A class of binary mixtures of Janus fluids formed by colloidal spheres with the hydrophobic hemispheres constrained to point either up or down are studied by means of Gibbs ensemble Monte Carlo simulations and simple analytical approximations. These fluids can be experimentally realized by the application of an external static electrical field. The gas-liquid and demixing phase transitions in five specific models with different patch-patch affinities are analyzed. It is found that a gas-liquid transition is present in all the models, even if only one of the four possible patch-patch interactions is attractive. Moreover, provided the attraction between like particles is stronger than between unlike particles, the system demixes into two subsystems with different composition at sufficiently low temperatures and high densities.

I. INTRODUCTION

Engineering new materials through direct self-assembly processes has recently become a new concrete possibility due to the remarkable developments in the synthesis of patchy colloids with different shapes and functionalities. Nowadays, both the synthesis and the aggregation process of patchy colloids can be experimentally controlled with a precision and reliability that were not possible until a few years ago. Within the general class of patchy colloids, a particularly interesting case is provided by the so-called Janus fluid, where the surface of the colloidal particle is evenly partitioned between the hydrophobic and the hydrophilic moieties, so that attraction between two spheres is possible only if both hydrophobic patches are facing one another. Several experimental and theoretical studies have illustrated the remarkable properties of this paradigmatic case.

The behavior of patchy particles under external fields has received recent attention. By applying an external electrical or magnetic field, appropriately synthesized dipolar Janus particles may be made to align orientationally, so as to expose their functionally active hemisphere either all up or all down (See Ref. 9, Secs. 1.4.3.1 and 1.4.3.2, and references therein). By mixing the two species one could have in the laboratory a binary mixture of Janus particles where the functionally active patch points in opposite directions for each species.

While theoretical studies have been keeping up with, and sometimes even anticipated, experimental developments, the complexities of the anisotropic interactions in patch colloids have mainly restricted these investigations to numerical simulations, which have revealed interesting specificities in the corresponding phase diagrams.

Motivated by the above scenario, we have recently introduced a simplified binary-mixture model of a fluid of Janus spheres (interacting via the anisotropic Kern–Frenkel potential) where the hydrophobic patches on each sphere could point only either up (species 1) or down (species 2). This orientational restriction, which is reminiscent of Zwanzig’s model for liquid crystals, clearly simplifies the theoretical description while still distilling out the main features of the original Janus model.

In the present paper, we generalize the above Janus fluid model by assuming arbitrary values for the energy scales $\epsilon_{ij}$ of the attractive interactions associated with the four possible pair configurations (see Fig. 1), which allows for a free tuning of the strength of the patch-patch attraction. In some cases this can effectively mimic the
reduction of the coverage in the original Kern–Frenkel model. Note that, in Fig. 1, \( \epsilon_{ij} \) is the energy associated with the (attractive) interaction between a particle of species \( i \) (at the left) and a particle of species \( j \) (at the right) when the former is below the latter, with the arrow always indicating the hydrophobic (i.e., attractive) patch. The original Kern–Frenkel model then corresponds to \( \epsilon_{12} > 0 \) and \( \epsilon_{11} = \epsilon_{22} = \epsilon_{21} = 0 \), whereas the full coverage limit is equivalent to \( \epsilon_{11} = \epsilon_{22} = \epsilon_{12} = \epsilon_{21} > 0 \). On the other hand, the effect of reducing the coverage from the full to the Janus limit, can be effectively mimicked by fixing \( \epsilon_{12} > 0 \) and progressively decreasing \( \epsilon_{21} \) and \( \epsilon_{11} = \epsilon_{22} \). Moreover, the class of models depicted in Fig. 1 allows for an interpretation more general and flexible than the hydrophobic-hydrophilic one. For instance, one may assume that attraction is only possible when patches of different type are facing one another (i.e., \( \epsilon_{11} = \epsilon_{22} > 0 \) and \( \epsilon_{12} = \epsilon_{21} = 0 \)). As shown below, this will provide a rich scenario of intermediate cases with a number of interesting features in the phase diagram of both the gas-liquid and the demixing transitions.

We emphasize the fact that in the simulation part of the present study we will always assume “global” equimolarity, that is, the combined number of particles \( N_1 \) is always equal to the combined number of particles of species 2 \( N_2 \), so that \( N_1 = N_2 = N/2 \), where \( N \) is the total number of particles. On the other hand, the equimolarity condition is not imposed on each coexisting phase.

The organization of the paper is as follows. The class of models is briefly described in Sec. II. Next, in Sec. III we present our Gibbs ensemble Monte Carlo (GEMC) results for the gas-liquid and demixing transitions. The complementary theoretical approach is presented in Sec. IV. The paper is closed with some concluding remarks in Sec. V.

