Wetting behavior of a colloidal particle trapped at a composite liquid-vapor interface of a binary liquid mixture

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A partially miscible binary liquid mixture, composed of *A* and *B* particles, is considered theoretically under conditions for which a stable *A*-rich liquid phase is in thermal equilibrium with the vapor phase. The *B*-rich liquid is metastable. The liquids and the thermodynamic conditions are chosen such that the interface between the *A*-rich liquid and the vapor contains an intervening wetting film of the *B*-rich phase. In order to obtain information about the large-scale fluid structure around a colloidal particle, which is trapped at such a composite liquid-vapor interface, three related and linked wetting phenomena at planar liquid-vapor, wall-liquid, and wall-vapor interfaces are studied analytically, using classical density functional theory in conjunction with the sharp-kink approximation for the number density profiles of the *A* and *B* particles. If in accordance with the so-called mixing rule the strength of the *A*-*B* interaction is given by the geometric mean of the strengths of the *A*-*A* and the *B*-*B* interactions, and similarly the ratio between the wall-*A* and the wall-*B* interaction, the scenario, in which the colloid is enclosed by a film of the *B*-rich liquid, can be excluded. Up to six distinct wetting scenarios are possible, if the above mixing rules for the fluid-wall and for the fluid-fluid interactions are relaxed. The way the space of system parameters is divided into domains corresponding to the six scenarios, and which of the domains actually appear, depends on the signs of the deviations from the mixing rule prescriptions. Relevant domains, corresponding, e.g., to the scenario in which the colloid is enclosed by a film of the *B*-rich liquid, emerge, if the ratio between the strengths of the wall-*A* and the wall-*B* interactions is reduced as compared to the mixing rule prescription, or if the strength of the *A*-*B* interaction is increased to values above the one from the mixing rule prescription. The range, within which the contact angle may vary inside the various domains, is also studied.

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I. INTRODUCTION

Interfaces involving fluids, i.e., fluid-fluid and fluid-wall (solid) interfaces, are very common and thus their study has received much interest for decades (see, e.g., Refs. [1,2]). In this context, wetting transitions are of particular interest [3]. Numerous studies have been devoted to the classification of the wetting behavior at individual, planar fluid-fluid and fluid-solid interfaces, including binary liquid mixtures [4–11]. Wetting in more complicated surface geometries [12–18] and at chemically inhomogeneous surfaces [19–22] has been extensively studied as well. In addition, premelting of ice [23] and wetting of a substrate [24] close to three-phase coexistence are of current interest. In these studies the adsorption equilibrium depends on the thicknesses of two intervening wetting layers.

Wetting-induced or fluid-mediated effective interactions between spherical particles [25,26] located inside a fluid are related topics, too. In the context of fluid interfaces, further studies are devoted to cylindrical particles approaching the interface between two coexisting liquid phases in binary liquid mixtures close to the critical point [27] or to colloidal particle located at the interface between two fluids [28,29]. We also mention a practical example in which a meniscus acts as a capillary filter for colloidal particles. The thickness of the liquid film on the surface of a solid object determines the effectivity of the filter, as demonstrated in recent experimental studies [30,31].

Despite numerous investigations concerning wetting of liquid-vapor and fluid-solid interfaces in binary liquid mixtures, a number of seemingly simple questions remain unanswered. For instance, considering a partially miscible binary liquid mixture, composed of *A* and *B* particles, one may think of the following scenario: A stable *A*-rich liquid phase in equilibrium and in contact with the vapor phase allows for the formation of a composite liquid-vapor interface containing an intervening film of the *B*-rich liquid phase, which is metastable in bulk. This scenario can be realized by properly selecting the liquids and by tuning the thermodynamic conditions. For such a setup one can pose the question as to what kind of fluid structures emerge if such a composite liquid-vapor interface meets a solid wall, for instance, the

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one provided by a large colloidal particle trapped at such an interface. A film of the *B*-rich phase at the liquid-vapor interface for instance could surround the colloidal particle completely. Alternatively, it could extend into the liquid α phase only, or only into the colloid-vapor interface, or it could disappear completely around the colloid. Here we are not interested in the detailed, molecular structure in close vicinity of the three-phase contact line; instead, we focus on the large-scale structures. Therefore, we can make use of studies for extended liquid-vapor and wall-fluid interfaces (see, e.g., Ref. [8]) and combine the results of those in order to develop a picture describing the entire scenario around a colloid at a composite liquid-vapor interface. In order to obtain analytical expressions, which are urgently needed in view of the many parameters involved, we use a reduced version of classical density functional theory (DFT) in which only the long-ranged van der Waals type of interactions are taken into account explicitly and in which the number density profiles are assumed to vary only steplike between their corresponding bulk values, which is known as the so-called sharp-kink approximation (see, e.g., Ref. [8]). The above scheme is designed to produce reasonably accurate free-energy differences of configurations involving wetting films with thicknesses above several times the diameter of the fluid particles. These are the configurations considered here. In order to reduce the number of cases to be considered, we assume certain inequalities for the number densities of the two components forming the three phases. They are satisfied for typical partially miscible liquids at liquid-vapor coexistence. The analytical results allow us to find the domains in the space of system parameters which correspond to the various conceivable wetting scenarios. We also analyze whether there are connections between these wetting domains and the contact angle, considered to be either smaller or larger than 90°. The aim of this study is also to provide a basis for a broader understanding of capillarity induced interactions between colloidal particles and eventually to design the self-assembly of colloidal particles at liquid-vapor interfaces.

II. MODEL

We consider a region of the bulk phase diagram of a binary liquid mixture, composed of *A* and *B* particles, in which the vapor phase (γ phase) coexists with a stable *A*-rich liquid phase (α phase), whereas the *B*-rich liquid phase (β phase) is metastable. We focus on the special situation in which the interface between the coexisting phases (i.e., the α-γ interface) is composite in the sense that between the α phase and the vapor a film of the β phase intrudes. The thermodynamic state is taken to be only slightly off α-β coexistence, such that the thickness of the β film is larger than a few molecular diameters and the β film can be treated like a genuine β phase.

Here, we analyze the kind of fluid structures which form if the composite liquid-vapor interface meets a solid wall. In this study we address the simple situation in which the composite liquid-vapor interface meets a *planar* solid wall, and we explore which of the conceivable wall-liquid and wall-vapor structures are compatible with the aforementioned composite liquid-vapor interface. We consider the wall-liquid (wall-α) interface, which is either wetted by a film of the β phase or, alternatively, is a plain interface without any wetting film, the wall-vapor (wall-γ) interface, which is either wetted by a β film or by an α film or is a plain interface without a wetting film. The issue as to what happens to the β film of the composite liquid-vapor interface once it meets the solid wall, can be resolved if one knows which combination of interfacial structures is realized for a given case. The type of structure which emerges depends on the fluid-fluid and the fluid-wall interactions as well as on the thermodynamic state. These parameters can be varied within certain limits imposed by the presupposed liquid-vapor interfacial structure. The results directly apply to the case in which the wall is the curved surface of a colloid. The linear size of the colloidal particle should exceed the thicknesses of the wetting films. In turn, the thicknesses of the films should be above several times the diameters of the fluid particles, otherwise the concepts used in the following discussion are not safely applicable. For molecular fluids this implies that the size of the colloidal particle should be tens of nanometers or larger. In our discussion, the shape of the particles does not play a particular role. We only assume that the curvature radii are in the same range as the particle size. Given that, curvature effects for interfacial tensions can be safely disregarded. The considered configurations are sketched in Fig. 1. In order to simplify these sketches and also the ones shown later in Fig. 2, there the liquid-vapor interface meets the wall at an angle of 90°. However, in our analysis, there is no assumption concerning the value of this angle; the actual angle is given by Young's contact angle.

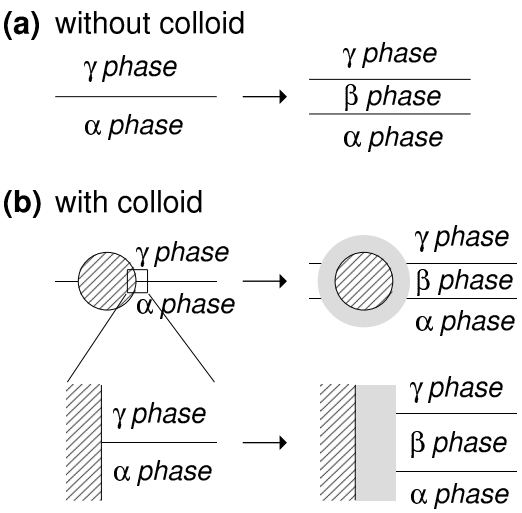

FIG. 1. A binary liquid mixture exhibits three fluid bulk phases: vapor (γ), an *A*-rich liquid (α), and a *B*-rich liquid (β). (a) Liquid-vapor interface in a binary liquid mixture which is wetted by the β phase. (b) The composite liquid-vapor interface from (a) meets the surface of a colloidal particle. In the gray area various interfacial structures are conceivable. The second row in (b) magnifies the structure within the square of the first row.

In order to rephrase the issue, it is our goal to find out which wall-vapor (wall-γ) interfacial structure and which wall-liquid (wall-α) interfacial structure are realized together for a certain fluid at given thermodynamic conditions and for a given wall, under the proposition that for the chosen fluid

and the given thermodynamic conditions the α-γ interface is a composite one with an intervening film of phase β. Moreover, we want to identify various domains in the space of system parameters, each of which can be related to a particular combination of the structures of the three interfaces involved. In order to proceed we make use of previous results [8] in which wetting of individual planar interfaces has been studied based on a simplified version of classical density functional theory (DFT). In these studies, long-ranged van der Waals type of interactions are treated explicitly within a mean-field approximation whereas other contributions to the free energy are treated within a local-density approximation. Furthermore, the so-called sharp-kink approximation has been used according to which the number densities of the A and B particles are considered to be piecewise constant and to vary discontinuously, at the interface positions, between their respective bulk values. The corresponding analytic expressions, which can be derived based on these approximations, contain the interaction parameters as well as the equilibrium number densities of the A and B particles in the various phases. These equilibrium number densities follow from minimizing the bulk free energy with respect to the bulk number densities. The equilibrium number densities depend on both the fluid-fluid interaction parameters as well as on the thermodynamic state (i.e., the thermodynamic variables). We do not try to express the equilibrium number densities in terms of the thermodynamic variables and the fluid-fluid interaction parameters, as this would require to introduce a specific expression for the free energy contribution, which is local in the densities. Instead, we introduce variables which combine interaction parameters and densities, and we identify various domains in the space of these parameters. In addition, we use knowledge and plausible assumptions concerning certain inequalities between the two number densities characterizing each of the phases and inequalities between the number densities in different phases.

For the long-ranged part of the fluid-fluid interaction we choose the Lennard-Jones potential $\tilde{w}_{ij}(\mathbf{r}) = 4\epsilon_{ij}[(a_{ij}/r)^{12} - (a_{ij}/r)^{6}]$ or, rather, in order to avoid spurious singularities in certain expressions, a modified (shifted) version of it: $\tilde{w}_{ij}(\mathbf{r}) = 4\epsilon_{ij}[(\frac{a_{ij}}{r+a_{ij}})^{12} - (\frac{a_{ij}}{r+a_{ij}})^{6}]$, where ϵ_{ij} and a_{ij} represent the interaction strengths and the length parameters for the interaction between the i and j components, respectively. For reasons of simplicity we assume that all length parameters are equal ($a_{AA} = a_{AB} = a_{BB}$). However, we provide an approximate mapping of the general case onto this specific case. This mapping is highly accurate for the scenarios to which our analysis applies. Thus, the relevant parameters describing the fluid-fluid interaction are the three interaction strengths ϵ_{AA}, ϵ_{AB}, and ϵ_{BB}. The interaction strength ϵ_{AB} between unlike particles is expressed in terms of those between the two sorts of like particles: $\epsilon_{AB} = \xi_f\sqrt{\epsilon_{AA}\epsilon_{BB}}$ for the fluid-fluid interactions [2,9,32,33]. The case of $\xi_f = 1$ is called the strict mixing rule [34–36]; simplified expressions for the dispersion forces give rise to the strict mixing rule. Similar expressions can be put forward for the strengths of the interactions between a wall particle and a fluid particle of sort A or B, respectively; i.e., $\epsilon_{wA} = \xi_{wA}\sqrt{\epsilon_{ww}\epsilon_{AA}}$ and $\epsilon_{wB} = \xi_{wB}\sqrt{\epsilon_{ww}\epsilon_{BB}}$. Introducing $\xi_w = \xi_{wA}/\xi_{wB}$, the ratio between the wall-A and the wall-B interaction can be expressed as $\epsilon_{wA}/\epsilon_{wB} = \xi_w\sqrt{\epsilon_{AA}/\epsilon_{BB}}$. Again, the case $\xi_w = 1$ is called the strict mixing rule for the fluid-wall interaction. We first assume that the strict mixing rules apply to both the fluid-fluid and the fluid-wall interactions, which cuts in half the dimension of the parameter space. We then identify domains in the space of reduced parameters such that each domain represents a particular combination of the structures of the three interfaces involved. Next, we relax the strict mixing rules and keep track of the consequences for the map of domains. Before presenting in the next section the map of domains, in the next two subsections we provide the presently available results for the three different interfaces and express them in a form which is suitable for our discussion.

A. Planar liquid-vapor interface

In order to determine the conditions for which a planar α-γ interface is wetted by a film of the β phase, we introduce a wetting parameter $W_{\alpha\beta\gamma}$ defined as

$$W_{\alpha\beta\gamma} := \sigma_{\alpha\beta\gamma} - \sigma_{\alpha\gamma}, \tag{1}$$

where $\sigma_{\alpha\beta\gamma}$ is the surface free energy (surface tension) of a composite configuration in which an intervening wetting film of the β phase occurs at the α-γ interface; $\sigma_{\alpha\gamma}$ is the surface free energy (surface tension) of a plain configuration in which such a film is absent. If $W_{\alpha\beta\gamma} < 0$, the stable configuration is the one in which the α-γ interface is wetted by a film of the β phase. Otherwise, if $W_{\alpha\beta\gamma} > 0$, the liquid ($\alpha$ phase) and the vapor (γ phase) are in direct spatial contact and the α-γ interface is a plain one without an intruding β film.

We now follow the discussion in Ref. [8] and first separate the grand canonical potential functional Ω into a bulk (b) and a surface (s) contribution:

$$\Omega[\{\rho_i(\mathbf{r})\}, T, \{\mu_i\}] = V\Omega_b + S\Omega_s, \tag{2}$$

where $i = A$ and B denote the two types of fluid particles and V and S denote the volume and the surface area, respectively; T is the temperature, and μ_i is the chemical potential of species i. In the next step, the surface contribution to the grand canonical potential for a composite configuration of the α-γ interface with an intruding film of the β phase can be written as

$$\Omega_s^{\alpha\beta\gamma}(l) = l(\Omega^\beta - \Omega^\gamma) + \omega_{\alpha\beta\gamma}(l) + \sigma_{\alpha\beta} + \sigma_{\beta\gamma}. \tag{3}$$

The first term in Eq. (3) is the bulk free energy needed to replace a slab of thickness l of the γ phase by the β phase. The second term in Eq. (3) is the correction to the surface free energy due to the finite thickness l of the slab. The terms $\sigma_{\alpha\beta}$ and $\sigma_{\beta\gamma}$ denote the surface tensions of plain interfaces between the bulk phases α, β and β, γ, respectively.

In thermal equilibrium the thickness l of the slab of the β phase attains its equilibrium value $l_{\alpha\beta\gamma}$. The surface tension of the composite configuration, i.e., the first term in Eq. (1), is determined in terms of this equilibrium configuration by

$$\begin{aligned}\sigma_{\alpha\beta\gamma} &= \min_{\{\rho_i(\mathbf{r})\}} \Omega_s^{\alpha\beta\gamma}[\{\rho_i(\mathbf{r})\}, T, \{\mu_i\}] \\ &= \min_{l} \Omega_s^{\alpha\beta\gamma}(l, T, \{\mu_i\}) \\ &= \Omega_s^{\alpha\beta\gamma}(l_{\alpha\beta\gamma}, T, \{\mu_i\})\end{aligned} \tag{4}$$

and

$$\left.\frac{\partial \Omega_{\rm s}^{\alpha\beta\gamma}(l)}{\partial l}\right|_{l=l_{\alpha\beta\gamma}} = 0. \tag{5}$$

(Note that $\Omega_{\rm s}^{\alpha\beta\gamma}[\{\rho_i(\mathbf{r})\}]$ and $\Omega_{\rm s}^{\alpha\beta\gamma}(l)$ are distinct functionals and functions, respectively, as indicated by their arguments.) It should be stressed that $l_{\alpha\beta\gamma}$ is a solution of Eq. (5) corresponding to a minimum of the free energy. Furthermore, the subdivision of the free energy used in Eq. (3) is applicable only if $l_{\alpha\beta\gamma}$ is sufficiently large such that the β film can be treated like a piece of genuine β phase. By inserting Eqs. (3) and (4) into Eq. (1), the wetting parameter defined in Eq. (1) for the α-γ interface can be expressed as

$$\begin{aligned} W_{\alpha\beta\gamma} =& l_{\alpha\beta\gamma}(\Omega^{\beta} - \Omega^{\gamma}) + \omega_{\alpha\beta\gamma}(l_{\alpha\beta\gamma}) \\ &+ \sigma_{\alpha\beta} + \sigma_{\beta\gamma} - \sigma_{\alpha\gamma}. \end{aligned} \tag{6}$$

Further, using Eq. (3) one can rewrite Eq. (5) as

$$\Omega^{\beta} - \Omega^{\gamma} = -\left.\frac{\partial \omega_{\alpha\beta\gamma}(l)}{\partial l}\right|_{l=l_{\alpha\beta\gamma}}. \tag{7}$$

From here onwards the sharp-kink approximation is used. Within this approximation the following expressions are obtained for $\omega_{\alpha\beta\gamma}(l)$ and the interfacial tensions of the various plain interfaces:

$$\omega_{\alpha\beta\gamma}(l) = -\sum_{i,j}(\rho_{i,\alpha} - \rho_{i,\beta})(\rho_{j,\beta} - \rho_{j,\gamma})\int_{l}^{\infty} dy\, t_{ij}(y), \tag{8}$$

$$\sigma_{\alpha\beta} = -\frac{1}{2}\sum_{i,j}(\rho_{i,\alpha} - \rho_{i,\beta})(\rho_{j,\alpha} - \rho_{j,\beta})\int_{0}^{\infty} dy\, t_{ij}(y), \tag{9}$$

$$\sigma_{\beta\gamma} = -\frac{1}{2}\sum_{i,j}(\rho_{i,\beta} - \rho_{i,\gamma})(\rho_{j,\beta} - \rho_{j,\gamma})\int_{0}^{\infty} dy\, t_{ij}(y), \tag{10}$$

and

$$\sigma_{\alpha\gamma} = -\frac{1}{2}\sum_{i,j}(\rho_{i,\alpha} - \rho_{i,\gamma})(\rho_{j,\alpha} - \rho_{j,\gamma})\int_{0}^{\infty} dy\, t_{ij}(y), \tag{11}$$

respectively, where

$$t_{ij}(y) = \int_{y}^{\infty} dx \int d^2\mathbf{r}_{\parallel}\, \tilde{w}_{ij}\left[\left(\mathbf{r}_{\parallel}^2 + x^2\right)^{\frac{1}{2}}\right].$$

Here, i and j denote the species A and B forming the binary liquid mixture and $\rho_{i,\zeta}$ is the number density of particles of species i in the bulk phase $\zeta = \alpha,\ \beta,$ and γ.

