of initial guess we put the C-rich phase in between the A- and B-rich phases. In panel b we show a similar result, now for $\chi_{AB} = \chi_{AC} = \chi_{BC} = 0.6935$ which is close to, but slightly above, the triple point value $(4/N)\ln 2$. Close inspect shows that the B molecules accumulate a little at the A-C interface and the A molecules accumulate at the C-B interface. This adsorption effect becomes relatively larger when the χ-values are reduced as will be discussed below (cf Fig. 5). In panels c and d, we give examples for the density profiles for some asymmetric choice of the interaction parameters. In both cases $\chi_{AB} = 0.8$, $\chi_{AC} = 0.7$. The third variable is $\chi_{BC} = 0.6$ in panel c and slightly smaller (closer to the critical value) 0.59 in panel d. We like to draw attention to the profile of C at the A-C interface. The small inset in panel c shows that

the profile increases monotonically. In d the C-profile goes through a local maximum. As we argued above, our conclusion is that the C-phase does not wet the A-B interface in conditions for panel c, whereas the A-B interface is wet by C in conditions in panel d. A closer inspection reveals a wetting transition at $\chi_{BC} \approx 0.597$. Note that the interface A-C is much 'sharper' than the B-C interface, and the B-C interface in panel d is even wider than the B-C interface in panel c. The widening of the B-C interface is a visual indication that one approaches the B-C critical point. In line with the Cahn argument, upon the approach towards the bulk critical point (where B and C phases become the 'BC' phase) the system suffers a wetting transition.

It is somewhat unconventional to decide on the wetting state of a system based on the observation of a single 'bump' in the profile of the wetting component. That is why we present (as an example) a more classical analysis based on adsorption isotherms in Fig. 2. In an isotherm the adsorbed amount (Gibbs excess) Γ_C as a function of the bulk volume fraction φ_C^b (bulk is defined as the B-rich phase). The Gibbs excess for component X is found by:

$$\Gamma_X = (\varphi_X[M] - \varphi_X[1])R^{\text{Gibbs}} + \sum_z (\varphi_X(z) - \varphi_X^b) \tag{11}$$

In Eqn (11) $\varphi_X[1]$ is the volume fraction of X near the lower-bound and $\varphi_X[M]$ is the volume fraction of X near the upper-bound of the system. R^{Gibbs} is defined by setting $\Gamma_B = 0$.

In Fig. 2 the adsorption isotherms (bottom panels) are accompanied by a corresponding plot of the grand potential per unit area (interfacial tension) as a function of the logarithm of the bulk concentration of C (bulk phase is defined as the phase rich in B) (top panels). In Fig. 2a the results for $\chi_{AB} = 0.8$, $\chi_{AC} = 0.7$ and $\chi_{BC} = 0.6$ are given. Both the isotherms and the grand potential plot are indicating that C does not wet the interface. This is concluded because the isotherm has a super-saturated excursion, and the grand potential has a cusp in the super-saturated region. The conclusion is in line with the profile result discussed above in Fig. 1c. As there is no indication of a pre-wetting step, the corresponding wetting transition is second order. For higher values of $\chi_{AB} = 1$ we did record a first-order wetting transition (not presented). The partial wetting situation is understood from the grand potential curve because the grand potential at the end-point of the curve (at the bulk binodal) is *above* the grand potential at the first crossing of the bulk binodal (the spreading parameter $S < 0$ cf. Eqn (10)).

The results for Fig. 2b are for $\chi_{AB} = 0.8$, $\chi_{AC} = 0.7$ and $\chi_{BC} = 0.59$. Both the adsorption isotherm and the grand potential curve indicate that in this case C wets the A-B interface. The isotherm increases monotonically and diverges at the bulk binodal. The grand potential monotonically decreases and terminates at the bulk binodal. Again this result is consistent with the profiles discussed above in Fig. 1d.

At this point we established that there is a strong correlation between the adsorption isotherm characteristics (Fig. 2) and the profile characteristics (Fig. 1c,d) and that both routes can be used to locate wetting transitions. As the profile route is computationally more efficient, we have use this approach below in most cases. However, it must be mentioned that the isotherm route is the most general. In particular it was found that for a symmetric setting $\chi_{BC} = \chi_{AC}$ the profile information generally signals partial wetting, as a local maximum in the C-profile can not develop, while the isotherm route is indicating either partial or complete wetting. For this reason, we used the isotherm route when $\chi_{BC} \approx \chi_{AC}$. Indeed, routinely we used alternative ways to determine the location of the wetting transitions, simply to be sure that results that are reported are accurate.

Wetting transitions for $\chi > (4/N)\ln 2$

In the symmetric system A_4, B_4, C_4, without loosing generality we can choose the interaction parameters $\chi_{AB} \geq \chi_{AC} \geq \chi_{BC}$. Hence we consider the situation that a decrease of χ_{BC} will eventually merge the two phases (B-rich and C-rich) into one homogeneous 'BC' phase. This is the
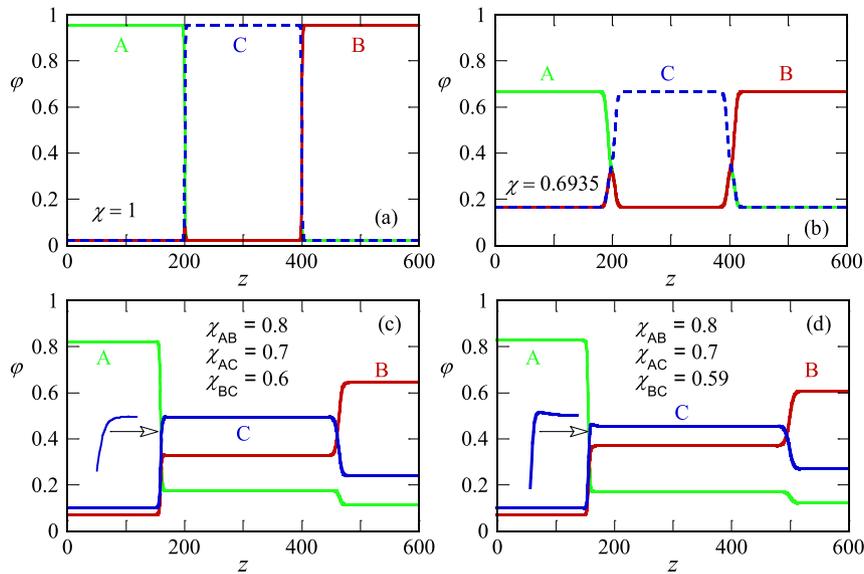
Fig. 1. Segment density profiles $\varphi_X(z)$ for $X = A, B, C$, showing two interfaces, A-C and C-B, for systems with equal composition $\theta_A = \theta_B = \theta_C = 200$. ($\theta_X = n_X N$) All molecular components are equally long $N = 4$. At the system boundary we have reflecting boundary conditions. a) $\chi_{AB} = \chi_{AC} = \chi_{BC} = 1.0$. b) $\chi_{AB} = \chi_{AC} = \chi_{BC} = 0.6935$ slightly above the triple point value $\ln 2$. c) A system for which C is partially wetting the A-B interface. As a 'proof', the inset shows that the profile grows monotonically. d) A system for which C is complete wetting the A-B interface. As a 'proof', the inset shows that the profile has a local maximum.
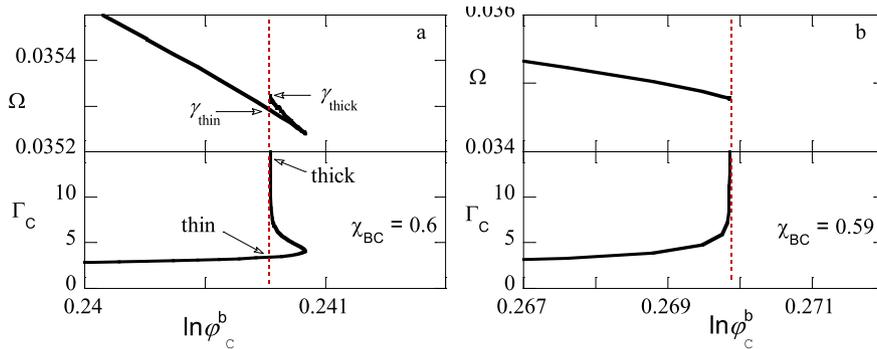
Fig. 2. (i) bottom graphs: the Gibbs adsorbed amount Γ_C with the Gibbs plane determined by component B (in units amount of segments per lattice site) (ii) top graphs: the grand potential (in units of $k_B T$ per lattice site), as a function of the bulk volume fraction φ_C^b (in the B-rich phase) for the systems presented in Fig. 1c,d: $\chi_{AB} = 0.8$, $\chi_{AC} = 0.7$. a) $\chi_{BC} = 0.6$; the isotherm is characteristic for partial wetting as the bulk concentration enters the super-saturated region and the grand potential has a cusp. The 'thin' and 'thick' terminology is illustrated by arrows pointing to the first crossing of the binodal (thin) and the high Γ region (thick). The red dotted line is the binodal volume fraction. b) $\chi_{BC} = 0.59$; the isotherm is characteristic for complete wetting; the isotherm increases monotonically and grand potential decreases monotonically. As no pre-wetting step is detected, it is concluded that the wetting transition which occurs between conditions for a and b is of second order type. (For interpretation of the colours in the figure(s), the reader is referred to the web version of this article.)