Regular analytic expressions are obtained by replacing in Eqs. (9)–(11), for the long-ranged part $\tilde{w}_{ij}(\mathbf{r})$ of the fluid-fluid interaction, the simple Lennard-Jones potential by its shifted version:

$$\tilde{w}_{ij}(\mathbf{r}) = 4\epsilon_{ij}\left[\left(\frac{a_{ij}}{r + a_{ij}}\right)^{12} - \left(\frac{a_{ij}}{r + a_{ij}}\right)^{6}\right], \tag{12}$$

where ϵ_{ij} and a_{ij} denote the strength of the interaction energy and the length parameters for the interactions between the components i and j. In order to evaluate Eq. (8) we use the additional assumption $l \gg a_{ij}$, which is justified by the above requirement of a sufficiently thick β film. Eventually the following results are obtained:

$$\begin{aligned} \omega_{\alpha\beta\gamma}(l) =& \pi\sum_{i,j}\left\{\epsilon_{ij}a_{ij}^4(\rho_{i,\alpha} - \rho_{i,\beta})(\rho_{j,\beta} - \rho_{j,\gamma})\right. \\ &\left.\times\left[\frac{1}{3}\left(\frac{a_{ij}}{l}\right)^2 - \frac{4}{5}\left(\frac{a_{ij}}{l}\right)^3\right]\right\}, \end{aligned} \tag{13}$$

$$\sigma_{\alpha\beta} = \frac{13}{132}\pi\sum_{i,j}\epsilon_{ij}a_{ij}^4(\rho_{i,\alpha} - \rho_{i,\beta})(\rho_{j,\alpha} - \rho_{j,\beta}), \tag{14}$$

$$\sigma_{\beta\gamma} = \frac{13}{132}\pi\sum_{i,j}\epsilon_{ij}a_{ij}^4(\rho_{i,\beta} - \rho_{i,\gamma})(\rho_{j,\beta} - \rho_{j,\gamma}), \tag{15}$$

and

$$\sigma_{\alpha\gamma} = \frac{13}{132}\pi\sum_{i,j}\epsilon_{ij}a_{ij}^4(\rho_{i,\alpha} - \rho_{i,\gamma})(\rho_{j,\alpha} - \rho_{j,\gamma}). \tag{16}$$

Due to Eq. (13), we can rewrite Eq. (7) as

$$\begin{aligned} \Omega^{\beta} - \Omega^{\gamma} =& \pi\sum_{i,j}\left\{\epsilon_{ij}a_{ij}^3(\rho_{i,\alpha} - \rho_{i,\beta})(\rho_{j,\beta} - \rho_{j,\gamma})\right. \\ &\left.\times\left[\frac{2}{3}\left(\frac{a_{ij}}{l_{\alpha\beta\gamma}}\right)^3 - \frac{12}{5}\left(\frac{a_{ij}}{l_{\alpha\beta\gamma}}\right)^4\right]\right\}. \end{aligned} \tag{17}$$

Using Eqs. (13)–(17), Eq. (6) for $W_{\alpha\beta\gamma}$ can be rewritten as

$$W_{\alpha\beta\gamma} = \pi\sum_{i,j}\epsilon_{ij}a_{ij}^4(\rho_{i,\beta} - \rho_{i,\alpha})(\rho_{j,\beta} - \rho_{j,\gamma})F_{ij}(l_{\alpha\beta\gamma}), \tag{18}$$

where

$$F_{ij}(l) = \frac{13}{66} - \left(\frac{a_{ij}}{l}\right)^2 + \frac{16}{5}\left(\frac{a_{ij}}{l}\right)^3, \tag{19}$$

and $l_{\alpha\beta\gamma}$ is the equilibrium thickness of the β film intruding the α-γ interface.

If the components A and B of the binary liquid mixture have equal molecular radii, the length parameters in Eq. (12) are all equal, i.e., $a_{AA} = a_{AB} = a_{BB}$. In this case Eq. (18) reduces to

$$W_{\alpha\beta\gamma} = \pi a_{AA}^4 S_{\alpha\beta\gamma}F_{AA}(l_{\alpha\beta\gamma}), \tag{20}$$

where

$$\begin{aligned} S_{\alpha\beta\gamma} =& (\rho_{A,\beta} - \rho_{A,\alpha})(\rho_{A,\beta} - \rho_{A,\gamma})\epsilon_{AA} \\ &+ (\rho_{A,\beta} - \rho_{A,\alpha})(\rho_{B,\beta} - \rho_{B,\gamma})\epsilon_{AB} \\ &+ (\rho_{B,\beta} - \rho_{B,\alpha})(\rho_{A,\beta} - \rho_{A,\gamma})\epsilon_{BA} \\ &+ (\rho_{B,\beta} - \rho_{B,\alpha})(\rho_{B,\beta} - \rho_{B,\gamma})\epsilon_{BB}. \end{aligned} \tag{21}$$

The sign of $F_{AA}(l_{\alpha\beta\gamma})$ in Eq. (20) is always positive if $l_{\alpha\beta\gamma} > 0$ [see Eq. (19), actually the relation $l_{\alpha\beta\gamma} \gg a$ should hold, otherwise there is no composite interface]. The sign of $W_{\alpha\beta\gamma}$ is therefore entirely determined by the sign of $S_{\alpha\beta\gamma}$, which depends on the bulk number densities of the two species in the various phases and on the three interaction strengths. If $S_{\alpha\beta\gamma} < 0$, the stable configuration is a composite α-γ interface with an intruding β film between the α and the γ phase. If $S_{\alpha\beta\gamma} > 0$, the stable configuration is a plain α-γ interface.

Equations (20) and (21) can be generalized to the case in which the length parameters are not all equal, if one takes into

account the fact that the functions F_{ij} are not very sensitive to the actual values of the length parameters in cases in which the film thicknesses exceed several diameters of the fluid particles; this is the range of film thicknesses to which our study applies. For example, for a film thickness of 10 times the diameters of a fluid particle A (a_{AA}), F_{ij} varies by only a few percent if the length parameter is varied by a factor of 2. Therefore, it is a good approximation to replace the various functions F_{ij} by just one function F_{AA}. Using this approximation, Eq. (20) remains intact, if in Eq. (21) one introduces rescaled interaction strengths

$$\bar{\epsilon}_{ij} = (a_{ij}/a_{AA})^4 \epsilon_{ij}$$

instead of the original ϵ_{ij}.

In order to obtain a statement concerning the sign of $S_{\alpha\beta\gamma}$, we inspect the various contributions in Eq. (21). First, all interaction strengths ϵ_{AA}, ϵ_{AB}, and ϵ_{BB} are positive. The prefactors may be positive or negative depending on the relations between the various number densities. Since the β phase is a liquid phase, the γ phase is vapor, and the number densities in the liquid phases are much higher than in the vapor (at least away from the critical point), and $\rho_{B,\beta} - \rho_{B,\gamma}$ is always positive. Typically, $\rho_{A,\beta} - \rho_{A,\gamma}$ should be positive as well. On the other hand, because by definition the β phase is a B-rich phase, it cannot be excluded that the component A is very diluted in the β phase but present in a much higher concentration in the vapor, such that $\rho_{A,\beta} - \rho_{A,\gamma}$ could be negative. We exclude such exceptional cases from our discussion and always assume in the following that $\rho_{A,\beta} - \rho_{A,\gamma}$ is positive.

Next, we consider the sign of $\rho_{A,\beta} - \rho_{A,\alpha}$ and $\rho_{B,\beta} - \rho_{B,\alpha}$. The possibility that $\rho_{A,\beta} - \rho_{A,\alpha} > 0$ and $\rho_{B,\beta} - \rho_{B,\alpha} > 0$ would result in a positive sign of $S_{\alpha\beta\gamma}$, irrespective of the values of the interaction strengths. This case is not of interest to our present study because it excludes the occurrence of an intervening β film at the liquid-vapor interface. In the following we consider the case $\rho_{A,\beta} - \rho_{A,\alpha} < 0$ and $\rho_{B,\beta} - \rho_{B,\alpha} > 0$. In this case the sign of $S_{\alpha\beta\gamma}$ depends on the values of the interaction strengths and the magnitude of the density differences. A case in which both $\rho_{A,\beta} - \rho_{A,\alpha} < 0$ and $\rho_{B,\beta} - \rho_{B,\alpha} < 0$, which would always lead to a negative sign of $S_{\alpha\beta\gamma}$, we consider as an untypical case for a liquid-liquid mixture. In this case $\rho_{B,\beta} < \rho_{B,\alpha}$, i.e., the number density of the B particles in the B-rich β phase would be smaller than the number density of the B particles in the A-rich α phase. This would require that the total number density in the α phase is substantially higher than the one in the β phase and that the β phase is only marginally rich in B particles and the α phase only marginally rich in A particles. The remaining case $\rho_{A,\beta} - \rho_{A,\alpha} > 0$ and $\rho_{B,\beta} - \rho_{B,\alpha} < 0$ is not possible. This can be seen as follows. The definition of the A-rich α phase implies $\rho_{A,\alpha} > \rho_{B,\alpha}$. Next, we use the first of the two conditions, i.e., $\rho_{A,\beta} - \rho_{A,\alpha} > 0$, which leads to the sequence $\rho_{A,\beta} > \rho_{A,\alpha} > \rho_{B,\alpha}$ of inequalities. Finally, using the definition of the B-rich β phase, i.e., $\rho_{B,\beta} > \rho_{A,\beta}$, one obtains $\rho_{B,\beta} > \rho_{A,\beta} > \rho_{A,\alpha} > \rho_{B,\alpha}$, i.e., $\rho_{B,\beta} - \rho_{B,\alpha} > 0$, which is in contradiction to the second of the two conditions, which means that both conditions cannot be satisfied together. To conclude the above discussion, from here onwards the following inequalities between the various number densities are assumed:

$$\begin{aligned} &\rho_{A,\alpha} > \rho_{A,\beta}, \quad \rho_{B,\alpha} < \rho_{B,\beta}, \\ &\rho_{A,\beta} > \rho_{A,\gamma}, \quad \text{and} \quad \rho_{B,\beta} > \rho_{B,\gamma}. \end{aligned} \tag{22}$$

Now, given the inequalities in Eq. (22), the sign of $S_{\alpha\beta\gamma}$ is studied. First, the (rescaled) interaction parameter ϵ_{AB} ($\bar{\epsilon}_{AB}$) between unlike particles is expressed in terms of the corresponding ones between like particles ϵ_{AA} and ϵ_{BB} ($\bar{\epsilon}_{AA}$ and $\bar{\epsilon}_{BB}$) as

$$\epsilon_{AB} = \xi_f \sqrt{\epsilon_{AA}\epsilon_{BB}} \qquad (\bar{\epsilon}_{AB} = \bar{\xi}_f \sqrt{\bar{\epsilon}_{AA}\bar{\epsilon}_{BB}}), \tag{23}$$

with $\xi_f > 0$ ($\bar{\xi}_f > 0$); the bracketed part of Eq. (23) applies to the general case and defines a modified "mixing parameter" $\bar{\xi}_f$, where $\bar{\xi}_f = (a_{AB}/a_{AA})^2 (a_{AB}/a_{BB})^2 \xi_f$. Next, we introduce the dimensionless variable

$$X = \frac{\rho_{B,\beta}}{\rho_{A,\beta}} \sqrt{\frac{\epsilon_{BB}}{\epsilon_{AA}}} \qquad \left(\bar{X} = \frac{\rho_{B,\beta}}{\rho_{A,\beta}} \sqrt{\frac{\bar{\epsilon}_{BB}}{\bar{\epsilon}_{AA}}} \right), \tag{24}$$

which characterizes the relative strengths of the (rescaled) A-A and the (rescaled) B-B interactions, weighted according to the abundance of the two species in the β phase. X ($\bar{X}$) is always positive. In the following we do not distinguish X and $\bar{X}$ or ξ_f and $\bar{\xi}_f$; X always can be understood as representing also $\bar{X}$ and ξ_f as representing $\bar{\xi}_f$. Using Eq. (23) and the dimensionless variable X, Eq. (21) can be expressed as

$$\begin{aligned} S_{\alpha\beta\gamma} = \epsilon_{AA} \rho_{A,\beta}^2 \Bigg[&\left(1 - \frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right)\left(1 - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right) X^2 \\ &+ \left(1 - \frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right)\left(1 - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right) \xi_f X \\ &+ \left(1 - \frac{\rho_{A,\alpha}}{\rho_{A,\beta}}\right)\left(1 - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right) \xi_f X \\ &+ \left(1 - \frac{\rho_{A,\alpha}}{\rho_{A,\beta}}\right)\left(1 - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right) \Bigg]. \end{aligned} \tag{25}$$

Based on Eq. (25), the range of X is determined for which $S_{\alpha\beta\gamma} < 0$ (see Appendix A). Equivalently, one can state that at a planar α-γ interface a β film can occur if X is in the range

$$\begin{aligned} 0 < X < &\sqrt{\left[\frac{\xi_f}{2}(D_{\alpha\beta} + D_{\beta\gamma})\right]^2 - D_{\alpha\beta} D_{\beta\gamma}} \\ &+ \frac{\xi_f}{2}(D_{\alpha\beta} + D_{\beta\gamma}), \end{aligned} \tag{26}$$

where

$$D_{\alpha\beta} = \left(\frac{\rho_{A,\alpha}}{\rho_{A,\beta}} - 1\right) \Big/ \left(1 - \frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right) \tag{27}$$

and

$$D_{\beta\gamma} = \left(1 - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right) \Big/ \left(\frac{\rho_{B,\gamma}}{\rho_{B,\beta}} - 1\right). \tag{28}$$

Otherwise, given the inequalities in Eq. (22), no β film can occur at the planar α-γ interface. In the case that the strict mixing rule applies ($\xi_f = 1$), the condition in Eq. (26) for the occurrence of a β film reduces to [note that the inequalities in Eq. (22) imply $D_{\alpha\beta} > 0$ and $D_{\beta\gamma} < 0$]

$$0 < X < D_{\alpha\beta}.$$

B. Planar wall-fluid interfaces

In analogy to Eq. (1) we introduce three additional wetting parameters, the signs of which determine whether a configuration with an intruding wetting film at the wall-α or the wall-γ interface, respectively, has a lower free energy than the corresponding one without such a wetting film. The configurations considered are a β film wetting the wall-α interface, a β film wetting the wall-γ interface, and an α film wetting the wall-γ interface. The corresponding three wetting parameters $W_{w\beta\alpha}$, $W_{w\beta\gamma}$, and $W_{w\alpha\gamma}$ are given by

$$W_{w\beta\alpha} = \sigma_{w\beta\alpha} - \sigma_{w\alpha}, \tag{29}$$

$$W_{w\beta\gamma} = \sigma_{w\beta\gamma} - \sigma_{w\gamma}, \tag{30}$$

and

$$W_{w\alpha\gamma} = \sigma_{w\alpha\gamma} - \sigma_{w\gamma}. \tag{31}$$

Here, w represents the wall; $\sigma_{w\beta\alpha}$ is the surface tension (surface free energy) of the wall-α interface which is wetted by a β film; $\sigma_{w\beta\gamma}$ and $\sigma_{w\alpha\gamma}$ are the surface tensions (surface free energies) of the wall-γ interface which is wetted by a β or an α film, respectively; $\sigma_{w\alpha}$ and $\sigma_{w\gamma}$ are the surface tensions (surface free energies) of the wall-α and the wall-γ interface, respectively, without any intruding wetting film. If $W_{w\beta\alpha} < 0$, the wall-α interface is wetted by the β phase. If $W_{w\beta\gamma} < 0$, it is more favorable to have a film of the β phase at the wall-γ interface than to have a direct wall-γ contact without an intruding wetting film. If $W_{w\alpha\gamma} < 0$, a wetting film of the α phase at the wall-γ interface is more favorable than a direct wall-γ contact. Additional considerations might be necessary in order to decide whether wetting of a wall-γ interface by a film of the β phase or by a film of the α phase renders the more favorable configuration.