bulk critical point that we will approach in order to induce a wetting transition according to the Cahn conjecture. Again, when $\chi_{AB} = \chi_{AC}$ the wetting transition is maximally postponed (this is the neutral value for which the contact angle remains 90 degrees until the bulk critical point is reached). This motivates us to introduce $\Delta\chi \equiv \chi_{AB} - \chi_{AC}$ a disparity of interactions between the (no-critical) phase components away from the 'neutral value'. For each combination of χ_{AB} and χ_{AC} there is a critical value for χ_{BC}. Our interest is in the critical value of χ_{BC} when the other two parameters are equal to each other (that is, the neutral value condition). Let's refer to this one as $\chi_{BC}^{cr'}$. We record the value for χ_{BC} for which the wetting transition occurs as χ_{BC}^{wet}. We expect that $\chi_{BC}^{wet} > \chi_{BC}^{cr}$ and thus also $\chi_{BC}^{wet} > \chi_{BC}^{cr'}$. The latter turns into an equal sign when we have the situation that $\Delta\chi = 0$. ($\chi_{AB} = \chi_{AC}$ -the neutral value-). This motivates to define $\Delta\chi_W \equiv \chi_{BC}^{wet} - \chi_{BC}^{cr'}$ to give a measure for how far from the critical point (that is the special critical point where $\chi_{AB} = \chi_{AC}$) the system suffers the wetting transition. These coordinates ($\Delta\chi_W, \Delta\chi$) ware used for the wetting phase diagrams.

In Fig. 3 we present a set of wetting phase diagrams (each one for a different value of χ_{AB} as indicated in double logarithmic scale. In these coordinates the wetting transition lines are straight implying power-law dependencies. Again a line in a wetting phase diagram divides the parameter space into two regions (one representing partial wetting and the other representing complete wetting). When the combination of χ-parameter is such that the system is above this line, it is in the partial wet regime; inversely, systems with χ-parameters below this line are in the complete wet state. We present only a piece of each of the wetting transition lines (that is, we show the lines connected the wetting transitions that we explicitly computed; we did not extrapolate the curves yet) but it is expected that all presented wetting phase transition lines continue as straight lines all the way up to $\Delta\chi \to 0$ and $\Delta\chi_W \to 0$. The lines to not arbitrarily continue to higher values of $\Delta\chi$. They 'start' when $\chi_{BC} = \chi_{AC}$. We have plotted the lines to (approximately) this point.

We find a wetting phase diagram for each specified χ_{AB}-value and this value was varied from very far from-, to relatively close to the triple point value $\chi = (4/N)\ln 2$. The wetting transition lines obey to the power-law dependence $\Delta\chi_W \propto (\Delta\chi)^\alpha$. The slopes α of these curves vary from case to case and thus the slope is not universal. The closer χ_{AB} to the value $(4/N)\ln 2$, the lower the value is of the slope α. Again,
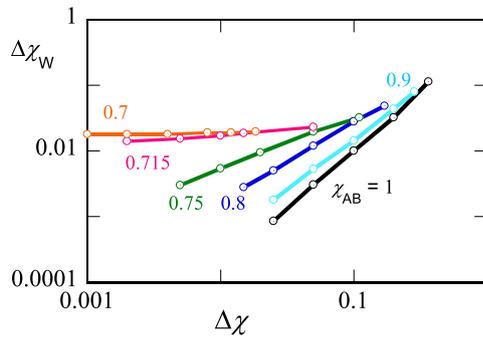
Fig. 3. Set of wetting phase diagrams for systems with specified value of χ_{AB} as indicated. The coordinates in these wetting phase diagrams are $\Delta\chi_W \equiv \chi_{BC} - \chi_{BC}^{cr'}$ as a function of $\Delta\chi \equiv \chi_{AB} - \chi_{AC}$ (double logarithmic scale). Each curve represents the location of the wetting transition, i.e., $\chi_{BC}^{wet}, \chi_{AC}^{wet}$) as for each curve both χ_{AB} and $\chi_{BC}^{cr'}$ are constants. The curves obey the scaling relation $\Delta\chi_W \propto (\Delta\chi)^\alpha$ and this power-law scaling is expected to hold up to the 'neutral value' conditions (which are at negative infinity) The bulk critical point when $\chi_{AB} = \chi_{BC}$ (the neutral value) is indicated by $\chi_{BC}^{cr'}$. In Fig. 4 the power-law coefficients α and the (fitted) value for $\chi_{BC}^{cr'}$ are presented as a function of χ_{AB}.

all lines in Fig. 3 are expected to follow the power-law scaling in the limit $\Delta\chi \to 0$.

As mentioned above, at high values of $\Delta\chi$ the curves approach the limit that $\chi_{BC}^{wet} = \chi_{AC}^{wet}$ (starting point of the curves). These wetting transitions (found by the isotherm route) have been discussed earlier. [9] For sufficiently large values of χ_{AB}, the wetting transition is expected when $\chi_{AB} = 2\chi_{AC}$ as in this limit the interfacial tension is proportional to the interaction parameter $\gamma \propto \chi$.

One benefit of collecting a full set of wetting transition lines into one graph is that it becomes possible to see how these curves are positioned with respect to each other. We mentioned already that the wetting phase transition lines extend towards the neutral value where the wetting transition is at $\chi_{BC} = \chi^{cr'}$ but not to larger values, because these parts of the parameter space correspond to a different order of the values of the χ-parameters (role of A, B and C components are iteratively cyclic changed). It then is relevant to notice that the wetting curves do not cross each other. A crossing of lines would have implied that two systems may have similar values for the control parameters for wetting while their value for χ_{AB} would be different. This does not happen.

The fact that all wetting transitions can systematically be collected in power-law dependencies (cf Fig. 3) implies that all wetting transitions are (mathematically) linked to a critical point $\chi_{BC}^{cr'}$ and as such we can say that all wetting transitions are critical point related and can be rationalised using the Cahn conjecture.

It must be noted that these power-law curves were constructed with a limited number of points and one may know from experience that the fitted values for α do depend on the exact value for $\chi_{BC}^{cr'}$ chosen (or vice versa). For this reason we present the collected fitting values in Fig. 4 in an attempt to show that the fitting values are not random.

The critical values $\chi_{BC}^{cr'}$ -equal AB and AC interactions- was estimated (in 4 significant digits) in a separate calculation and presented by the solid line in Fig. 4a. The points in this graph are the $\chi_{BC}^{cr'}$-values that gave the best power-law fits in the phase diagrams of Fig. 3. The correspondence is satisfactory albeit that near the triple point there are minor deviations which are attributed to fitting uncertainties. For very large values of χ_{AB}, the limiting value $\chi_{BC}^{cr} = 2/N$, or $\chi_{BC}^{cr} = 0.5$ as $N = 4$ in our case. The curve terminates at a value $\chi \approx 0.693$ where (for our symmetric system) all χ-values are equal to each other. We believe that this fitted and extrapolated value is a numerical approximation of the triple point value $\chi^{tr} = (4/N)\ln 2 = \ln 2$ as $N = 4$. [10]

In Fig. 4b the corresponding α values, the slopes of the power-law fits in Fig. 3, are presented as a function of χ_{AB}. Again, the exact values for α does depend on fitting details and the relative uncertainty in α is

significant especially for small values of α. At large values of χ_{AB}, $\alpha \approx 2$. In the limit of weak segregation $\alpha \approx 0$. This seems to take place in the vicinity of $\chi = 0.693$ (indicated by the vertical dotted line).

As there is no analytical method available to pinpoint the wetting transitions, we can use the fitting values for presented in Fig. 4 to predict the wetting transition χ_{BC}^{wet} for any specified set of χ_{AB} and χ_{AC} values. With confidence we can say that the Cahn conjecture appears operational for all conditions that we have encountered for $\chi > (4/N)\ln 2$. This means that up to the neutral value all systems obey to the Cahn conjecture. Beyond the neutral value we should rename the phase names because then the role of the B-rich phase is taken over by either the A-rich or C-rich phase. Hence the neutral value is where the system switches to another wetting component.