By using the shifted Lennard-Jones potential [see Eq. (12)] for the fluid-fluid interaction $\tilde{w}_{ij}(\mathbf{r})$, and also for the fluid-wall interaction potential $\tilde{v}_i(\mathbf{r})$,

$$\tilde{v}_i(\mathbf{r}) = 4\epsilon_{wi}\left[\left(\frac{a_{wi}}{r + a_{wi}}\right)^{12} - \left(\frac{a_{wi}}{r + a_{wi}}\right)^{6}\right], \tag{32}$$

with the length parameters a_{wi} and the strengths ϵ_{wi} of the wall-i interactions, the above wetting parameters can be expressed as (see Appendix B)

$$W_{w\beta\alpha} = \pi \sum_{i,j} (\rho_{i,\beta} - \rho_{i,\alpha})\left[\epsilon_{ij} a_{ij}^4 \rho_{j,\beta} F_{ij}(l_{w\beta\alpha}) - \delta_{ij}\epsilon_{wi} a_{wi}^4 \rho_w F_{wi}(l_{w\beta\alpha})\right], \tag{33}$$

$$W_{w\beta\gamma} = \pi \sum_{i,j} (\rho_{i,\beta} - \rho_{i,\gamma})\left[\epsilon_{ij} a_{ij}^4 \rho_{j,\beta} F_{ij}(l_{w\beta\gamma}) - \delta_{ij}\epsilon_{wi} a_{wi}^4 \rho_w F_{wi}(l_{w\beta\gamma})\right], \tag{34}$$

and

$$W_{w\alpha\gamma} = \pi \sum_{i,j} (\rho_{i,\alpha} - \rho_{i,\gamma})\left[\epsilon_{ij} a_{ij}^4 \rho_{j,\alpha} \hat{F}_{ij}(l_{w\alpha\gamma}) - \delta_{ij}\epsilon_{wi} a_{wi}^4 \rho_w \hat{F}_{wi}(l_{w\alpha\gamma})\right], \tag{35}$$

respectively, where i, j represent the fluid components A and B, δ_{ij} is the Kronecker symbol, $F_{ij}(l)$ is defined in Eq. (19), and $F_{wi}(l)$ is defined by the same equation but with the length parameters a_{wi}. The functions $\hat{F}_{ij}(l)$ and $\hat{F}_{wi}(l)$ in Eq. (35) are defined by

$$\hat{F}_{ij}(l) = \frac{13}{66} - \frac{1}{3}\left(\frac{a_{ij}}{l}\right)^2 + \frac{4}{5}\left(\frac{a_{ij}}{l}\right)^3; \tag{36}$$

the functional form of $\hat{F}_{wi}(l)$ is the same but with the length parameters a_{wi}. Here, $l_{w\beta\alpha}$ is the equilibrium thickness of the intruding β film at the wall-α interface and $l_{w\beta\gamma}$ ($l_{w\alpha\gamma}$) is the equilibrium thickness of the intruding β (α) film at the wall-γ interface. (We only consider films with thicknesses much larger than the length parameters of the interactions.)

If the length parameters of all interactions, i.e., the ones between the components A and B of the binary liquid mixture and those between the two components and the wall, are all equal, i.e., $a_{AA} = a_{AB} = a_{BB} = a_{wA} = a_{wB}$, Eqs. (33)–(35) reduce to

$$W_{w\beta\alpha} = \pi a_{AA}^4 S_{w\beta\alpha} F_{AA}(l_{w\beta\alpha}), \tag{37}$$

$$W_{w\beta\gamma} = \pi a_{AA}^4 S_{w\beta\gamma} F_{AA}(l_{w\beta\gamma}), \tag{38}$$

and

$$W_{w\alpha\gamma} = \pi a_{AA}^4 S_{w\alpha\gamma} \hat{F}_{AA}(l_{w\alpha\gamma}), \tag{39}$$

where

$$\begin{aligned} S_{w\beta\alpha} = {} & (\rho_{A,\beta} - \rho_{A,\alpha})(\epsilon_{AA}\rho_{A,\beta} - \epsilon_{wA}\rho_w) \\ & + (\rho_{A,\beta} - \rho_{A,\alpha})(\epsilon_{AB}\rho_{B,\beta}) \\ & + (\rho_{B,\beta} - \rho_{B,\alpha})(\epsilon_{BA}\rho_{A,\beta}) \\ & + (\rho_{B,\beta} - \rho_{B,\alpha})(\epsilon_{BB}\rho_{B,\beta} - \epsilon_{wB}\rho_w), \end{aligned} \tag{40}$$

$$\begin{aligned} S_{w\beta\gamma} = {} & (\rho_{A,\beta} - \rho_{A,\gamma})(\epsilon_{AA}\rho_{A,\beta} - \epsilon_{wA}\rho_w) \\ & + (\rho_{A,\beta} - \rho_{A,\gamma})(\epsilon_{AB}\rho_{B,\beta}) \\ & + (\rho_{B,\beta} - \rho_{B,\gamma})(\epsilon_{BA}\rho_{A,\beta}) \\ & + (\rho_{B,\beta} - \rho_{B,\gamma})(\epsilon_{BB}\rho_{B,\beta} - \epsilon_{wB}\rho_w), \end{aligned} \tag{41}$$

and

$$\begin{aligned} S_{w\alpha\gamma} = {} & (\rho_{A,\alpha} - \rho_{A,\gamma})(\epsilon_{AA}\rho_{A,\alpha} - \epsilon_{wA}\rho_w) \\ & + (\rho_{A,\alpha} - \rho_{A,\gamma})(\epsilon_{AB}\rho_{B,\alpha}) \\ & + (\rho_{B,\alpha} - \rho_{B,\gamma})(\epsilon_{BA}\rho_{A,\alpha}) \\ & + (\rho_{B,\alpha} - \rho_{B,\gamma})(\epsilon_{BB}\rho_{B,\alpha} - \epsilon_{wB}\rho_w). \end{aligned} \tag{42}$$

The signs of the various wetting parameters in Eqs. (37)–(39) and thus the structures of the wall-α and the wall-γ interfaces are determined by the signs of the various quantities S given by Eqs. (40)–(42) because F_{AA} and $\hat{F}_{AA}$ are positive within the range of film thicknesses of interest [see Eqs. (19) and (36)]. The signs of the various quantities S depend on various differences between bulk densities and on the strengths of the interactions. As discussed above we only consider binary liquid mixtures and conditions such that the inequalities in Eq. (22) between the number densities of the two species in different phases hold. In order to identify the regions in the parameter space corresponding to a negative or a positive sign of the various wetting parameters, we use the notation already introduced in the description of our model. We write $\epsilon_{AB} = \xi_f\sqrt{\epsilon_{AA}\epsilon_{BB}}$, $\epsilon_{wA} = \xi_{wA}\sqrt{\epsilon_{ww}\epsilon_{AA}}$, and $\epsilon_{wB} = \xi_{wB}\sqrt{\epsilon_{ww}\epsilon_{BB}}$. Introducing $\xi_w = \xi_{wA}/\xi_{wB}$ the ratio

between the wall-A and the wall-B interaction can be expressed as $\epsilon_{wA}/\epsilon_{wB} = \xi_w\sqrt{\epsilon_{AA}/\epsilon_{BB}}$. The case $\xi_f = 1$ ($\xi_w = 1$) is called the strict fluid-fluid (fluid-wall) mixing rule.

In order to complete the approximate mapping of the general case onto the specific case, we again replace the various functions F_{ij} by one function F_{AA} as well as the functions $\hat{F}_{ij}$ by just one function $\hat{F}_{AA}$. Furthermore, once the rescaled interaction strengths $\bar{\epsilon}_{wi} = (a_{wi}/a_{AA})^4\epsilon_{wi}$ and the modified "mixing parameter" $\bar{\epsilon}_{wA}/\bar{\epsilon}_{wB} = \bar{\xi}_w\sqrt{\bar{\epsilon}_{AA}/\bar{\epsilon}_{BB}}$, with $\bar{\xi}_w = (a_{BB}/a_{AA})^2(a_{wA}/a_{wB})^4\xi_w$, are introduced, the equations derived for the special case remain unchanged if they are expressed in terms of the rescaled quantities.

We now consider the reduced space spanned by the two dimensionless variables $X = (\rho_{B,\beta}/\rho_{A,\beta})\sqrt{\epsilon_{BB}/\epsilon_{AA}}$ [$\bar{X} = (\rho_{B,\beta}/\rho_{A,\beta})\sqrt{\bar{\epsilon}_{BB}/\bar{\epsilon}_{AA}}$ in the general case, see Eq. (24)] and

$$Y = \frac{\rho_w}{\rho_{A,\beta}}\frac{\epsilon_{wA}}{\epsilon_{AA}} \qquad \left(\bar{Y} = \frac{\rho_w}{\rho_{A,\beta}}\frac{\bar{\epsilon}_{wA}}{\bar{\epsilon}_{AA}}\right), \tag{43}$$

characterizing the parameter space of the system; one has $X > 0$ ($\bar{X} > 0$) and $Y > 0$ ($\bar{Y} > 0$). X ($\bar{X}$) characterizes the relative strengths of the (rescaled) A-A and the (rescaled) B-B interactions in the β phase, Y ($\bar{Y}$) gives the relative strengths of the (rescaled) wall-A interaction and the (rescaled) A-A interaction in the β phase. The two additional parameters ξ_f and ξ_w ($\bar{\xi}_f$ and $\bar{\xi}_w$) eventually determine how the reduced parameter space (X, Y) or $(\bar{X}, \bar{Y})$ is subdivided into various "wetting domains". In the following X, Y, ξ_f, and ξ_w should be always understood as representing $\bar{X}$, $\bar{Y}$, $\bar{\xi}_f$, and $\bar{\xi}_w$, respectively, if the equations and figures are applied to the general case. In the general case the modified strict mixing rules $\bar{\xi}_f = 1$ and $\bar{\xi}_w = 1$ refer to the relations between the rescaled interaction strengths, which means that the original interaction strengths, in general, do not obey the strict mixing rules. We divide the (X, Y) parameter space, for each wall-fluid interface separately, into regions within which the wall is wetted by an intruding phase (wet state) and regions within which there is no intruding phase (nonwet state) (see Appendix C).

The planar wall-α interface is wetted by a β film ($S_{w\beta\alpha} < 0$) if

$$\begin{aligned} &0 < X < \xi_w D_{\alpha\beta} \quad \text{and} \\ &0 < Y < X + 1 + (\xi_w - 1)\frac{X}{(X - \xi_w D_{\alpha\beta})}(X + 1) \\ &\quad + \xi_w(\xi_f - 1)(1 - D_{\alpha\beta})\frac{X}{(X - \xi_w D_{\alpha\beta})} \end{aligned} \tag{44}$$

or if

$$\begin{aligned} &X > \xi_w D_{\alpha\beta} \quad \text{and} \\ &Y > X + 1 + (\xi_w - 1)\frac{X}{(X - \xi_w D_{\alpha\beta})}(X + 1) \\ &\quad + \xi_w(\xi_f - 1)(1 - D_{\alpha\beta})\frac{X}{(X - \xi_w D_{\alpha\beta})} \end{aligned} \tag{45}$$

[with $D_{\alpha\beta}$ as given in Eq. (27)]. Otherwise, the wall is in direct contact with the α phase without an intruding film of the β phase.

A wall-γ interface which is wetted by an intervening β film is more favorable than a wall-γ interface without any wetting film ($S_{w\beta\gamma} < 0$) if

$$\begin{aligned} &X > 0 \quad \text{and} \\ &Y > X + 1 + (\xi_w - 1)\frac{X}{(X - \xi_w D_{\beta\gamma})}(X + 1) \\ &\quad + \xi_w(\xi_f - 1)(1 - D_{\beta\gamma})\frac{X}{(X - \xi_w D_{\beta\gamma})} \end{aligned} \tag{46}$$

[with $D_{\beta\gamma}$ as given in Eq. (28)]. Otherwise, the wall which is in direct contact with the γ phase, i.e., without a β film gives rise to a lower free energy.

A wall-γ interface which is wetted by an intruding α film is more favorable than a wall-γ interface without any wetting film ($S_{w\alpha\gamma} < 0$) if

$$\begin{aligned} &X > 0 \quad \text{and} \\ &Y > \frac{\rho_{B,\alpha}}{\rho_{B,\beta}}X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} \\ &\quad + (\xi_w - 1)\frac{X}{(X - \xi_w D_{\alpha\gamma})}\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}}\right) \\ &\quad + \xi_w(\xi_f - 1)\left(\frac{\rho_{A,\alpha}}{\rho_{A,\beta}} - \frac{\rho_{B,\alpha}}{\rho_{B,\beta}}D_{\alpha\gamma}\right)\frac{X}{(X - \xi_w D_{\alpha\gamma})}, \end{aligned} \tag{47}$$

where

$$D_{\alpha\gamma} = \left(\frac{\rho_{A,\alpha}}{\rho_{A,\beta}} - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\Big/\left(\frac{\rho_{B,\gamma}}{\rho_{B,\beta}} - \frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right). \tag{48}$$

Otherwise, the wall which is in direct contact with the γ phase, i.e., without an α film, leads to a lower free energy. In regions, in which wetting of the wall-γ interface with both a film of the β phase and a film of the α phase is more favorable than a configuration without any wetting film, a direct comparison of these two wetting scenarios is required. This is discussed below.

III. DISCUSSION

A. Colloid particle at a composite α-β-γ interface: Possible wetting scenarios

In Fig. 2 we sketch the possible wetting scenarios around a colloid floating at a composite α-γ interface with a β film intruding between the adjacent phases. In addition we depict the simplified system actually studied, which is a composite α-γ interface meeting a planar wall, instead of a curved wall as provided by the surface of a colloid. The information obtained in the previous chapter on the individual interfacial wetting problems in binary liquid mixtures, can now be combined in order to assign to each of the six scenarios sketched in Fig. 2 a domain in the parameter space (X, Y).

The images shown in Fig. 2 are simplified in several respects. The α-γ interface meets the wall at Young's contact angle; for simplicity in the drawings we use a contact angle of 90°. In general the film thickness at the wall-vapor (wall-γ) interface is different from the one at the wall-liquid (wall-α) interface and not equal as drawn in Fig. 2. From the information on the individual interfaces, only the gross features can be deduced. The fluid structure in the spatial region close to the core of the three-phase contact line cannot

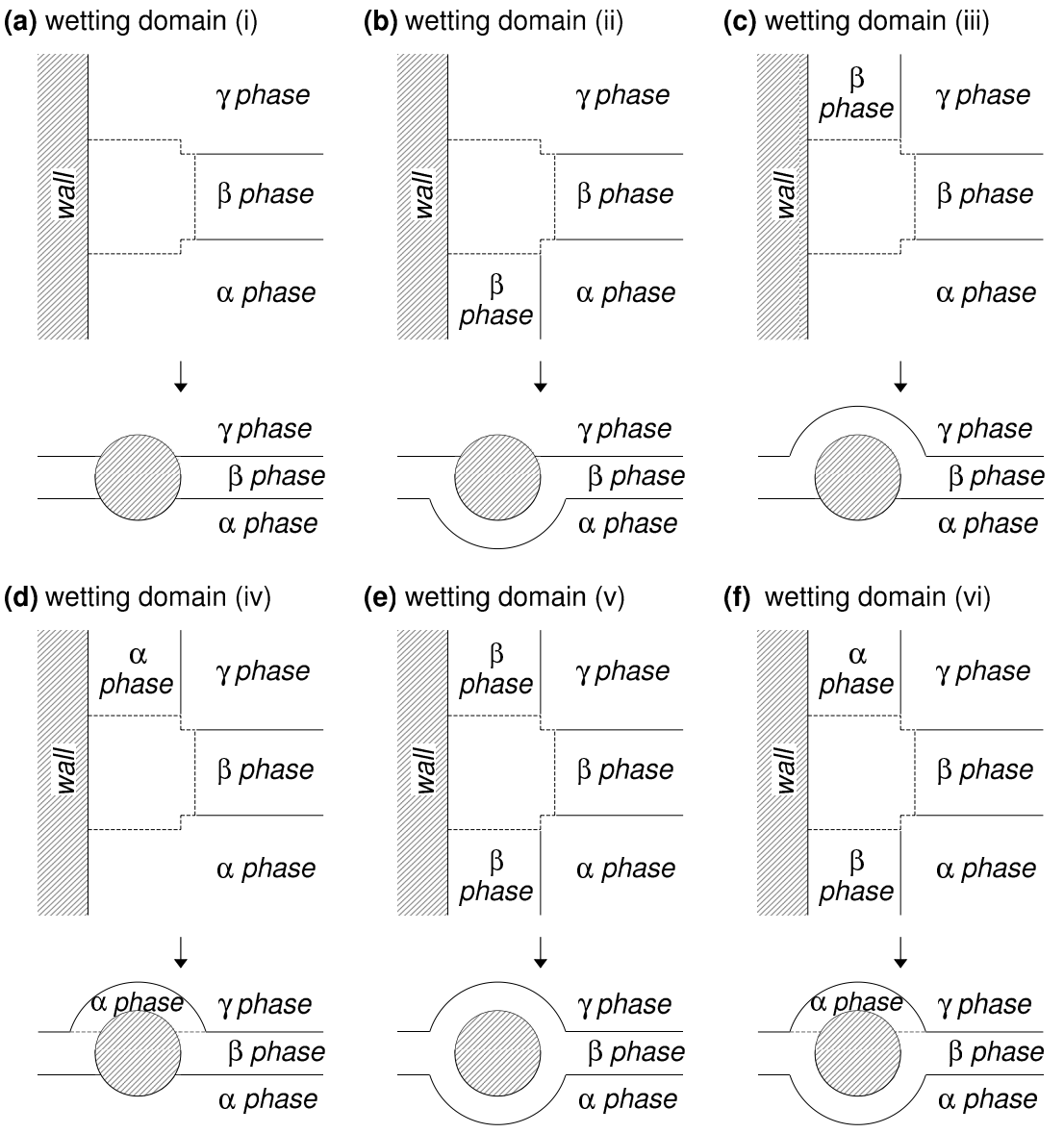

FIG. 2. Possible wetting scenarios around a colloid floating at a composite α-γ interface with an intruding β film. (a) Wetting domain (i): the β film terminates near the wall. (b) Wetting domain (ii): the β film extends down into the wall-α interface. (c) Wetting domain (iii): the β film extends up into the wall-γ interface. (d) Wetting domain (iv): the β film terminates near the wall, and a film of the α phase forms at the wall-γ interface. (e) Wetting domain (v): the β film extends into the wall-α interface and into the wall-γ interface, surrounding the colloid entirely. (f) Wetting domain (vi): the β film extends into the wall-α interface, and a wetting film of the α phase forms at the wall-γ interface. Within our approach the fluid structure around the three-phase contact line (indicated by dashed lines) remains unknown. In the wetting domains (iv) and (vi) the wall-α-γ interface actually might be replaced by one involving in addition a wetting film of the β phase, thus resulting in a wall-α-β-γ interface.

be determined within the present approach but requires a fully fledged density functional calculation.

The first possible wetting scenario is shown in Fig. 2(a). In this case the β film at the α-γ interface neither extends up into the wall-γ interface nor down into the wall-α interface. The β film just terminates near the wall. This scenario is called wetting domain (i).

The wetting scenarios shown in Figs. 2(b)–2(d) [wetting domains (ii)–(iv)] are characterized by a thick wetting film at just one of the two wall-fluid interfaces, either at the wall-α or at the wall-γ interface. In the wetting domain (ii) the β film at the α-γ interface extends down into the wall-α interface whereas no wetting film is present at the wall-γ interface. In the wetting domain (iii) the β film extends up into the wall-γ interface whereas no wetting film is present at the wall-α interface. In the wetting domain (iv) the β film at the α-γ interface terminates near the wall, but a film of the α phase intrudes at the wall-γ interface.

If wetting films are present at both wall-fluid interfaces, two scenarios are conceivable. In the wetting domain (v) the β film at the α-γ interface extends into the wall-α interface as well as into the wall-γ interface; a colloid would be com-

pletely surrounded by a film of the β phase [see Fig. 2(e)]. In the wetting domain (vi) the β film at the α-γ interface extends into the wall-α interface, but at the wall-γ interface a wetting film of the α phase forms [see Fig. 2(f)].

In the wetting domains (iv) and (vi) the α wetting film at the wall-γ interface might split into two wetting films with a β film forming at the α-γ interface, eventually resulting in a wall-α-β-γ interface. This interfacial structure is similar to the one discussed in Refs. [23,24]. In the following fluid structures involving two subsequent wetting films are not considered.

B. Fluid-fluid and fluid-wall interactions exhibiting the strict mixing rules

The relations between the strengths of the fluid-fluid and the fluid-wall interactions imposed by the strict mixing rules lead to a number of simplifications. The strict mixing rule $\xi_f = 1$ for the fluid-fluid interactions together with the inequalities in Eq. (22) between the number densities constrain the range of X, which we have to consider, to $0 < X < D_{\alpha\beta}$. Here, $D_{\alpha\beta}$ is given by Eq. (27). Otherwise, there is no β film at the α-γ interface [see Eq. (26)]. We do not pursue this latter case.

Second, the condition for the formation of a β film at a wall-α interface simplifies if the strict mixing rules for the fluid-fluid as well as for the fluid-wall interactions are valid ($\xi_f = 1$ and $\xi_\mathrm{w} = 1$). Within the range $0 < X < D_{\alpha\beta}$ one obtains from Eq. (44)

$$0 < Y < X + 1.$$

Third, for the wall-γ interface, the two distinct comparisons which have been made [see Eqs. (46) and (47)] also simplify if the strict mixing rules $\xi_f = 1$ and $\xi_\mathrm{w} = 1$ apply.

From Eq. (46) one finds that the formation of a β film is more favorable than having a plain wall-γ interface without an interleaving film if

$$Y > X + 1.$$

The formation of an α film at the wall-γ interface is favored with respect to a plain wall-γ interface without an interleaving film if

$$Y > \frac{\rho_{B,\alpha}}{\rho_{B,\beta}} X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}},$$

which follows from Eq. (47) and the strict mixing rules.

Within the range $0 < X < D_{\alpha\beta}$, on which we can focus here, the inequality

$$\frac{\rho_{B,\alpha}}{\rho_{B,\beta}} X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} > X + 1$$

is satisfied. This inequality leads to the following sequence of wetting scenarios at the wall-γ interface.

(a) $0 < Y < X + 1$: both a β wetting film and an α wetting film can be excluded and a plain wall-γ interface is the preferred structure.

(b) $X + 1 < Y < \frac{\rho_{B,\alpha}}{\rho_{B,\beta}} X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}}$: a β wetting film is the preferred structure; a plain wall-γ interface and wetting by the α phase can be excluded.

(c) $Y > \frac{\rho_{B,\alpha}}{\rho_{B,\beta}} X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}}$: wetting by the α phase becomes possible in addition to wetting by the β phase; a plain wall-γ interface can be excluded.

In the range $Y > \frac{\rho_{B,\alpha}}{\rho_{B,\beta}} X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}}$, one still has to find another boundary which determines whether wetting of the wall-γ interface by a film of the β phase or by a film of the α phase is the preferred configuration. In order to find this boundary we introduce a further wetting parameter $W_{\mathrm{w}\beta(\alpha)\gamma} = \sigma_{\mathrm{w}\beta\gamma} - \sigma_{\mathrm{w}\alpha\gamma}$, which is the difference between the surface tensions of a wall-γ interface with an intruding β film and of one with an intruding α film. If $W_{\mathrm{w}\beta(\alpha)\gamma} > 0$, the wall-$\gamma$ interface is wetted by the α phase. Otherwise, an intruding β phase wets the wall-γ interface. By using Eqs. (30) and (31), $W_{\mathrm{w}\beta(\alpha)\gamma}$ can be written as $W_{\mathrm{w}\beta\gamma} - W_{\mathrm{w}\alpha\gamma}$. Again we make the simplifying assumption that all length parameters are equal: $a_{AA} = a_{AB} = a_{BB} = a_{\mathrm{w}A} = a_{\mathrm{w}B}$. Under this condition, by using Eqs. (38) and (39) one finds

$$\begin{aligned} W_{\mathrm{w}\beta(\alpha)\gamma} &= \pi a_{AA}^4 \left[S_{\mathrm{w}\beta\gamma} F_{AA}(l_{\mathrm{w}\beta\gamma}) - S_{\mathrm{w}\alpha\gamma} \hat{F}_{AA}(l_{\mathrm{w}\alpha\gamma}) \right] \\ &=: \pi a_{AA}^4 K(X, Y). \end{aligned} \tag{49}$$

Expressing $S_{\mathrm{w}\beta\gamma}$ and $S_{\mathrm{w}\alpha\gamma}$, as given in Eqs. (C7) and (C8), one finds

$$\begin{aligned} K(X,Y) = \epsilon_{AA} \rho_{A,\beta}^2 \Bigg\{ & \left[\left(1 - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}} \right) X + 1 - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}} \right] (X + 1 - Y) F_{AA}(l_{\mathrm{w}\beta\gamma}) \\ & - \left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}} - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}} \right) X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}} \right] \left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}} X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} - Y \right) \hat{F}_{AA}(l_{\mathrm{w}\alpha\gamma}) \Bigg\}. \end{aligned} \tag{50}$$

The sign of $W_{\mathrm{w}\beta(\alpha)\gamma}$ is determined by the sign of $K(X, Y)$. Accordingly, for $K(X, Y) > 0$ a configuration with an intruding α film at the wall-γ interface is more stable than one with an intruding β film. For $K(X, Y) < 0$ the configuration with an intruding β film becomes more stable. (However, for $Y < X + 1$ a plain wall-γ interface without any wetting film is the configuration preferred most.) The condition $K(X, Y) < 0$ can be rewritten as

$$\begin{aligned} P_{K(X,Y)} \times Y > & \left[\left(1 - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}} \right) X + 1 - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}} \right] (X + 1) F_{AA}(l_{\mathrm{w}\beta\gamma}) - \left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}} - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}} \right) X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}} \right] \left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}} X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} \right) \hat{F}_{AA}(l_{\mathrm{w}\alpha\gamma}), \end{aligned} \tag{51}$$

where

$$P_{K(X,Y)} = \left[\left(1 - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}} \right) X + 1 - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}} \right] F_{AA}(l_{\mathrm{w}\beta\gamma}) - \left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}} - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}} \right) X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}} \right] \hat{F}_{AA}(l_{\mathrm{w}\alpha\gamma}). \tag{52}$$

In order to determine the sign of $P_{K(X,Y)}$ within the relevant range of X values it is convenient to rewrite Eq. (52) as

$$P_{K(X,Y)} = \left(1 - \frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right)(X - D_{\alpha\beta})F_{AA}(l_{w\beta\gamma}) - \left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}} - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)(X - D_{\alpha\gamma})[\hat{F}_{AA}(l_{w\alpha\gamma}) - F_{AA}(l_{w\beta\gamma})]. \tag{53}$$

Given the inequalities in Eq. (22) between the number densities we have $\rho_{B,\alpha}/\rho_{B,\beta} < 1$, $D_{\alpha\beta} > 0$, $\rho_{B,\alpha}/\rho_{B,\beta} - \rho_{B,\gamma}/\rho_{B,\beta} > 0$, and $D_{\alpha\gamma} < 0$. Moreover, we have $0 < F_{AA}(l_{w\beta\gamma}) < \hat{F}_{AA}(l_{w\alpha\gamma})$. As a result, $P_{K(X,Y)}$ is negative in the range $0 < X < D_{\alpha\beta}$.

The inequality in Eq. (51) can be rewritten as $Y < Y_{K(X,Y)}$, where the separatrix $Y_{K(X,Y)}$ between the β phase and the α phase wetting of the wall-γ interface is given by [see Eq. (53)]

$$Y_{K(X,Y)} = \frac{\rho_{B,\alpha}}{\rho_{B,\beta}}X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} + \left[\left(1 - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X + 1 - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right]\left[\left(1 - \frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right)X + 1 - \frac{\rho_{A,\alpha}}{\rho_{A,\beta}}\right]\frac{F_{AA}(l_{w\beta\gamma})}{P_{K(X,Y)}}. \tag{54}$$

In the X range of interest, i.e., $0 < X < D_{\alpha\beta}$, $Y_{K(X,Y)}$ is always located above the straight line $Y = \frac{\rho_{B,\alpha}}{\rho_{B,\beta}}X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}}$, which in turn is located above $Y = X + 1$. Interestingly, the three curves $Y_{K(X,Y)}$, $Y = X + 1$, and $Y = \frac{\rho_{B,\alpha}}{\rho_{B,\beta}}X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}}$ meet at the same point ($X = D_{\alpha\beta}$, $Y = D_{\alpha\beta} + 1$), at that X value above which the β wetting film at the α-γ interface ceases to exist.

We now consider the special case of three-phase (α-β-γ) coexistence. In this case one has both $l_{w\beta\gamma} \to \infty$ and $l_{w\alpha\gamma} \to \infty$ (see Appendix D), and $F_{AA}(l_{w\beta\gamma}) = \hat{F}_{AA}(l_{w\alpha\gamma}) = \frac{13}{66}$. Thus, the sign of $K(X, Y)$ depends only on the sign of $S_{w\beta\gamma} - S_{w\alpha\gamma}$. By inspecting this expression, one finds that wetting of the wall-γ interface by the β phase is more favorable than wetting by the α phase ($0 < X < D_{\alpha\beta}$) if

$$Y < \frac{\rho_{B,\alpha}}{\rho_{B,\beta}}X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} + \left[\left(1 - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X + 1 - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right]. \tag{55}$$

The curve represented by the right hand side of the inequality in Eq. (55) is, for $0 < X < D_{\alpha\beta}$, always located above the curve $Y_{K(X,Y)}$. Thus, the separatrix $Y_{K(X,Y)}$ must be located in the interval given by

$$\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} < Y_{K(X,Y)} < \frac{\rho_{B,\alpha}}{\rho_{B,\beta}}X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} + \left[\left(1 - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X + 1 - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right].$$

Accordingly, in the X range of interest, i.e., $0 < X < D_{\alpha\beta}$, the wetting behavior at the wall-γ interface can now be classified as follows:

(a) $0 < Y < X + 1$: the wall-γ interface is a plain one without any intervening wetting film.

(b) $X + 1 < Y < Y_{K(X,Y)}$: the wall-γ interface is wetted by a film of the β phase.

(c) $Y > Y_{K(X,Y)}$: the wall-γ interface is wetted by a film of the α phase.

Finally, the information about wetting at the three individual interfaces can be combined in order to deliminate a domain in the space (X, Y) of system parameters, which correspond to a certain wetting scenario as sketched in Fig. 2. We only have to consider the interval $0 < X < D_{\alpha\beta}$ because only in this X range a composite α-γ interface with an intervening wetting film of the β phase can occur. This subspace is divided into three different domains as indicated in Fig. 3. In domain (ii) [see the corresponding scenario depicted in Fig. 2(b)], below the straight line $Y = X + 1$ (red line in Fig. 3), the wall-α interface is wetted by the β phase. On the other hand below $Y = X + 1$ no film of the β phase can occur at the wall-γ interface. Thus, this interface is a plain one without any wetting film. The domain (iii), which corresponds to the scenario depicted in Fig. 2(c), is bounded from below by $Y = X + 1$ (straight red line in Fig. 3) and from above by $Y = Y_{K(X,Y)}$ (curved blue line in Fig. 3). In this domain the wall-α interface is a plain one without an intervening wetting

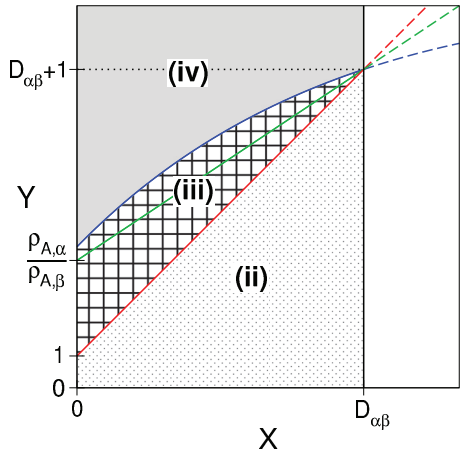

FIG. 3. Wetting domains in the space (X, Y) of system parameters, in the case that the fluid-fluid and the fluid-wall interactions obey the strict mixing rules. Further, the inequalities in Eq. (22) between the number densities are assumed to hold. The domains (ii), (iii), and (iv) correspond to the scenarios depicted in Figs. 2(b)–2(d). The domains (i), (v), and (vi) are not realized in this case. Only to the left of the black line ($X = D_{\alpha\beta}$), the desired composite α-γ interface with an intruding β film can occur. Below the red line ($Y = X + 1$), the wall-α interface is wetted by a film of the β phase whereas the wall-γ interface is a plain one without an intervening wetting film. Between the straight red line and the curved blue line [$Y = Y_{K(X,Y)}$, see Eq. (54)], a β film occurs at the wall-γ interface, whereas the wall-α interface is a plain one. Above the blue line the wall-γ interface is wetted by an α film. The curved blue line [$Y = Y_{K(X,Y)}$] is always located above the straight green line ($Y = \frac{\rho_{B,\alpha}}{\rho_{B,\beta}}X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}}$). All curves meet at the special point ($X = D_{\alpha\beta}$, $Y = D_{\alpha\beta} + 1$) (see the main text). The dashed lines extend the domain boundaries into the region where the α-γ interface is a plain one without an intruding β film; this region is beyond the interest of this study. The curves correspond to the choices $\rho_{A,\alpha}/\rho_{A,\beta} = 4$, $\rho_{B,\alpha}/\rho_{B,\beta} = \frac{2}{3}$, which implies $D_{\alpha\beta} = 9$, $F_{AA}(l_{w\beta\gamma}) = \frac{13}{132}$, and $\hat{F}_{AA}(l_{w\alpha\gamma}) = \frac{13}{66}$.

film, whereas the wall-γ interface is wetted by a film of the β phase. The domain (iv) above the curve $Y = Y_{K(X,Y)}$ corresponds to the scenario shown in Fig. 2(d). In this domain the wall-α interface is a plain one, whereas the wall-γ interface is wetted by a film of the α phase. The remaining three scenarios depicted in Fig. 2 are not realized if the strict mixing rules are imposed on both the strengths of the fluid-fluid and the fluid-wall interactions (the corresponding domains are absent in Fig. 3). In particular, the scenario depicted in Fig. 2(e) cannot occur, featuring wetting films of the β phase at all three interfaces, i.e., with a β film completely surrounding a colloid.

Some of the lines shown in Fig. 3, which separate the domains, depend on the ratios of various number densities. These ratios are not independent of X, but are also not uniquely determined by X; these ratios also depend on the thermodynamic state. The fluid model used here is also not complete and does not allow one to predict the number densities in the different phases at given thermodynamic conditions. Thus, the boundaries between the domains still depend parametrically on ratios between the number densities; we only made use of the inequalities in Eq. (22). Moreover, the equation defining the separatrix $Y_{K(X,Y)}$ implicitly depends even on Y via the equilibrium thicknesses $l_{w\beta\gamma}$ and $l_{w\alpha\gamma}$ of the wetting films. Nevertheless, strict statements about possible and impossible wetting scenarios can be made.

C. Relaxed mixing rule for the fluid-wall interactions and strict mixing rule for the fluid-fluid interactions

Here, we consider the case in which the relations between the strengths of the fluid-fluid interactions still follow the strict mixing rule $\xi_f = 1$; this constraint, however, is no longer imposed on the fluid-wall interactions (i.e., $\xi_w \neq 1$). Since the condition for the formation of a composite α-γ interface with an intervening β film is still the same as in the previous subsection, the parameter space can again be constrained to the interval $0 < X < D_{\alpha\beta}$, where $D_{\alpha\beta}$ is given by Eq. (27). The conditions for the formation of an intruding β film at the wall-α interface follow from Eqs. (44) and (45) and are given by

$$0 < Y < Y_{w\beta\alpha}(X) \quad \text{for} \quad 0 < X < \xi_w D_{\alpha\beta}$$

with

$$Y_{w\beta\alpha}(X) = X + 1 + (\xi_w - 1)\frac{X}{(X - \xi_w D_{\alpha\beta})}(X + 1) \tag{56}$$

and

$$Y > Y_{w\beta\alpha}(X) \quad \text{for} \quad X > \xi_w D_{\alpha\beta}.$$

In the above conditions, the following distinctions have to be made in accordance with the magnitude of ξ_w.