We have discussed above that $\chi = 0.69$ is not the lowest possible value to have three-phase coexistence. Indeed the lowest point (the tri-critical value) is at $N\chi = 18/7$. We will address this weak segregation regime below in a separate section. But first we will discuss what happens near the triple point (where the three phases give way to a homogeneous ABC phase).

When we insist that the three coexisting phases are compositionally similar (iterative renaming components), we have a limiting value for the $\chi = (4/N)\ln 2$ (all components have the same interaction parameter). It thus is of interest to study what happens 'wetting-wise' in the fully symmetric system, that is with all compounds having the same amount in the system, and all interaction parameters are kept the same in this specific limit. To this end we consider $\chi \equiv \chi_{AB} = \chi_{BC} = \chi_{AC}$ (recall all N the same as well). A few density profiles for these systems are shown in Fig. 5 for different values of the interaction parameter χ. In these graphs we have taken periodic boundary conditions and the system has three interfaces: A-B, A-C and C-B. When the interaction parameters are sufficiently high, the interfaces are as expected: at the A-B interface a little of C is 'adsorbed', and the similar adsorption are found at other interfaces, cf Fig. 5a. Upon the approach towards the $\chi = (4/N)\ln 2$, the adsorbed amounts gradually increase (panel b, c). When the adsorbed densities approach the value 1/3, we see a sudden growth of these adsorption layers, turning into wetting layers (cf Fig. 5d). Indeed in this situation we have 4 phases that coexist. (i) An A-rich phase (density of A = 2/3 and both B and C have density 1/6), (ii) an B-rich phase with similar densities and (iii) a C-rich phase (also with similar densities) and (iv) an ABC-phase (wherein all components have the same density value 1/3). As anticipated this occurs at $\chi = \ln 2 \approx 0.693$. It is easily checked numerically that the (Flory-Huggins) free energy density for the ABC homogeneous phase is identical to the free energy density of the A-rich, B-rich or C-rich phases at this particular case ($\chi = \ln 2$) and mentioned densities.

An additional argument in favour of this idea is that the wetting layers found for $\chi_{AB} = 0.7$ (wetting transitions presented in Fig. 3) are composition-wise very similar to the ones reported in Fig. 5, that is the densities of A,B and C approach the value 1/3 gradually when $\chi_{AB} \to ln2$. So the wetting transitions in asymmetric cases smoothly converge to the symmetric wetting layers with ideal composition that all densities are equal to 1/3. With respect to the applicability of the Cahn argument, the triple point may have the same 'exception' status as the 'neutral value' systems discussed earlier.