(1) For $0 < \xi_w < 1$, $Y_{w\beta\alpha}(X)$ is positive within the interval $0 < X < \xi_w D_{\alpha\beta}$ and negative within $\xi_w D_{\alpha\beta} < X < D_{\alpha\beta}$. Therefore, a β film wets the wall-α interface if the following conditions are fulfilled:

$$0 < Y < Y_{w\beta\alpha}(X) \quad \text{for} \quad 0 < X < \xi_w D_{\alpha\beta}$$

or

$$Y_{w\beta\alpha}(X) < 0 < Y \quad \text{for} \quad \xi_w D_{\alpha\beta} < X < D_{\alpha\beta}.$$

(2) For $\xi_w > 1$, $Y_{w\beta\alpha}(X)$ is positive in the whole range $0 < X < D_{\alpha\beta}$ of interest. Therefore, a β film wets the wall-α interface if the following condition is satisfied:

$$0 < Y < Y_{w\beta\alpha}(X)$$
$$\text{for the whole range } 0 < X < D_{\alpha\beta}.$$

A wetting film of the β phase at the wall-γ interface is more favorable than a plain interface without a wetting film if [see Eq. (46)]

$$Y > Y_{w\beta\gamma}(X)$$

with

$$Y_{w\beta\gamma}(X) = X + 1 + (\xi_w - 1)\frac{X}{(X - \xi_w D_{\beta\gamma})}(X + 1). \tag{57}$$

Here, $D_{\beta\gamma}$ is given by Eq. (28).

A wetting film of the α phase at the wall-γ interface is more favorable than a plain interface if [see Eq. (47)]

$$Y > Y_{w\alpha\gamma}(X)$$

with

$$Y_{w\alpha\gamma}(X) = \frac{\rho_{B,\alpha}}{\rho_{B,\beta}}X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} + (\xi_w - 1)\frac{X}{(X - \xi_w D_{\alpha\gamma})}\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}}\right). \tag{58}$$

Here, $D_{\alpha\gamma}$ is given by Eq. (48).

In order to figure out whether the configuration with an α film or the one with a β film at the wall-γ interface is more favorable, one has to inspect the sign of $W_{w\beta(\alpha)\gamma}$ [see Eq. (49)]. By applying Eqs. (C7) and (C8), with $W_{w\beta(\alpha)\gamma} =: \pi a_{AA}^4 L(X, Y)$, one has

$$L(X,Y) = \epsilon_{AA}\rho_{A,\beta}^2\left(\left\{\left[\left(1 - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X + 1 - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right](X+1) - \left[\left(1 - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)\frac{X}{\xi_w} + 1 - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right]Y\right\}F_{AA}(l_{w\beta\gamma})\right.$$
$$\left. - \left\{\left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}} - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right]\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}}\right) - \left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}} - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)\frac{X}{\xi_w} + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right]Y\right\}\hat{F}_{AA}(l_{w\alpha\gamma})\right).$$

Wetting of the wall-γ interface by the β phase is preferred as compared to wetting by the α phase, if $L(X, Y) < 0$. The condition $L(X, Y) < 0$ can be expressed as

$$P_{L(X,Y)} \times Y > \left[\left(1 - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X + 1 - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right](X+1)F_{AA}(l_{w\beta\gamma}) - \left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}} - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right]\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}}\right)\hat{F}_{AA}(l_{w\alpha\gamma}),$$

where

$$P_{L(X,Y)} = \left[\left(1-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)\frac{X}{\xi_{\rm w}}+1-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right]F_{AA}(l_{{\rm w}\beta\gamma})-\left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)\frac{X}{\xi_{\rm w}}+\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right]\hat{F}_{AA}(l_{{\rm w}\alpha\gamma})$$
$$=\frac{1}{\xi_{\rm w}}\left\{\left(1-\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right)(X-\xi_{\rm w}D_{\alpha\beta})F_{AA}(l_{{\rm w}\beta\gamma})-\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)(X-\xi_{\rm w}D_{\alpha\gamma})[\hat{F}_{AA}(l_{{\rm w}\alpha\gamma})-F_{AA}(l_{{\rm w}\beta\gamma})]\right\}.$$

The inequalities between the number densities [Eq. (22)] imply $\rho_{B,\alpha}/\rho_{B,\beta}<1$, $D_{\alpha\beta}>0$, $\rho_{B,\alpha}/\rho_{B,\beta}-\rho_{B,\gamma}/\rho_{B,\beta}>0$, and $D_{\alpha\gamma}<0$. Furthermore, we have $0<F_{AA}(l_{{\rm w}\beta\gamma})<\hat{F}_{AA}(l_{{\rm w}\alpha\gamma})$.

If $0<X<\xi_{\rm w}D_{\alpha\beta}$, one has $P_{L(X,Y)}<0$. If $X>\xi_{\rm w}D_{\alpha\beta}$, $P_{L(X,Y)}$ can be positive or negative. Which possibility prevails depends on the magnitude of $\xi_{\rm w}$.

(1) If $0<\xi_{\rm w}<1$, the inequalities $0<\xi_{\rm w}D_{\alpha\beta}<D_{\alpha\beta}$ hold. For $0<X<\xi_{\rm w}D_{\alpha\beta}$, $P_{L(X,Y)}$ is negative. Within the interval $\xi_{\rm w}D_{\alpha\beta}<X<D_{\alpha\beta}$, $P_{L(X,Y)}$ can be positive or negative.

(2) If $\xi_{\rm w}>1$, one has $\xi_{\rm w}D_{\alpha\beta}>D_{\alpha\beta}$. Thus, $P_{L(X,Y)}<0$ in the whole range of X values of interest, i.e., for $0<X<D_{\alpha\beta}$.

In the case $P_{L(X,Y)}<0$ and if $0<Y<Y_{L(X,Y)}$, an intruding β film at the wall-γ interface is more favorable than a wetting film of the α phase; here,

$$Y_{L(X,Y)}=\left[\left(1-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X+1-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right](X+1)\frac{F_{AA}(l_{{\rm w}\beta\gamma})}{P_{L(X,Y)}}-\left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X+\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right]\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}X+\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}\right)\frac{\hat{F}_{AA}(l_{{\rm w}\alpha\gamma})}{P_{L(X,Y)}}. \tag{59}$$

If $P_{L(X,Y)}>0$ and if $Y>Y_{L(X,Y)}$, the β wetting film at the wall-γ interface is preferred.

The separatrix $Y=Y_{L(X,Y)}$ [Eq. (59)] is always located above the curve $Y_{{\rm w}\alpha\gamma}(X)$ [Eq. (58)] as long as $Y_{{\rm w}\beta\gamma}(X)<Y_{{\rm w}\alpha\gamma}(X)$ [$Y_{{\rm w}\beta\gamma}(X)$ is defined in Eq. (57)]. Otherwise, $Y_{L(X,Y)}$ is located below the line $Y_{{\rm w}\alpha\gamma}(X)$. The intersection between $Y_{L(X,Y)}$ and $Y_{{\rm w}\alpha\gamma}(X)$ lies on the curve $Y_{{\rm w}\beta\gamma}(X)$, i.e., the three curves have a common intersection.

By admitting deviations from the strict mixing rule for the fluid-wall interactions, additional wetting scenarios may be realized as compared to those which are possible in the case that the strict mixing rules apply to both the fluid-fluid and the fluid-wall interactions (see Fig. 3). The main reason for this is that in the latter case the domain boundary for wetting of the wall-α interface by the β phase and the domain boundary for wetting of the wall-γ interface by the β phase (red line in Fig. 3) coincide, whereas these two boundaries are different (orange and red lines in Fig. 4) once the mixing rules for the fluid-wall interactions are relaxed.

If $0<\xi_{\rm w}<1$ (i.e., the wall-A interaction is weaker than the one prescribed by the strict mixing rule) the two additional scenarios (v) and (vi) [Figs. 2(e) and 2(f)] become possible in their corresponding domains in the parameter space (X,Y) [see Fig. 4(a)]. In scenario (v) the β wetting film extends into both the wall-α interface and into the wall-γ interface. In this case the surface of a colloidal particle floating at the α-γ interface would be fully covered by a film of the β phase [see Fig. 2(e)]. In scenario (vi) the wall-α interface is wetted by a film of the β phase, whereas the wall-γ interface is wetted by the α phase [see Fig. 2(f)].

If $\xi_{\rm w}>1$ (i.e., the wall-A interaction is stronger than the one prescribed by the strict mixing rule) only the additional domain (i) appears [see Fig. 4(b)]. In this scenario, the wall-α and the wall-γ interfaces are both plain ones without an intruding wetting film [see Fig. 2(a)].

D. Relaxed mixing rule for the fluid-fluid interactions and strict mixing rule for the fluid-wall interactions

Here, we consider deviations from the strict mixing rule for the fluid-fluid interactions $\xi_f\neq 1$, whereas the ratio of the strengths of the interactions of the A and B particles with the wall is strictly fixed by the fluid-wall mixing rule ($\xi_{\rm w}=1$). The condition for the formation of a composite α-γ interface with an intervening β film is now given by the general expression in Eq. (26), and thus the parameter space of interest is constrained to $0<X<X_{\xi_f}$, with

$$X_{\xi_f}=\sqrt{\left[\frac{\xi_f}{2}(D_{\alpha\beta}+D_{\beta\gamma})\right]^2-D_{\alpha\beta}D_{\beta\gamma}}+\frac{\xi_f}{2}(D_{\alpha\beta}+D_{\beta\gamma}). \tag{60}$$

Here, $D_{\alpha\beta}$ and $D_{\beta\gamma}$ are given by Eqs. (27) and (28), respectively. Depending on whether $\xi_f<1$ or $\xi_f>1$, one has $X_{\xi_f}<D_{\alpha\beta}$ or $X_{\xi_f}>D_{\alpha\beta}$.

The conditions for the formation of an intruding β film at the wall-α interface follow from Eqs. (44) and (45) and can be expressed as

$$0<Y<\widetilde{Y}_{{\rm w}\beta\alpha}(X)\ \text{ for }\ 0<X<D_{\alpha\beta}$$

with

$$\widetilde{Y}_{{\rm w}\beta\alpha}(X)=X+1+(\xi_f-1)(1-D_{\alpha\beta})\frac{X}{(X-D_{\alpha\beta})} \tag{61}$$

and

$$Y>\widetilde{Y}_{{\rm w}\beta\alpha}(X)\ \text{ for }\ X>D_{\alpha\beta}.$$

Within the interesting range $0<X<X_{\xi_f}$ of X, depending on the magnitude of ξ_f, the following distinctions can be made in the above conditions:

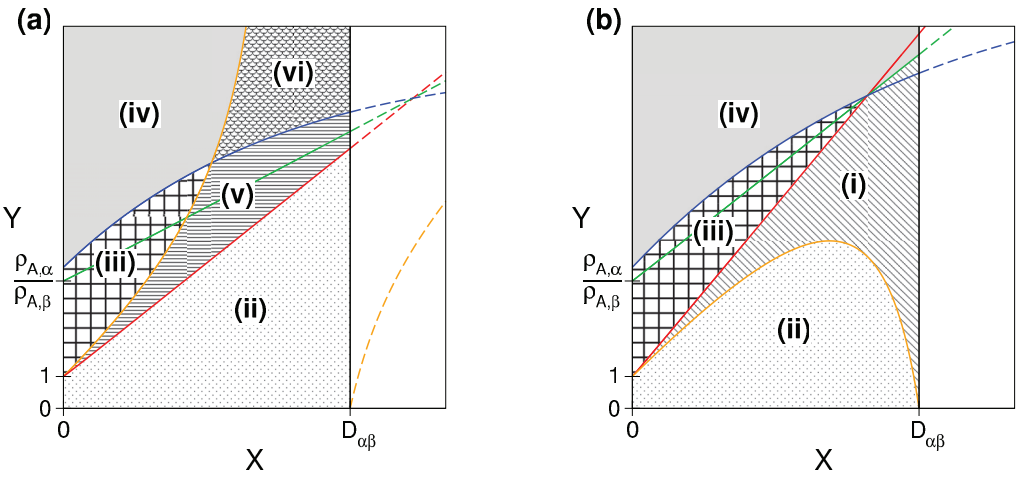

FIG. 4. Wetting domains (i)–(vi) in the parameter space (X, Y), in the case that the fluid-fluid interactions obey the strict mixing rule, but the fluid-wall interactions are not constrained ($\xi_w \neq 1$). Further, the inequalities between the number densities [Eq. (22)] are assumed. The domains correspond to the scenarios depicted in Fig. 2. Two distinct scenarios emerge, depending on whether (a) $0 < \xi_w < 1$ or (b) $\xi_w > 1$. Only to the left of the black line ($X = D_{\alpha\beta}$) one encounters the composite α-γ interface of interest with an intruding β film. Above the red line $Y_{w\beta\gamma}(X)$ [Eq. (57)] the wall-γ interface is potentially wetted by a β film. Above the green line $Y_{w\alpha\gamma}(X)$ [Eq. (58)] the wall-γ interface is potentially wetted by an α film. The separatrix between wetting of this interface by the β phase and wetting by the α phase is given by the blue line $Y_{L(X,Y)}$ [Eq. (59)]. Depending on whether the green line lies above the red line or below, wetting of the wall-γ interface by an α film is found above or below the blue line. Below the orange line $Y_{w\beta\alpha}(X)$ [Eq. (56)] the wall-α interface is wetted by a film of the β phase. The dashed lines extend the domain boundaries into the region within which the α-γ interface is a plain one without an intruding β film; this region is beyond the interest of this study. In particular, the dashed orange line in (a) represents $Y_{w\beta\alpha}(X)$ for $X > D_{\alpha\beta}$. $Y_{w\beta\alpha}(X)$ has a vertical asymptote and changes sign at $X = \xi_w D_{\alpha\beta}$; it returns to positive values for $X > D_{\alpha\beta}$ [see Eq. (56)]. The lines correspond to the choices $\rho_{A,\alpha}/\rho_{A,\beta} = 4$, $\rho_{B,\alpha}/\rho_{B,\beta} = \frac{2}{3}$, which implies $D_{\alpha\beta} = 9$, $F_{AA}(l_{w\beta\gamma}) = \frac{13}{132}$, and $\hat{F}_{AA}(l_{w\alpha\gamma}) = \frac{13}{66}$. In (a) we have $\xi_w = 0.8$ and in (b) $\xi_w = 1.2$.

(1) For $0 < \xi_f < 1$ and thus $X_{\xi_f} < D_{\alpha\beta}$, the wall-$\alpha$ interface is wetted by an intruding film of the β phase if

$$0 < Y < \widetilde{Y}_{w\beta\alpha}(X)$$
$$\text{for the whole range } 0 < X < X_{\xi_f}.$$

(2) For $\xi_f > 1$ and thus for $X_{\xi_f} > D_{\alpha\beta}$, an intruding β film at the wall-α interface occurs if

$$0 < Y < \widetilde{Y}_{w\beta\alpha}(X) \text{ for } 0 < X < D_{\alpha\beta}$$
or
$$Y > \widetilde{Y}_{w\beta\alpha}(X) \text{ for } D_{\alpha\beta} < X < X_{\xi_f}.$$

From Eq. (46) one obtains that a wetting film of the β phase at the wall-γ interface is more favorable than a plain interface without a wetting film if

$$Y > \widetilde{Y}_{w\beta\gamma}(X)$$

with

$$\widetilde{Y}_{w\beta\gamma}(X) = X + 1 + (\xi_f - 1)(1 - D_{\beta\gamma})\frac{X}{(X - D_{\beta\gamma})}. \quad (62)$$

From Eq. (47) one finds that an intruding α film at the wall-γ interface is more favorable than a plain interface if

$$Y > \widetilde{Y}_{w\alpha\gamma}(X)$$

with

$$\widetilde{Y}_{w\alpha\gamma}(X) = \frac{\rho_{B,\alpha}}{\rho_{B,\beta}}X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} + (\xi_f - 1)\left(\frac{\rho_{A,\alpha}}{\rho_{A,\beta}} - \frac{\rho_{B,\alpha}}{\rho_{B,\beta}}D_{\alpha\gamma}\right)\frac{X}{(X - D_{\alpha\gamma})}. \quad (63)$$

Here, $D_{\alpha\gamma}$ is given by Eq. (48). We recall that in addition we are interested only in X values within the interval $0 < X < X_{\xi_f}$.

In the parameter region, in which wetting of the wall-γ interface both by the α and by the β phase is more favorable than a plain wall-γ interface without any wetting film, we still have to determine whether wetting by a film of the α phase or of the β phase is preferred. This distinction hinges on the sign of $W_{w\beta(\alpha)\gamma} =: \pi a_{AA}^4 M(X, Y)$ [see Eq. (49)] with

$$M(X,Y) = \epsilon_{AA}\rho_{A,\beta}^2\left(\left\{\left[\left(1 - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X + 1 - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right](X + 1 - Y) + \left[\left(1 - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right) + \left(1 - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\right](\xi_f - 1)X\right\}F_{AA}(l_{w\beta\gamma})\right.$$
$$\left. - \left\{\left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}} - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right]\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} - Y\right)\right.$$

$$+\left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}+\left(\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right](\xi_f-1)X\Bigg\}\hat{F}_{AA}(l_{w\alpha\gamma})\Bigg).$$

For $M(X,Y)>0$ wetting of the wall-γ interface by an α film is more favorable than wetting by a β film; for $M(X,Y)<0$ wetting by the β phase is preferred. The condition $M(X,Y)<0$ can be rewritten as

$$\begin{aligned}P_{M(X,Y)}\times Y>&\left\{\left[\left(1-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X+1-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right](X+1)+\left[\left(1-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)+\left(1-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\right](\xi_f-1)X\right\}F_{AA}(l_{w\beta\gamma})\\&-\left\{\left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X+\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right]\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}X+\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}\right)\right.\\&\left.+\left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}+\left(\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right](\xi_f-1)X\right\}\hat{F}_{AA}(l_{w\alpha\gamma}),\end{aligned}$$

with $P_{M(X,Y)}=P_{K(X,Y)}$, where $P_{K(X,Y)}$ is given by Eqs. (52) and (53).

Depending on the magnitude of ξ_f, the following distinctions can be made:

(1) For $0<\xi_f<1$ and thus $X_{\xi_f}<D_{\alpha\beta}$, $P_{M(X,Y)}$ is negative in the whole range $0<X<X_{\xi_f}$ of interest, because $P_{M(X,Y)}<0$ for $0<X<D_{\alpha\beta}$.

(2) For $\xi_f>1$ and thus $X_{\xi_f}>D_{\alpha\beta}$, two regions have to be distinguished: $P_{M(X,Y)}<0$ for $0<X<D_{\alpha\beta}$, whereas within $D_{\alpha\beta}<X<X_{\xi_f}$ $P_{M(X,Y)}$ can be positive or negative.

For $P_{M(X,Y)}>0$ the wall-γ interface is wetted by a β film only if $Y>Y_{M(X,Y)}$, with

$$\begin{aligned}Y_{M(X,Y)}=&\left\{\left[\left(1-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X+1-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right](X+1)+\left[\left(1-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)+\left(1-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\right](\xi_f-1)X\right\}\frac{F_{AA}(l_{w\beta\gamma})}{P_M(X,Y)}\\&-\left\{\left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X+\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right]\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}X+\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}\right)\right.\\&\left.+\left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}+\left(\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right](\xi_f-1)X\right\}\frac{\hat{F}_{AA}(l_{w\alpha\gamma})}{P_{M(X,Y)}}.\end{aligned}\tag{64}$$

If $P_{M(X,Y)}<0$, wetting of the wall-γ interface by a β film is preferred only if $0<Y<Y_{M(X,Y)}$.

For

$$\widetilde{Y}_{w\beta\gamma}(X)<\widetilde{Y}_{w\alpha\gamma}(X),$$

$Y_{M(X,Y)}$ [Eq. (64)] lies always above $\widetilde{Y}_{w\alpha\gamma}(X)$. Otherwise, $Y_{M(X,Y)}$ lies below $\widetilde{Y}_{w\alpha\gamma}(X)$ [Eq. (63)]. The intersection between $Y_{M(X,Y)}$ and $\widetilde{Y}_{w\alpha\gamma}(X)$ is located on the curve $\widetilde{Y}_{w\beta\gamma}(X)$ [Eq. (62)], which means that $\widetilde{Y}_{w\alpha\gamma}(X)$, $\widetilde{Y}_{w\beta\gamma}(X)$, and $Y_{M(X,Y)}$ have a common intersection point.

In Fig. 5 we illustrate how the parameter space (X,Y) is subdivided into domains, which are associated with the various wetting scenarios, in the case that deviations from the strict mixing rule for the fluid-fluid interactions are admitted. In Fig. 5(a) the division into domains for $0<\xi_f<1$ (i.e., the strength of the A-B interaction is smaller than prescribed by the strict mixing rule) is shown. Figure 5(a) resembles closely Fig. 4(b) (i.e., deviations from the mixing rule concerning the fluid-wall interactions and $\xi_w>1$). However, in the present case an additional domain associated with the wetting scenario (v) appears, although only in a very small region of the parameter space. In the case $\xi_f>1$ [see Fig. 5(b)] one obtains a picture which is very similar to the one shown in Fig. 4(a), but with an additional domain, occupying also only a very small region of the parameter space, corresponding to scenario (i).

E. Contact angles

The equilibrium contact angle θ, with which the liquid-vapor (α-γ) interface meets the wall, is a measurable observable. It can be expressed via Young's equation

$$\cos\theta=\frac{\sigma_{w\gamma}^{eq}-\sigma_{w\alpha}^{eq}}{\sigma_{\alpha\gamma}^{eq}},\tag{65}$$

in terms of the interfacial tensions of the wall-γ, wall-α, and α-γ interfaces. The tensions correspond to the respective equilibrium structures. The various wetting domains introduced above are characterized by combinations of interfacial structures at the wall-γ and the wall-α interfaces. One may pose the question whether this is reflected by the possible values of the contact angle θ. For instance, it might be the case that in one domain the wall must be lyophilic (i.e., $\theta<\frac{\pi}{2}$) whereas in another domain the wall must be lyophobic (i.e., $\theta>\frac{\pi}{2}$). However, it is also conceivable that in one domain both lyophilic and lyophobic behaviors are possible and that there is a dividing line, inside the domain, separating the two behaviors.

Here, we focus on the case in which the mixing rules apply to both the fluid-fluid and the fluid-wall interactions. In this particular case the parameter space is divided into three distinct wetting domains. Now we relate Eq. (65) to this case and to the three wetting domains (ii), (iii), and (iv) by inserting

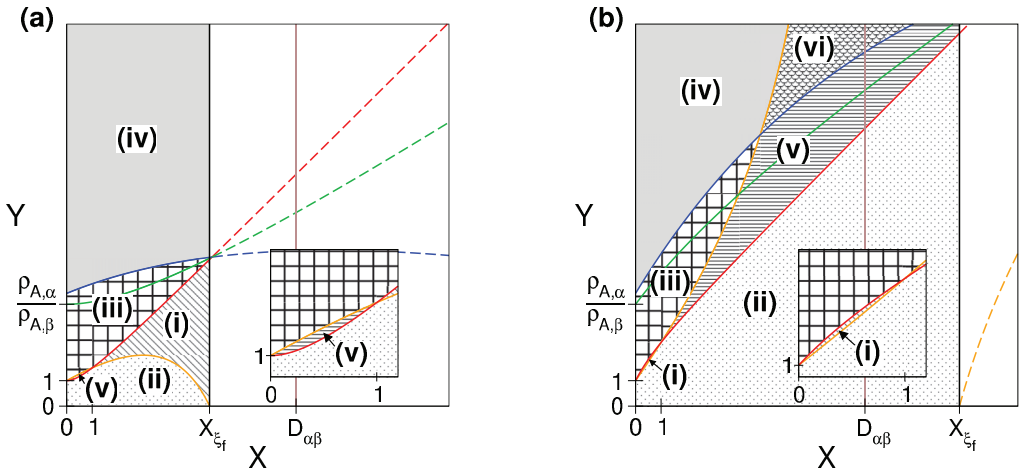

FIG. 5. Wetting domains in the parameter space (X, Y), in the case that the fluid-wall interactions obey the strict mixing rule, but that the fluid-fluid interactions are not constrained ($\xi_f \neq 1$). Furthermore the inequalities in Eq. (22) between the number densities are respected. The domains correspond to the wetting scenarios depicted in Fig. 2. Two different scenarios emerge in addition, depending on whether (a) $0 < \xi_f < 1$ or (b) $\xi_f > 1$. Only to the left of the black line $X = X_{\xi_f}$ [Eq. (60)], the desired composite α-γ interface with an intruding β film can occur. Above the red line $\widetilde{Y}_{w\beta\gamma}(X)$ [Eq. (62)] the wall-γ interface is potentially wetted by a β film. Above the green line $\widetilde{Y}_{w\alpha\gamma}(X)$ [Eq. (63)] the wall-γ interface is potentially wetted by an α film. The separatrix between wetting by the β phase and the α phase, respectively, is given by the blue line $Y_{M(X,Y)}$ [Eq. (64)]. Depending on whether the green line lies above the red line or below, wetting of the wall-γ interface by an α film is found above or below the blue line. Below the orange line $\widetilde{Y}_{w\beta\alpha}(X)$ [Eq. (61)] the wall-α interface is wetted by a film of the β phase. The dashed lines extend the domain boundaries into the region within which the α-γ interface is a plain one without an intruding β film. In particular, the dashed orange line in (b) represents $\widetilde{Y}_{w\beta\alpha}(X)$ for $X > X_{\xi_f}$. The vertical asymptote of $\widetilde{Y}_{w\beta\alpha}(X)$, at which in addition this function changes sign, is located at $X = D_{\alpha\beta}$. $\widetilde{Y}_{w\beta\alpha}(X)$ returns to positive values for $X > X_{\xi_f}$ [see Eq. (61)]. The brown vertical line shows $X = D_{\alpha\beta}$. The lines are drawn using $\rho_{A,\alpha}/\rho_{A,\beta} = 4$, $\rho_{B,\alpha}/\rho_{B,\beta} = \frac{2}{3}$, which implies $D_{\alpha\beta} = 9$, $F_{AA}(l_{w\beta\gamma}) = \frac{13}{132}$, and $\hat{F}_{AA}(l_{w\alpha\gamma}) = \frac{13}{66}$. In (a) we have chosen $\xi_f = 0.5$ and in (b) $\xi_f = 1.5$ so that $X_{\xi_f} = 5.605$ in (a) and $X_{\xi_f} = 12.709$ in (b). The insets are magnifications of the regions indicated by arrows in the main figures.

the interfacial tensions for the respective interfacial structures and by using the notation introduced above. This leads to the three expressions

$$\cos\theta_{(ii)} = \frac{\sigma_{w\gamma} - \sigma_{w\beta\alpha}}{\sigma_{\alpha\beta\gamma}},$$

$$\cos\theta_{(iii)} = \frac{\sigma_{w\beta\gamma} - \sigma_{w\alpha}}{\sigma_{\alpha\beta\gamma}},$$

and

$$\cos\theta_{(iv)} = \frac{\sigma_{w\alpha\gamma} - \sigma_{w\alpha}}{\sigma_{\alpha\beta\gamma}}.$$

Here, θ_κ is the contact angle according to Young's equation specialized to domain κ, with $\kappa =$ (ii), (iii), and (iv). If $\cos\theta_\kappa > 0$, we have $\theta_\kappa < \frac{\pi}{2}$. Otherwise, $\theta_\kappa > \frac{\pi}{2}$. The sign of $\cos\theta_\kappa$ is determined by the numerators in the above expressions because $\sigma_{\alpha\beta\gamma}$ is positive. By using Eqs. (29)–(31), these numerators, called ψ_κ, can be expressed as follows:

$$\begin{aligned}\psi_{(ii)} &= \sigma_{w\gamma} - \sigma_{w\beta\alpha} \\ &= \sigma_{w\gamma} - \sigma_{w\alpha} - W_{w\beta\alpha},\end{aligned} \tag{66}$$

$$\begin{aligned}\psi_{(iii)} &= \sigma_{w\beta\gamma} - \sigma_{w\alpha} \\ &= W_{w\beta\gamma} + \sigma_{w\gamma} - \sigma_{w\alpha},\end{aligned} \tag{67}$$

and

$$\begin{aligned}\psi_{(iv)} &= \sigma_{w\alpha\gamma} - \sigma_{w\alpha} \\ &= W_{w\alpha\gamma} + \sigma_{w\gamma} - \sigma_{w\alpha}.\end{aligned} \tag{68}$$

Preliminary conclusions regarding the sign of $\cos\theta$ can be drawn based already on the sign of $\sigma_{w\gamma} - \sigma_{w\alpha}$ and our knowledge that $W_{w\beta\alpha}$, $W_{w\beta\gamma}$, and $W_{w\alpha\gamma}$ are negative within the respective domain for which Eqs. (66), (67), and (68) are applicable. We find $\sigma_{w\gamma} - \sigma_{w\alpha} = 0$ if $Y = Y_{ref}(X)$ with

$$Y_{ref}(X) = \frac{1}{2}\left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}} + \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} + \frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right] \tag{69}$$

(see Appendix E). The difference $\sigma_{w\gamma} - \sigma_{w\alpha}$ is positive if $Y > Y_{ref}$, and it is negative if $0 < Y < Y_{ref}$. Based on the inequalities in Eq. (22) between the number densities, we also know that $Y_{ref}(X)$ lies above $Y = X + 1$, which is the boundary between the domains (ii) and (iii) for small X. $Y_{ref}(X)$ intersects $Y = X + 1$ at X_{int} [see, cf., Eq. (73)] and is located below $Y = X + 1$ for $X > X_{int}$. It also follows that $Y_{ref}(X)$ is located below the green line in Fig. 3 and thus it is located below the domain (iv). From Eq. (68) and the sign of $W_{w\alpha\gamma}$ we infer that the line, above which $\theta_\kappa < \frac{\pi}{2}$, must be located above $Y_{ref}(X)$; only if this shift is unexpectedly large this boundary would move up into domain (iv). Thus, it is very likely that domain (iv) does not contain a boundary between lyophilic and lyophobic behavior so that the whole domain

(iv) is linked to lyophilic walls. The knowledge acquired up to this point can be summarized as follows:

(a) In the wetting domain (ii) one has $\theta_{(\mathrm{ii})} < \frac{\pi}{2}$ for $Y > Y_{\mathrm{ref}}(X)$; the actual boundary $\theta_{(\mathrm{ii})} = \frac{\pi}{2}$ is located below $Y_{\mathrm{ref}}(X)$.

(b) In the wetting domain (iii) one has $\theta_{(\mathrm{iii})} > \frac{\pi}{2}$ within the interval $0 < Y < Y_{\mathrm{ref}}(X)$; the actual boundary $\theta_{(\mathrm{iii})} = \frac{\pi}{2}$ is located above $Y_{\mathrm{ref}}(X)$.

(c) In the wetting domain (iv), it is likely that $\theta_{(\mathrm{iv})} < \frac{\pi}{2}$ inside the entire domain.

In order to locate the boundary $\theta_\kappa = \frac{\pi}{2}$ precisely, we study the full expressions on the right hand sides of Eqs. (66)–(68) and determine the separatrix Y_{G_κ} between lyophilic behavior ($\theta_\kappa < \frac{\pi}{2}$, $\psi_\kappa > 0$) and lyophobic behavior ($\theta_\kappa > \frac{\pi}{2}$, $\psi_\kappa < 0$) in each case.

For the domain (ii) we find

$$Y_{G_{(\mathrm{ii})}(X,Y)} = X + 1 + \frac{13}{132}\left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}} - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right]\left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}} + \frac{\rho_{B,\gamma}}{\rho_{B,\beta}} - 2\right)X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} + \frac{\rho_{A,\gamma}}{\rho_{A,\beta}} - 2\right]\frac{1}{P_{G_{(\mathrm{ii})}(X,Y)}} \tag{70}$$

with

$$P_{G_{(\mathrm{ii})}(X,Y)} = \frac{13}{66}\left[\left(1 - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X + 1 - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right] + \left[\frac{13}{66} - F_{AA}(l_{\mathrm{w}\beta\alpha})\right]\left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}} - 1\right)X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} - 1\right].$$

$P_{G_{(\mathrm{ii})}(X,Y)}$ is positive in the relevant interval $0 < X < D_{\alpha\beta}$. In these terms we can state that $\theta_{(\mathrm{ii})} < \frac{\pi}{2}$ for $Y > Y_{G_{(\mathrm{ii})}(X,Y)}$ and $\theta_{(\mathrm{ii})} > \frac{\pi}{2}$ for $0 < Y < Y_{G_{(\mathrm{ii})}(X,Y)}$.

For the domain (iii) we find

$$Y_{G_{(\mathrm{iii})}(X,Y)} = X + 1 + \frac{13}{132}\left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}} - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right]\left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}} + \frac{\rho_{B,\gamma}}{\rho_{B,\beta}} - 2\right)X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} + \frac{\rho_{A,\gamma}}{\rho_{A,\beta}} - 2\right]\frac{1}{P_{G_{(\mathrm{iii})}(X,Y)}} \tag{71}$$

with

$$P_{G_{(\mathrm{iii})}(X,Y)} = \frac{13}{66}\left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}} - 1\right)X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} - 1\right] + \left[\frac{13}{66} - F_{AA}(l_{\mathrm{w}\beta\gamma})\right]\left[\left(1 - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X + 1 - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right].$$

$P_{G_{(\mathrm{iii})}(X,Y)}$ is positive in the relevant interval $0 < X < D_{\alpha\beta}$. Accordingly, we obtain $\theta_{(\mathrm{iii})} < \frac{\pi}{2}$ for $Y > Y_{G_{(\mathrm{iii})}(X,Y)}$ and $\theta_{(\mathrm{iii})} > \frac{\pi}{2}$ for $0 < Y < Y_{G_{(\mathrm{iii})}(X,Y)}$.

Finally, for the domain (iv) we find

$$Y_{G_{(\mathrm{iv})}(X,Y)} = \frac{1}{2}\left\{\left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}} + \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} + \frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right] + \left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}} - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right]\hat{F}_{AA}(l_{\mathrm{w}\alpha\gamma})\right\}. \tag{72}$$

Because $\hat{F}_{AA}(l_{\mathrm{w}\alpha\gamma}) \leqslant \frac{13}{66}$ and due to the inequalities in Eq. (22) we find that $Y_{G_{(\mathrm{iv})}(X,Y)}$ is always located below the green line in Fig. 3 and thus below the domain (iv). This confirms that $\theta_{(\mathrm{iv})} < \frac{\pi}{2}$ in the entire domain.

It is also interesting to note that $Y_{G_{(\mathrm{ii})}(X,Y)}$, $Y_{G_{(\mathrm{iii})}(X,Y)}$, and $Y = X + 1$ meet at the same point $(X_{\mathrm{int}}, Y_{\mathrm{int}})$ at which $Y_{\mathrm{ref}}(X)$ and $Y = X + 1$ intersect. This intersection point $(X_{\mathrm{int}}, Y_{\mathrm{int}})$ is given by

$$X_{\mathrm{int}} = \frac{\left(\frac{\rho_{A,\alpha}}{\rho_{A,\beta}} + \frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right) - 2}{2 - \left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}} + \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)} \quad \text{and}$$

$$Y_{\mathrm{int}} = \frac{\left(\frac{\rho_{A,\alpha}}{\rho_{A,\beta}} + \frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right) - \left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}} + \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)}{2 - \left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}} + \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)}. \tag{73}$$

Our findings are summarized in Fig. 6 where we show the three wetting domains in the parameter space (X, Y) together with the two domains corresponding to either lyophilic ($\theta < \frac{\pi}{2}$) or lyophobic ($\theta > \frac{\pi}{2}$) behavior.