There are no wetting transitions for $\frac{18}{7} < N\chi < 4\ln 2$

As mentioned above there are yet other ways to have three phase coexistence in three-fluid phase systems and these cases occur when $18/7 < N\chi < \frac{4}{N}\ln 2$. We refer to this as the weak segregation region. Characteristic for this range of parameters is that the three phases when in mutual equilibrium not all have the similar composition. The A and B phases are composition-like the same but phase relatively rich in C has a distinctly different composition. In order to consider possible violations of the Cahn conjecture in these systems we need to search for parameter settings that correspond to partial wetting first and then we can change
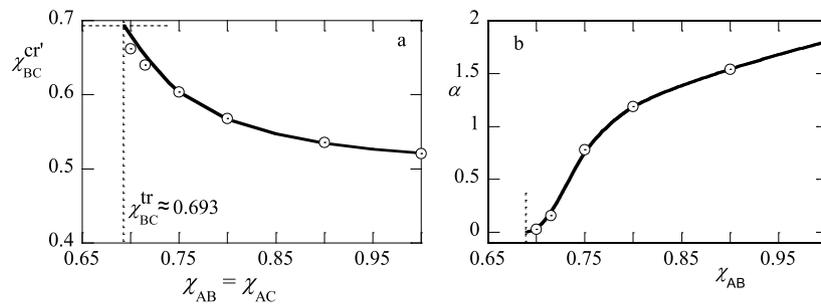
Fig. 4. a) The critical value $\chi_{BC}^{cr'}$, obtained in four significant digits, as a function of $\chi_{AB} = \chi_{AC}$ (line). The points are the values of $\chi_{BC}^{cr'}$ which were found from the fitting procedure leading to power-law dependencies in Fig. 3). The dotted lines represents the estimate value for the triple point $\chi^{tr} = \ln 2$. b) The fitted values of α obtained from the power-law fits of the data presented in Fig. 3 (points) as a function of χ_{AB}. The line is to guide the eye.
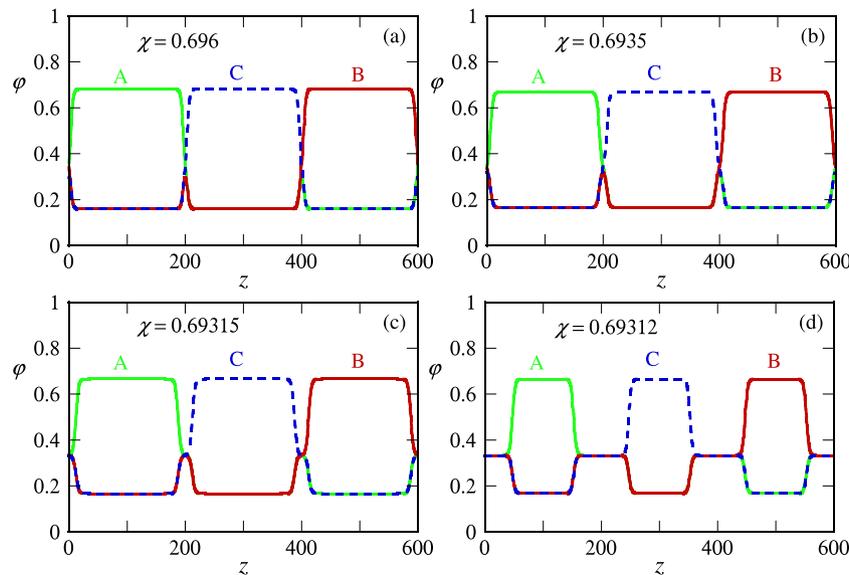
Fig. 5. Volume fraction profiles of A, B and C components for the symmetric system for various values of the $\chi \equiv \chi_{AB} = \chi_{AC} = \chi_{BC}$ as indicated. Periodic boundary conditions are applied. a) $\chi = 0.696$, b) $\chi = 0.6935$; the adsorption of the homogeneous ABC-phase reaches the value $\varphi = 1/3$ for A, B and C. c) $\chi = 0.69315$, d) $\chi = 0.69312 = \ln 2$: the A-rich, B-rich and C-rich phases have densities $\varphi(\text{majority}) = 2/3$ and $\varphi(\text{minorities}) = 1/6$.

parameters systematically to induce a wetting transition (for example using the Cahn strategy). This search strategy is frustrated because as it appears, in this regime there is no parameter setting that correspond to partial wetting!

To rationalise this we should elaborate that the phenomenological power-law lines of Fig. 3 can be seen as lines of wetting transitions in corresponding wetting phase diagrams, with $\chi_{BC} - \chi^{cr'}$ as the tuning parameter on the y-axis. So for given χ_{AB} and χ_{AC} one can consider the variation of χ_{BC}: when $\chi_{BC} > \chi_{BC}^{wet}$ (above the line) we have partial wetting, when $\chi_{BC} < \chi_{BC}^{wet}$ (below the line), the system is wet. As χ_{BC} by choice of our parameter setting is necessarily smaller than χ_{AB}, so the range for χ_{BC}-values is limited. Indeed, the closer α become to zero the more narrow the χ_{BC}-range is for which the system is found in the partial wet state. We believe that when $\alpha = 0$ this coincides with $\chi_{AB} = \chi_{BC} = \chi_{AC} = \chi^{tr} = (4/N) \ln 2$ the window χ_{BC} which causes the partial wetting to disappears completely from the wetting options. Stated otherwise, the system looses the ability to have partial wetting when $\alpha = 0$. Consequently, one can expect that for $N\chi_{AB} < 4 \ln 2$, we have complete wetting for all relevant parameter settings $\chi_{AB} \geq \chi_{AC} \geq \chi_{BC}$. To illustrate that this is exactly what happens we decided to illustrate that the complete wet case is found for arbitrary $18/7 < N\chi_{AB} < \frac{4}{N} \ln 2$ for relevant arbitrary choices for the other two parameters.

Fig. 6 gives for three cases for (systematically chosen values) $\chi_{AB} = 0.67$, 0.66 and 0.65 the volume fraction profiles for a three-phase coexis-
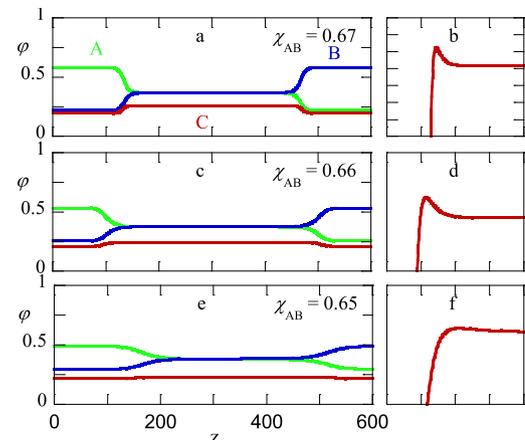
Fig. 6. Proof that the phase rich in C wets the A-B interface in the tricritical region. (a), (c), (e) Volume fraction profiles for A, B and C. (b), (d), (f) Volume fraction profile for the wetting component C zoomed in onto the part near the A-C interface. The x-axis have the same range of 200 layers. (a),(b) $\chi_{AB} = 0.67$, $\chi_{BC} = 0.599$, $\chi_{AC} = 0.66$, (c),(d) $\chi_{AB} = 0.66$, $\chi_{BC} = 0.5499$, $\chi_{AC} = 0.65$, (e),(f) $\chi_{AB} = 0.65$, $\chi_{BC} = 0.5489$, $\chi_{AC} = 0.649$.

tence cases. In the legend it is mentioned that the other two parameters are chosen below the χ_{AB} value, and relatively close to each other. This is the optimal choice to find partial wetting if this could exist in this region. However, as the panels b, d and f show, the profile for the wetting component C has a local maximum near the A-rich phase. As argued above this is characteristic for complete wetting. The adsorption isotherms for these cases (not shown) are in line with this result. In the phase triangle the value $N\chi = 8/3$, or for $N = 4$, $\chi = 2/3$, is special as here two three-phase coexistence regions touch. [10] Both slightly above, 0.67, or slightly below, 0.66, this value there is no sign whatsoever that partial wetting is possible, let-alone that it could persist until the critical point.

Although only three example χ_{AB}-values are presented in Fig. 6, other values that have been tested give corresponding results. Engels et al. [9] presented wetting transitions for parameters $\chi_{AC} = \chi_{BC}$. Their results fully support our findings: parameters in the weak segregation region invariably are below their line of wetting transitions and thus all these systems are in the wet-state. As in these symmetric parameter choice the system is already wet, we again conclude that in this weak segregation region all systems are wet by the C-rich phase: there exist no parameter choice for which there is partial wetting and thus the system can not be partial wet when the system suffers a critical point.

Upon close inspection of Fig. 6, we see that the width of the interfaces grows dramatically when $N\chi_{AB} \to 18/7$ (when $N = 4$, $\chi_{AB} \approx 0.64286$) and the phase relatively rich in C disappears. When this happens the density difference of C between the C-rich phase and that in the other phases has disappeared. Upon lowering the amount of C in the system the two-phase window between A and B rich phases may open up again and this two phase region vanishes when the C concentration is zero and $\chi_{AB} = 2/N$. Hence there are no lower values of χ_{AB} which need to be examined to find possible violations of the Cahn argument. In line with the data in the literature [10] the lowest possible value for χ_{AB} to find three-phase coexistence is found at this tricritical point.

Conclusions

Recently a suggestion appeared in the literature that in ternary systems with three fluid phases having short-ranged interactions, one can find large ranges of parameter space wherefore the Cahn argument to predict wetting transitions does not apply [5]. More specifically they report that in the vicinity of the neutral value, one can find a range of parameter settings that give partial wetting even up to the bulk critical point. In our set of results the only exception for the Cahn rule is at exactly the 'neutral value'. This trivial exception is usually not seen as a violation of the Cahn conjecture. Even the smallest of deviations from the neutral value will lead to a wetting transition before the bulk critical point is reached. This effect is beautifully captured by power-law wetting transition lines in our wetting phase diagrams: when you are infinitesimally below the neutral value, the wetting transition will be obviously very close to, but strictly below, the bulk critical point.