IV. CONCLUSIONS AND SUMMARY

A region of the bulk phase diagram of a binary liquid mixture, composed of A and B particles, has been considered in which the vapor phase (γ phase) coexists with a stable A-rich liquid phase (α phase), whereas the B-rich phase (β phase) is metastable. For such fluids possible scenarios have been discussed, which may occur, if a composite liquid-vapor (α-γ) interface with an intruding film of the β phase meets a solid wall. The study is based on classical density functional theory, using the so-called sharp-kink approximation for the fluid density profiles. Furthermore, certain inequalities [Eq. (22)] have been assumed among the number densities of the A and B particles in the three phases α, β, and γ. These are valid for typical mixtures of two partially miscible liquids. Within the theoretical framework presented here, we have considered also cases in which one or two of these inequalities are reversed. We refrain from including these into this presentation in order to avoid an unnecessary complexity of the discussion and because these cases correspond to very special situations, which should be discussed separately by focusing on a particular system. In order to simplify the analytical expressions, we have also assumed that the various length parameters, which characterize the range of the repulsive core of the various fluid-fluid and fluid-wall interactions, are all equal. However, the general case in which the length parameters are all different can be approximately mapped onto the special case. This mapping is accurate if the wetting films are of mesoscopic thicknesses.

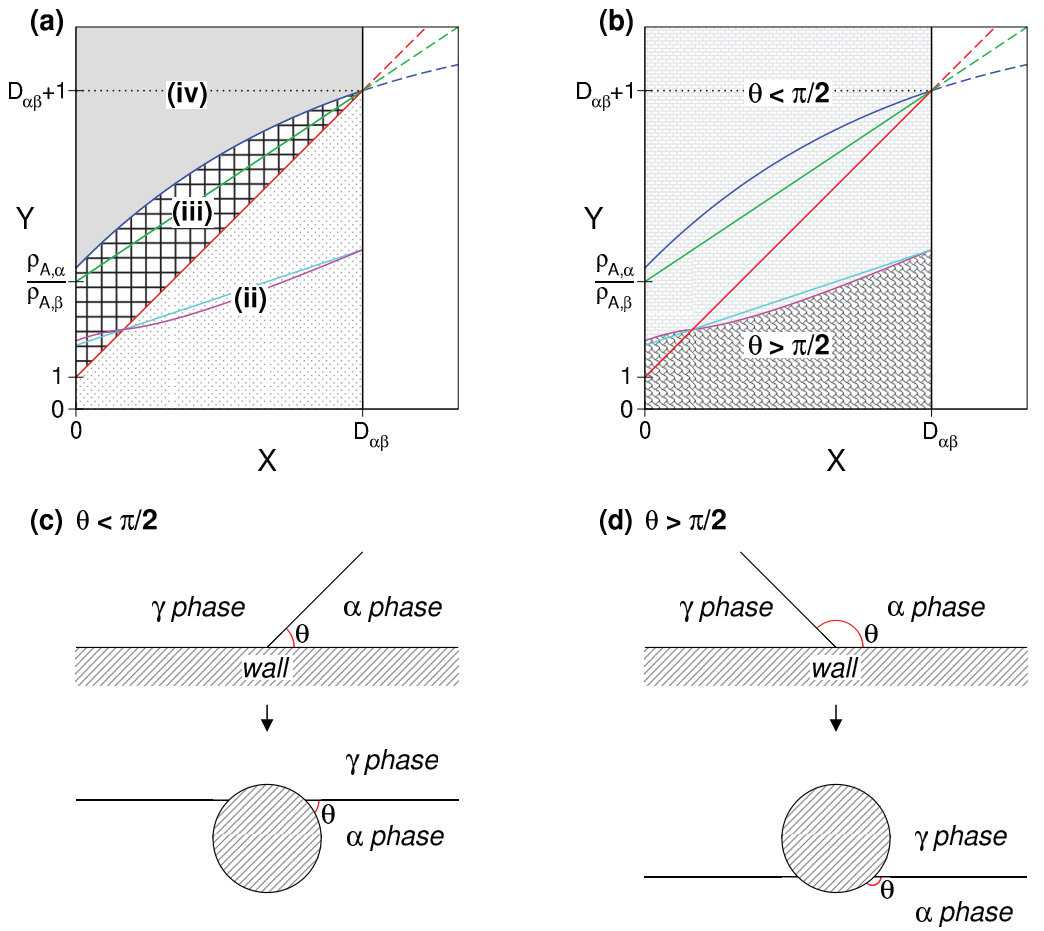

FIG. 6. In (a) the three wetting domains depicted in Fig. 3 are shown again together with $Y_{\rm ref}$ [cyan straight line, Eq. (69)] and $Y_{G_\kappa(X,Y)}$ [magenta curve, Eqs. (70) and (71)] for $\kappa =$ (ii) and (iii). The latter is the separatrix between lyophobic ($\theta > \frac{\pi}{2}$) and lyophilic ($\theta < \frac{\pi}{2}$) behavior; the first is an approximation to this separatrix. The model used here (such as the constraints to interaction parameters, etc.) is the same as the one explained in Fig. 3. In (b) the domains of lyophobic and lyophilic behavior are shown. In (c) and (d) sketches of the two contact angle scenarios are given, for a planar wall and for a colloid floating at a liquid-vapor interface, neglecting gravity effects. The wetting films at the α-γ interface as well as further wetting films which might be present, depending on the wetting domain under discussion, are suppressed for reasons of clarity. In (a) and (b) the curves correspond to the choices $\rho_{A,\alpha}/\rho_{A,\beta} = 4$, $\rho_{B,\alpha}/\rho_{B,\beta} = \frac{2}{3}$, which implies $D_{\alpha\beta} = 9$, $F_{AA}(l_{w\beta\gamma}) = \frac{13}{132}$, and $\hat{F}_{AA}(l_{w\alpha\gamma}) = \frac{13}{66}$.

In a first step we have assumed that the so-called mixing rule, or the modified version of it if the length parameters are not all equal, applies to both the fluid-fluid and the fluid-wall interactions. In this case the strength of the *A*-*B* interaction is the geometric mean of the strengths of the *A*-*A* and the *B*-*B* interactions, and the ratio of the wall-*A* and the wall-*B* interaction strengths is related to the ratio of the *A*-*A* and the *B*-*B* interactions by a corresponding relation. Given these relations, the three distinct wetting scenarios (ii), (iii), and (iv) sketched in Figs. 2(b)–2(d) can occur. These are tied to the three domains (ii), (iii), and (iv) in the two-dimensional space of system parameters as shown in Fig. 3. A scenario, in which the β film extends into both the wall-vapor (wall-γ) and the wall-liquid (wall-α) interface [i.e., the wetting domain (v) in Fig. 2(e)], is not possible.

As further steps we have relaxed the mixing rules for the fluid-wall and for the fluid-fluid interactions. Up to six different wetting scenarios can occur, if the mixing rules for the fluid-wall (see Fig. 4) and for the fluid-fluid interactions (see Fig. 5) are relaxed. It depends on the sign of the deviations from the mixing rule prescriptions how the space of system parameters is divided into the corresponding domains and which domains actually appear, e.g., whether a domain (v) is present.

For the special case that the mixing rules apply to both the fluid-fluid and the fluid-wall interactions, we searched for relations between these wetting domains and the contact angle θ. For the scenario in which the β film ends at the wall, but an α film forms at the wall-γ interface, one always finds $\theta < 90^{\rm o}$. Concerning the other two scenarios, the respective domains are subdivided into subdomains within which $\theta > 90^{\rm o}$ or $\theta < 90^{\rm o}$, respectively.

We note that the system parameters may be varied in two ways. Either via varying the various interaction strengths (i.e., by using different liquids or a wall with modified properties) or via changing the thermodynamic state and thus the bulk number densities, which enter into the definition of the dimensionless system parameters X and Y [Eqs. (24) and (43), respectively]. Both routes facilitate to switch between the

wetting domains. The insight we have gained concerning the wetting scenarios around a colloidal particle floating at a composite liquid-vapor interface, is potentially useful for tuning the capillarity induced interactions between such colloidal particles. The particles could be fabricated from the same or from different materials. Such knowledge is essential for designing the self-assembly of colloidal particles at liquid-vapor interfaces.

APPENDIX A: CONDITION FOR $S_{\alpha\beta\gamma} < 0$

In this Appendix, we determine the range of X values within which $S_{\alpha\beta\gamma} < 0$, which is the condition for having an intruding wetting film of the β phase at the α-γ interface. We start from Eq. (25), i.e.,

$$S_{\alpha\beta\gamma} = \epsilon_{AA}\rho_{A,\beta}^2\Bigg[\left(1-\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right)\left(1-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X^2 + \left(1-\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right)\left(1-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\xi_f X + \left(1-\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}\right)\left(1-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)\xi_f X + \left(1-\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}\right)\left(1-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\Bigg].$$

The condition $S_{\alpha\beta\gamma} < 0$ implies

$$\left(1-\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right)\left(1-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X^2 + \left(1-\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right)\left(1-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\xi_f X + \left(1-\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}\right)\left(1-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)\xi_f X + \left(1-\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}\right)\left(1-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right) < 0. \tag{A1}$$

In order to solve the inequality in Eq. (A1), we consider $S_{\alpha\beta\gamma} = 0$. There are two solutions X_1 and $X_2 > X_1$:

$$X_1 = -\sqrt{\left[\frac{\xi_f}{2}(D_{\alpha\beta}+D_{\beta\gamma})\right]^2 - D_{\alpha\beta}D_{\beta\gamma}} + \frac{\xi_f}{2}(D_{\alpha\beta}+D_{\beta\gamma})$$

and

$$X_2 = \sqrt{\left[\frac{\xi_f}{2}(D_{\alpha\beta}+D_{\beta\gamma})\right]^2 - D_{\alpha\beta}D_{\beta\gamma}} + \frac{\xi_f}{2}(D_{\alpha\beta}+D_{\beta\gamma}),$$

where $D_{\alpha\beta}$ and $D_{\beta\gamma}$ are given by Eqs. (27) and (28), respectively.

Here we use the assumed inequalities $\rho_{A,\alpha} > \rho_{A,\beta}$ and $\rho_{B,\alpha} < \rho_{B,\beta}$ [Eq. (22)], from which we infer that the prefactor of X^2 in Eq. (A1) is positive. In order to have $S_{\alpha\beta\gamma} < 0$, X must be in the range of $X_1 < X < X_2$. It is known that $X_1 < 0$ and $X_2 > 0$ because $D_{\alpha\beta} > 0$, $D_{\beta\gamma} < 0$, and $X > 0$ by definition. As a result, we have $S_{\alpha\beta\gamma} < 0$ within the range $0 < X < X_2$ [see Eq. (26)].

APPENDIX B: WALL-FLUID WETTING PARAMETERS

In this Appendix, the explicit expressions [see Eqs. (33)–(35)] for the wetting parameters $W_{\mathrm{w}\beta\alpha}$, $W_{\mathrm{w}\beta\gamma}$, and $W_{\mathrm{w}\alpha\gamma}$ are derived from the definitions in Eqs. (29)–(31).

By using relations similar to the ones in Eqs. (4) and (5), we find the surface tensions $\sigma_{\mathrm{w}\beta\alpha}$, $\sigma_{\mathrm{w}\beta\gamma}$, and $\sigma_{\mathrm{w}\alpha\gamma}$ of the partially wet interfaces (see below). With the corresponding equilibrium wetting film thicknesses $l = l_{\mathrm{w}\beta\alpha}$, $l_{\mathrm{w}\beta\gamma}$, and $l_{\mathrm{w}\alpha\gamma}$ one has

$$\sigma_{\mathrm{w}\beta\alpha} = \Omega_{\mathrm{s}}^{\mathrm{w}\beta\alpha}(l_{\mathrm{w}\beta\alpha}, T, \{\mu_i\}) \quad \text{with} \quad \left.\frac{\partial\Omega_{\mathrm{s}}^{\mathrm{w}\beta\alpha}(l)}{\partial l}\right|_{l=l_{\mathrm{w}\beta\alpha}} = 0, \tag{B1}$$

and similarly for $\sigma_{\mathrm{w}\beta\gamma}$ and $\sigma_{\mathrm{w}\alpha\gamma}$.

Using the sharp-kink approximation, the surface contributions to the grand canonical potential for the various partially wet interfaces are given by

$$\Omega_{\mathrm{s}}^{\mathrm{w}\beta\alpha}(l) = l(\Omega^\beta - \Omega^\alpha) + \omega_{\mathrm{w}\beta\alpha}(l) + \sigma_{\mathrm{w}\beta} + \sigma_{\beta\alpha}, \tag{B2}$$

and similarly for $\Omega_{\mathrm{s}}^{\mathrm{w}\beta\gamma}(l)$ and $\Omega_{\mathrm{s}}^{\mathrm{w}\alpha\gamma}(l)$, where $\sigma_{\mathrm{w}\beta}$ is the surface tension of the plain wall-β interface, without any intruding wetting film.

Therefore, Eq. (29), $W_{\mathrm{w}\beta\alpha}$, can be expressed as

$$W_{\mathrm{w}\beta\alpha} = l_{\mathrm{w}\beta\alpha}(\Omega^\beta - \Omega^\alpha) + \omega_{\mathrm{w}\beta\alpha}(l_{\mathrm{w}\beta\alpha}) + \sigma_{\mathrm{w}\beta} + \sigma_{\beta\alpha} - \sigma_{\mathrm{w}\alpha}, \tag{B3}$$

and similarly for $W_{\mathrm{w}\beta\gamma}$ and $W_{\mathrm{w}\alpha\gamma}$ [Eqs. (30) and (31), respectively]. We also make use of the relations

$$\Omega^\beta - \Omega^\alpha = -\left.\frac{\partial\omega_{\mathrm{w}\beta\alpha}(l)}{\partial l}\right|_{l=l_{\mathrm{w}\beta\alpha}}, \tag{B4}$$

and similarly for $\Omega^\beta - \Omega^\gamma$ and $\Omega^\alpha - \Omega^\gamma$.

The expressions for the surface tensions of various fluid interfaces have already been derived within the sharp-kink approximation [see Eqs. (9)–(11)]. In addition, the surface tensions and the various interface potentials ω characterizing the wall-fluid interfaces are given by

$$\sigma_{w\alpha} = -\frac{1}{2}\sum_{i,j}\rho_{i,\alpha}\rho_{j,\alpha}\int_0^\infty dy\, t_{ij}(y) + \sum_i \rho_{i,\alpha}\rho_w \int_0^\infty dy\, V_i(y), \tag{B5}$$

$$\omega_{w\beta\alpha}(l) = \sum_{i,j}(\rho_{i,\beta}-\rho_{i,\alpha})\rho_{j,\beta}\int_l^\infty dy\, t_{ij}(y) - \sum_i(\rho_{i,\beta}-\rho_{i,\alpha})\rho_w\int_l^\infty dy\, V_i(y), \tag{B6}$$

and similarly for $\sigma_{w\beta}$, $\sigma_{w\gamma}$, $\omega_{w\beta\gamma}(l)$, and $\omega_{w\alpha\gamma}(l)$, where

$$t_{ij}(y) = \int_y^\infty dx \int d^2\mathbf{r}_\parallel\, \tilde{w}_{ij}\left[\left(\mathbf{r}_\parallel^2 + x^2\right)^{\frac{1}{2}}\right]$$

and

$$V_i(y) = \int_y^\infty dx \int d^2\mathbf{r}_\parallel\, \tilde{v}_i\left[\left(\mathbf{r}_\parallel^2 + x^2\right)^{\frac{1}{2}}\right].$$

By taking the explicit expressions for $\tilde{w}_{ij}$ and $\tilde{v}_i$ [see Eqs. (12) and (32)], one obtains for Eqs. (B5) and (B6)

$$\sigma_{w\alpha} = \frac{13}{132}\pi\sum_{i,j}\epsilon_{ij}a_{ij}^4\rho_{i,\alpha}\rho_{j,\alpha} - \frac{13}{66}\pi\sum_i \epsilon_{wi}a_{wi}^4\rho_{i,\alpha}\rho_w, \tag{B7}$$

$$\begin{aligned}\omega_{w\beta\alpha}(l) = &-\pi\sum_{i,j}\epsilon_{ij}a_{ij}^4(\rho_{i,\beta}-\rho_{i,\alpha})\rho_{j,\beta}\left[\frac{1}{3}\left(\frac{a_{ij}}{l}\right)^2 - \frac{4}{5}\left(\frac{a_{ij}}{l}\right)^3\right]\\ &+\pi\sum_i \epsilon_{wi}a_{wi}^4(\rho_{i,\beta}-\rho_{i,\alpha})\rho_w\left[\frac{1}{3}\left(\frac{a_{wi}}{l}\right)^2 - \frac{4}{5}\left(\frac{a_{wi}}{l}\right)^3\right],\end{aligned} \tag{B8}$$

and similarly for $\sigma_{w\beta}$, $\sigma_{w\gamma}$, $\omega_{w\beta\gamma}(l)$, and $\omega_{w\alpha\gamma}(l)$.

Using the derivative of Eq. (B8) with respect to the wetting film thickness, Eq. (B4) turns into

$$\begin{aligned}\Omega^\beta - \Omega^\alpha = &-\pi\sum_{i,j}\epsilon_{ij}a_{ij}^3(\rho_{i,\beta}-\rho_{i,\alpha})\rho_{j,\beta}\left[\frac{2}{3}\left(\frac{a_{ij}}{l_{w\beta\alpha}}\right)^3 - \frac{12}{5}\left(\frac{a_{ij}}{l_{w\beta\alpha}}\right)^4\right]\\ &+\pi\sum_i \epsilon_{wi}a_{wi}^3(\rho_{i,\beta}-\rho_{i,\alpha})\rho_w\left[\frac{2}{3}\left(\frac{a_{wi}}{l_{w\beta\alpha}}\right)^3 - \frac{12}{5}\left(\frac{a_{wi}}{l_{w\beta\alpha}}\right)^4\right],\end{aligned} \tag{B9}$$

and similarly for $\Omega^\beta - \Omega^\gamma$ and $\Omega^\alpha - \Omega^\gamma$. Here, $\Omega^\alpha - \Omega^\gamma$ is zero because we consider the bulk phases α and γ to be in thermal equilibrium.