Here we used the Scheutjens-Fleer self-consistent field SF-SCF theory to study wetting transitions in similar ternary three-fluid phase equilibria. This method avoids Taylor-series expansions and therefore generates numerically exact results not only close to but also further away from the tricritical point. The quasi off-lattice version of the SF-SCF method implements a mean-field approximation wherein the short-range interactions are parameterised by Flory-Huggins χ-parameters. As such SF-SCF can be seen as a generalised Flory-Huggins theory extended to account for inhomogeneities as these occur at interfaces. We considered incompressible systems and zoomed in onto the choice that all three components have the same degree of polymerisation (we took $N = 4$, but results are expected to hold for any other combinations of values of N). This symmetric choice of N-values is of interest because it suffices to study the wetting characteristics in one corner of the phase triangle and by cyclic renaming of the components we know the results in the other two corners. The neutral value points (known

to formally escape the Cahn conjecture) are the pivoting points for the cyclic renaming procedure (moving to another corner). Here we took the C-rich phase as the wetting component, which sits in between the A-rich and B-rich phases. In line with this, we focused on parameters $\chi_{AB} \geq \chi_{AC} \geq \chi_{BC} > \chi^{tc} = 18/(7N)$. We record the value of χ_{BC} at the wetting transition and use the value of χ_{AC} (or χ_{BC} as our wetting control parameter(s)) (for given value of χ_{AB}.

Our key result is presented in Fig. 3, wherein we show power-law scaling relations that connect wetting transitions χ_{BC}^{wet} in the system to specified values for the other two parameters χ_{AB} and χ_{AC}. In this scaling relation the critical $\chi_{BC}^{cr'}$, that is the critical value of χ_{BC} in the special situation that $\chi_{AB} = \chi_{AC}$, plays a key role. It is found that $\chi_{BC}^{cr'} \to (4/N)\ln 2$ when $\chi_{AB} = \chi_{AC} = (4/N)\ln 2$. Furthermore, in this limit the power-law coefficient $\alpha = 0$ (cf Fig. 4) and $\alpha > 0$ for $\chi_{AB} > (4/N)\ln 2$. There are two important consequences of these trends: (i) because of the continuity of the fitting parameters, we understand that all wetting transitions in the system, that are found for relatively strong segregation, i.e. $\chi_{|AB} > (4/N)\ln 2$, are under control of nearby critical points. Hence, in this range of parameters there is no escape from critical point wetting. There cannot be a system that is partial wet when the system suffers a critical point; (ii) as the natural limiting value for $\alpha = 0$ is reached at $\chi = (4/N)\ln 2$, we conjectured that in the weak segregation region $18/7 < N\chi < 4\ln 2$ we cannot have any parameter setting corresponding to partial wetting. In line with this, although we tried hard to find partial wetting, we did not find any exception. So also in this regime of parameter space there is no partial wetting situation when the system suffers a critical point.

Knowing how one can switch in multi-component systems from having three- to two interfaces, that is inducing a wetting transition in a system, is important for many applications. In general one can do this by choosing a path toward the bulk critical point as suggested by Cahn. For example, if the molten wax would not wet the wick of a candle flame, the wax would not fill its capillaries and there would simply not be enough wax evaporation and subsequent oxidation to fuel the flame. However, we understand that when the molten wax is heated it will approach its critical point; the contact angle is lowered, triggering a Cassie Baxter- to Wenzel-state 'wetting' transition [20,21] upon its way towards the (true) wetting transition and then the wax will penetrate the wick (in the wet state is guaranteed to do so) for a wide variety of wick materials. Depending on porosity sufficient transport of wax into the flame is spontaneously established and the candle flame exists. Many other examples with large practical relevance can be listed: rinsing off dirt from interfaces is easier with, e.g., acetone (closer to it's critical point and therefore tends to wet a surface and lift off dirt) than with water (further from its critical point, and therefore rarely wets a surface and leaves on dirt), membrane fouling correlates with wettibility (or non-wettibility) [22], solder with good wettability will improve solderability. [23], the dispersion–aggregation transition of particles in a polymer matrix often correlates with the wetting/dewetting transition, [24]. More 'abstract' examples may trigger novel research directions, e.g. in medical science / biology, the amount of uptake of apolar molecules (drug) in the lipid bilayer membrane (relevant for anaesthesia) is either bounded (partial 'wetting') or unbounded (complete 'wetting') when the saturation concentration of the drug in water is reached. In formulation science, the transition from micelles swollen by oil-like molecules to (micro)emulsion-like droplets is governed by wetting-like transition.

Even though the true reason for the disparity in wetting predictions between the work of Indekeu and Koga [5] and the current SF-SCF ones remains to some extend unresolved, we argue that the 'old-fashioned' believe in the Cahn argument should not be put aside as yet.

CRediT authorship contribution statement

F.A.M. Leermakers: Writing – review & editing, Writing – original draft, Supervision, Software, Methodology, Investigation, Conceptual-

ization. **S.A.A. Egorov:** Writing – review & editing, Methodology, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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