Finally, based on Eq. (B7), Eq. (B3) can be expressed as

$$\begin{aligned}W_{w\beta\alpha} = &\pi\sum_{i,j}\epsilon_{ij}a_{ij}^4(\rho_{i,\beta}-\rho_{i,\alpha})\rho_{j,\beta}\left[\frac{13}{66} - \left(\frac{a_{ij}}{l_{w\beta\alpha}}\right)^2 + \frac{16}{5}\left(\frac{a_{ij}}{l_{w\beta\alpha}}\right)^3\right]\\ &-\pi\sum_i \epsilon_{wi}a_{wi}^4(\rho_{i,\beta}-\rho_{i,\alpha})\rho_w\left[\frac{13}{66} - \left(\frac{a_{wi}}{l_{w\beta\alpha}}\right)^2 + \frac{16}{5}\left(\frac{a_{wi}}{l_{w\beta\alpha}}\right)^3\right],\end{aligned}$$

and similarly for $W_{w\beta\gamma}$ and $W_{w\alpha\gamma}$. Upon changing notation and by introducing the Kronecker symbol δ, we arrive at the expressions in Eqs. (33)–(35).

APPENDIX C: DOMAINS CHARACTERIZED BY $S_{w\beta\alpha} < 0$, $S_{w\beta\gamma} < 0$, OR $S_{w\alpha\gamma} < 0$

In this Appendix, we search for domains in the (X, Y) parameter space within which the conditions $S_{w\beta\alpha} < 0$, $S_{w\beta\gamma} < 0$, or $S_{w\alpha\gamma} < 0$ hold. We start this discussion with the condition $S_{w\beta\alpha} < 0$. To this end we introduce the notations $\epsilon_{AB} = \xi_f\sqrt{\epsilon_{AA}\epsilon_{BB}}$, $\epsilon_{wA} = \xi_{wA}\sqrt{\epsilon_{ww}\epsilon_{AA}}$, and $\epsilon_{wB} = \xi_{wB}\sqrt{\epsilon_{ww}\epsilon_{BB}}$ so that $\epsilon_{wA}/\epsilon_{wB} = (\xi_{wA}/\xi_{wB})\sqrt{\epsilon_{AA}/\epsilon_{BB}} =: \xi_w\sqrt{\epsilon_{AA}/\epsilon_{BB}}$. Accordingly, we express $S_{w\beta\alpha}$ [Eq. (40)] as

$$\begin{aligned}S_{w\beta\alpha} = &(\rho_{A,\beta}-\rho_{A,\alpha})(\epsilon_{AA}\rho_{A,\beta} - \xi_{wA}\sqrt{\epsilon_{ww}\epsilon_{AA}}\rho_w + \xi_f\sqrt{\epsilon_{AA}\epsilon_{BB}}\rho_{B,\beta})\\ &+(\rho_{B,\beta}-\rho_{B,\alpha})(\xi_f\sqrt{\epsilon_{AA}\epsilon_{BB}}\rho_{A,\beta} + \epsilon_{BB}\rho_{B,\beta} - \xi_{wB}\sqrt{\epsilon_{ww}\epsilon_{BB}}\rho_w).\end{aligned}$$

In terms of the dimensionless parameters $X = \frac{\rho_{B,\beta}}{\rho_{A,\beta}}\sqrt{\frac{\epsilon_{BB}}{\epsilon_{AA}}}$ and $Y = \frac{\rho_{\rm w}}{\rho_{A,\beta}}\frac{\epsilon_{wA}}{\epsilon_{AA}}$, $S_{{\rm w}\beta\alpha}$ can be written as

$$S_{{\rm w}\beta\alpha} = \epsilon_{AA}\rho_{A,\beta}^2\Bigg\{\left[\left(1-\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right)X+\left(1-\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}\right)\right](X+1)+\left[\left(1-\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right)+\left(1-\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}\right)\right](\xi_f-1)X$$
$$-\left[\left(1-\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right)\frac{X}{\xi_{\rm w}}+\left(1-\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}\right)\right]Y\Bigg\}. \tag{C1}$$

The condition $S_{{\rm w}\beta\alpha} < 0$, together with Eq. (C1), leads to the inequality

$$\left[\left(1-\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right)\frac{X}{\xi_{\rm w}}+\left(1-\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}\right)\right]Y > \left[\left(1-\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right)X+\left(1-\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}\right)\right](X+1)+\left[\left(1-\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right)+\left(1-\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}\right)\right](\xi_f-1)X. \tag{C2}$$

In order to proceed we analyze the sign of the prefactor of Y. It is positive, if

$$\left(1-\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right)\frac{X}{\xi_{\rm w}} > -\left(1-\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}\right). \tag{C3}$$

Taking into account the assumed inequalities $\rho_{A,\alpha} > \rho_{A,\beta}$ and $\rho_{B,\alpha} < \rho_{B,\beta}$ [Eq. (22)], Eq. (C3) leads to $X > \xi_{\rm w}D_{\alpha\beta}$ with $D_{\alpha\beta} > 0$. Under this condition of a positive prefactor of Y, we find

$$Y > X+1+\frac{\left(1-\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right)\left(1-\frac{1}{\xi_{\rm w}}\right)X}{\left[\left(1-\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right)\frac{X}{\xi_{\rm w}}+\left(1-\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}\right)\right]}(X+1)+\frac{\left[\left(1-\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right)+\left(1-\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}\right)\right](\xi_f-1)}{\left[\left(1-\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right)\frac{X}{\xi_{\rm w}}+\left(1-\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}\right)\right]}X \tag{C4}$$

or, expressed in terms of $D_{\alpha\beta}$ [Eq. (27)],

$$Y > X+1+(\xi_{\rm w}-1)\frac{X}{(X-\xi_{\rm w}D_{\alpha\beta})}(X+1)+\xi_{\rm w}(\xi_f-1)(1-D_{\alpha\beta})\frac{X}{(X-\xi_{\rm w}D_{\alpha\beta})}. \tag{C5}$$

In the case of a negative prefactor of Y, i.e., within the X interval $0 < X < \xi_{\rm w}D_{\alpha\beta}$, we obtain the inequality

$$0 < Y < X+1+(\xi_{\rm w}-1)\frac{X}{(X-\xi_{\rm w}D_{\alpha\beta})}(X+1)+\xi_{\rm w}(\xi_f-1)(1-D_{\alpha\beta})\frac{X}{(X-\xi_{\rm w}D_{\alpha\beta})}. \tag{C6}$$

In summary, the conditions for wetting of the wall-α interface by a film of the β phase are given by

$$0 < X < \xi_{\rm w}D_{\alpha\beta} \text{ and } 0 < Y < X+1+(\xi_{\rm w}-1)\frac{X}{(X-\xi_{\rm w}D_{\alpha\beta})}(X+1)+\xi_{\rm w}(\xi_f-1)(1-D_{\alpha\beta})\frac{X}{(X-\xi_{\rm w}D_{\alpha\beta})}$$

or if

$$X > \xi_{\rm w}D_{\alpha\beta} \text{ and } Y > X+1+(\xi_{\rm w}-1)\frac{X}{(X-\xi_{\rm w}D_{\alpha\beta})}(X+1)+\xi_{\rm w}(\xi_f-1)(1-D_{\alpha\beta})\frac{X}{(X-\xi_{\rm w}D_{\alpha\beta})},$$

which coincide with Eqs. (44) and (45).

Now, we determine the domains in the (X, Y) parameter space within which the conditions $S_{{\rm w}\beta\gamma} < 0$ and $S_{{\rm w}\alpha\gamma} < 0$ are valid. By using the same notation as introduced above we can rewrite $S_{{\rm w}\beta\gamma}$ and $S_{{\rm w}\alpha\gamma}$ as

$$S_{{\rm w}\beta\gamma} = \epsilon_{AA}\rho_{A,\beta}^2\Bigg\{\left[\left(1-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X+\left(1-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\right](X+1)+\left[\left(1-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)+\left(1-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\right](\xi_f-1)X$$
$$-\left[\left(1-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)\frac{X}{\xi_{\rm w}}+\left(1-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\right]Y\Bigg\} \tag{C7}$$

and

$$S_{{\rm w}\alpha\gamma} = \epsilon_{AA}\rho_{A,\beta}^2\Bigg\{\left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X+\left(\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\right]\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}X+\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}\right)$$
$$+\left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}+\left(\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right](\xi_f-1)X$$
$$-\left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)\frac{X}{\xi_{\rm w}}+\left(\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\right]Y\Bigg\}. \tag{C8}$$

The condition $S_{w\beta\gamma} < 0$ leads to the inequality

$$\left[\left(1-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)\frac{X}{\xi_w}+\left(1-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\right]Y > \left[\left(1-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X+\left(1-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\right](X+1) + \left[\left(1-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)+\left(1-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\right](\xi_f-1)X. \tag{C9}$$

Analogously, the condition $S_{w\alpha\gamma} < 0$ leads to the inequality

$$\left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)\frac{X}{\xi_w}+\left(\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\right]Y > \left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X+\left(\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\right]\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}X+\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}\right) + \left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}+\left(\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right](\xi_f-1)X. \tag{C10}$$

In both inequalities [Eqs. (C9) and (C10)], the prefactors of Y are positive for all $X > 0$, due to the assumed inequalities between the number densities [Eq. (22)]. Therefore, one can reformulate Eqs. (C9) and (C10) as

$$Y > X+1+\frac{\left(1-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)\left(1-\frac{1}{\xi_w}\right)X}{\left[\left(1-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)\frac{X}{\xi_w}+\left(1-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\right]}(X+1)+\frac{\left[\left(1-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)+\left(1-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\right](\xi_f-1)}{\left[\left(1-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)\frac{X}{\xi_w}+\left(1-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\right]}X \tag{C11}$$

and

$$Y > \frac{\rho_{B,\alpha}}{\rho_{B,\beta}}X+\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}+\frac{\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)\left(1-\frac{1}{\xi_w}\right)X}{\left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)\frac{X}{\xi_w}+\left(\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\right]}\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}X+\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}\right)+\frac{\left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}+\left(\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}\right](\xi_f-1)}{\left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}}-\frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)\frac{X}{\xi_w}+\left(\frac{\rho_{A,\alpha}}{\rho_{A,\beta}}-\frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right)\right]}X. \tag{C12}$$

By introducing the expressions for $D_{\beta\gamma}$ [Eq. (28)] and $D_{\alpha\gamma}$ [Eq. (48)], Eqs. (C11) and (C12) render the conditions expressed via Eqs. (46) and (47), respectively.

APPENDIX D: EQUILIBRIUM WETTING FILM THICKNESSES

In this Appendix, we investigate the equilibrium wetting film thicknesses at fluid-fluid or wall-fluid interfaces. $\Omega_s(l)$ attains its minimum at the equilibrium wetting film thickness. First, we consider the case of a planar α-γ interface with an intruding β wetting film. From Eqs. (3) and (5), we find

$$\left.\frac{\partial\Omega_s^{\alpha\beta\gamma}(l)}{\partial l}\right|_{l=l_{\alpha\beta\gamma}} = \Omega^\beta-\Omega^\gamma+\left.\frac{\partial\omega_{\alpha\beta\gamma}(l)}{\partial l}\right|_{l=l_{\alpha\beta\gamma}} = 0. \tag{D1}$$

Here, $\Omega^\beta-\Omega^\gamma$ is positive, given that the α phase is the stable phase and the β phase is slightly off coexistence. Therefore, $\frac{\partial\omega_{\alpha\beta\gamma}(l)}{\partial l}$ must be negative at $l = l_{\alpha\beta\gamma}$. By using Eq. (13) and taking all length parameters to be equal, one obtains

$$\frac{\partial\omega_{\alpha\beta\gamma}(l)}{\partial l} = \pi a_{AA}^3 S_{\alpha\beta\gamma}\left[\frac{2}{3}\left(\frac{a_{AA}}{l}\right)^3-\frac{12}{5}\left(\frac{a_{AA}}{l}\right)^4\right]. \tag{D2}$$

We have to consider only the case that $S_{\alpha\beta\gamma}$ is negative because only then a sufficiently thick β wetting film can occur. This implies that the expression in square brackets in Eq. (D2) must be positive. As a result, $l_{\alpha\beta\gamma}$ is definitely larger than $\frac{18}{5}a_{AA}$.

By inserting Eq. (D2) into Eq. (D1), one finds that it is possible that Eq. (D1) has no solution, only one solution, or two solutions, depending on the magnitude of $\Omega^\beta-\Omega^\gamma$. If Eq. (D1) has no solution or one solution, $\Omega_s^{\alpha\beta\gamma}(l)$ has a minimum at $l\to 0$, i.e., there is no β wetting film.

If Eq. (D1) has two solutions l_1 and $l_2 > l_1$, one knows that $\frac{18}{5}a_{AA} < l_1 < l_2$ (see above). In order to find out which of the two solutions corresponds to a minimum or rather to a maximum, we explore the sign of $\frac{\partial\Omega_s^{\alpha\beta\gamma}(l)}{\partial l}$ near l_1 and l_2:

(1) If $l < l_1$, one has $\frac{\partial\Omega_s^{\alpha\beta\gamma}(l)}{\partial l} > 0$, i.e., the slope of $\Omega_s^{\alpha\beta\gamma}(l)$ is positive for $l < l_1$.

(2) If $l_1 < l < l_2$, $\frac{\partial\Omega_s^{\alpha\beta\gamma}(l)}{\partial l} < 0$, i.e., the slope of $\Omega_s^{\alpha\beta\gamma}(l)$ is negative for $l_1 < l < l_2$.

(3) If $l > l_2$, $\frac{\partial\Omega_s^{\alpha\beta\gamma}(l)}{\partial l} > 0$, i.e., the slope of $\Omega_s^{\alpha\beta\gamma}(l)$ is again positive for $l > l_2$.

Thus, $\Omega_s^{\alpha\beta\gamma}(l)$ has its maximum at $l = l_1$ and its minimum at $l = l_2$. Therefore, the equilibrium film thickness is given by $l_2 =: l_{\alpha\beta\gamma}$. At three-phase coexistence, we have $\Omega^\beta-\Omega^\gamma\to 0$ so that $l_1\to\frac{18}{5}a_{AA}$ and $l_2\to\infty$, i.e., $l_{\alpha\beta\gamma}\to\infty$.

Analogously the equilibrium thickness of the β wetting film at a planar wall-α interface is determined. Based on Eqs. (B1), (B2), and (B8) with equal length parameters for all interactions, one finds $l_{w\beta\alpha} > \frac{18}{5}a_{AA}$. At three-phase coexistence, i.e., $\Omega^\beta-\Omega^\alpha\to 0$, we have $l_{w\beta\alpha}\to\infty$.

In the case of a planar wall-γ interface wetted by a film of the β phase we find again $l_{w\beta\gamma} > \frac{18}{5}a_{AA}$ and $l_{w\beta\gamma} \to \infty$ at three-phase coexistence. For the planar wall-γ interface with an intruding α wetting film, we have

$$\left.\frac{\partial \Omega_s^{w\alpha\gamma}(l)}{\partial l}\right|_{l=l_{w\alpha\gamma}} = \Omega^\alpha - \Omega^\gamma + \left.\frac{\partial \omega_{w\alpha\gamma}(l)}{\partial l}\right|_{l=l_{w\alpha\gamma}} = 0, \tag{D3}$$

where

$$\frac{\partial \omega_{w\alpha\gamma}(l)}{\partial l} = \pi a_{AA}^3 S_{w\alpha\gamma}\left[\frac{2}{3}\left(\frac{a_{AA}}{l}\right)^3 - \frac{12}{5}\left(\frac{a_{AA}}{l}\right)^4\right]. \tag{D4}$$

Again, all length parameters are taken to be equal. Here, Ω^α and Ω^γ are equal because the system is at α-γ coexistence. With $S_{w\alpha\gamma} < 0$, the equilibrium wetting film thickness $l_{w\alpha\gamma} \to \infty$ is found.

APPENDIX E: CONDITION FOR $\sigma_{w\alpha} < \sigma_{w\gamma}$

In this Appendix, we determine the domain in the (X, Y) parameter space for which $\sigma_{w\alpha} < \sigma_{w\gamma}$ is satisfied. By using Eq. (B7) and the similar expression for $\sigma_{w\gamma}$, we find

$$\sigma_{w\alpha} - \sigma_{w\gamma} = \frac{13}{132}\pi\left[\sum_{i,j}\epsilon_{ij}a_{ij}^4(\rho_{i,\alpha}\rho_{j,\alpha} - \rho_{i,\gamma}\rho_{j,\gamma}) - 2\sum_i \epsilon_{wi}a_{wi}^4(\rho_{i,\alpha} - \rho_{i,\gamma})\rho_w\right] < 0. \tag{E1}$$

Assuming that all length parameters in Eq. (E1) are equal, i.e., $a_{AA} = a_{AB} = a_{BB} = a_{wA} = a_{wB}$, we find

$$(\rho_{A,\alpha} - \rho_{A,\gamma})[(\rho_{A,\alpha} + \rho_{A,\gamma})\epsilon_{AA} - 2\epsilon_{wA}\rho_w] + (\rho_{A,\alpha}\rho_{B,\alpha} - \rho_{A,\gamma}\rho_{B,\gamma})(2\epsilon_{AB}) + (\rho_{B,\alpha} - \rho_{B,\gamma})[(\rho_{B,\alpha} + \rho_{B,\gamma})\epsilon_{BB} - 2\epsilon_{wB}\rho_w] < 0. \tag{E2}$$

By introducing the dimensionless parameters X and Y, Eq. (E2) can be written as

$$\left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}} - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right]\left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}} + \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} + \frac{\rho_{A,\gamma}}{\rho_{A,\beta}} - 2Y\right] < 0.$$

Here, one has $(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}} - \frac{\rho_{B,\gamma}}{\rho_{B,\beta}})X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} - \frac{\rho_{A,\gamma}}{\rho_{A,\beta}} > 0$ for all $X > 0$.

In conclusion, $\sigma_{w\alpha} < \sigma_{w\gamma}$ is satisfied if

$$Y > \frac{1}{2}\left[\left(\frac{\rho_{B,\alpha}}{\rho_{B,\beta}} + \frac{\rho_{B,\gamma}}{\rho_{B,\beta}}\right)X + \frac{\rho_{A,\alpha}}{\rho_{A,\beta}} + \frac{\rho_{A,\gamma}}{\rho_{A,\beta}}\right].$$

Otherwise, we have $\sigma_{w\alpha} > \sigma_{w\gamma}$.

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