II. DESCRIPTION OF THE MODELS

In our class of binary-mixture Janus models, particles of species 1 (with a mole fraction \( x_1 \)) and 2 (with a mole fraction \( x_2 = 1 - x_1 \)) are dressed with two up-down hemispheres with different attraction properties, as sketched in Fig. 1. The pair potential between a particle of species \( i \) at \( r_1 \) and a particle of species \( j \) at \( r_2 \) is

\[
\phi_{ij}(r_{12}) = \varphi_{ij}(r_{12})\Theta(z_{12}) + \varphi_{ji}(r_{12})\Theta(-z_{12}),
\]

(1)

where \( \Theta(z) \) is the Heaviside step function, \( r_{12} = r_2 - r_1 \), \( z_{12} = z_2 - z_1 \), and

\[
\varphi_{ij}(r) = \begin{cases} 
\infty, & 0 \leq r < \sigma, \\
-\epsilon_{ij}, & \sigma \leq r < \sigma + \Delta, \\
0, & r \geq \sigma + \Delta,
\end{cases}
\]

(2)

is a standard square-well (SW) potential of diameter \( \sigma \), width \( \Delta \), and energy depth \( \epsilon_{ij} \), except that, in general, \( \epsilon_{12} \neq \epsilon_{21} \). By symmetry, one must have \( \epsilon_{22} = \epsilon_{11} \) (see Fig. 1), so that (for given values of \( \sigma \) and \( \Delta \)) the space parameter of the interaction potential becomes three-dimensional, as displayed in Fig. 2. Except in the case of the hard-sphere (HS) model \( (\epsilon_{ij} = 0) \), one can freely choose one of the non-zero \( \epsilon_{ij} \) to fix the energy scale. Thus, we call \( \epsilon = \max_{ij}\{\epsilon_{ij}\} \) and use the three independent ratios \( \epsilon_{ij}/\epsilon \) as axes in Fig. 2. The model represented by the coordinates \((1, 1, 1)\) is the fully isotropic SW fluid, where species 1 and 2 become indistinguishable. Next, without loss of generality, we choose \( \epsilon_{12} \geq \epsilon_{21} \). With those criteria, all possible models of the class lie either inside the triangle SW-I0-B0-SW or inside the square SW-B0-A0-J0-SW. One could argue that any point inside the cube displayed in Fig. 2 may represent a distinct model, but this is not so. First, the choice \( \epsilon = \max_{ij}\{\epsilon_{ij}\} \) restricts the models to those lying on one of the three faces \( \epsilon_{11}/\epsilon = 1 \), \( \epsilon_{12}/\epsilon = 1 \), or \( \epsilon_{21}/\epsilon = 1 \). Second, the choice \( \epsilon_{12} \geq \epsilon_{21} \) reduces the face \( \epsilon_{11}/\epsilon = 1 \) to the line SW-J0 and the face \( \epsilon_{11}/\epsilon = 1 \) to the half-face SW-I0-B0-SW. The vertices SW, I0, B0, A0, and J0 define the five distinguished models we will specifically study. Those models, together with the HS one, are summarized in Table I.

### TABLE I. Definition of the models.

| Model | \( \epsilon_{11} \) | \( \epsilon_{12} \) | \( \epsilon_{21} \) | \( \epsilon_{22} \) |
|-------|-----------------|-----------------|-----------------|-----------------|
| HS    | 0               | 0               | 0               | 0               |
| A0    | 0               | \( \epsilon \)  | 0               | 0               |
| I0    | \( \epsilon \)  | 0               | 0               | \( \epsilon \)  |
| J0    | 0               | \( \epsilon \)  | \( \epsilon \)  | 0               |
| B0    | \( \epsilon \)  | \( \epsilon \)  | 0               | \( \epsilon \)  |
| SW    | \( \epsilon \)  | \( \epsilon \)  | \( \epsilon \)  | \( \epsilon \)  |

FIG. 2. Parameter space of the class of Janus models defined in the paper.
The rationale behind our nomenclature for the models goes as follows. Models with $\epsilon_{12} = \epsilon_{21}$ are isotropic and so we use the letter I to denote the isotropic models with $0 \leq \epsilon_{12}/\epsilon = \epsilon_{21}/\epsilon \leq 1$ and $\epsilon_{11}/\epsilon = 1$. Apart from them, the only additional isotropic models are those with $\epsilon_{12}/\epsilon = \epsilon_{21}/\epsilon = 1$ and $0 \leq \epsilon_{11}/\epsilon \leq 1$, and we denote them with the letter (J) next to I. All the remaining models are anisotropic (i.e., $\epsilon_{12} \neq \epsilon_{21}$). Out of them, we use the letter A to denote the particular subclass of anisotropic models ($0 \leq \epsilon_{11}/\epsilon = \epsilon_{21}/\epsilon \leq 1$ and $\epsilon_{12}/\epsilon = 1$) which can be viewed as the anisotropic counterpart of the isotropic subclass I. Analogously, we employ the letter (B) next to A to refer to the anisotropic counterpart ($\epsilon_{11}/\epsilon = \epsilon_{12}/\epsilon = 1$ and $0 \leq \epsilon_{21}/\epsilon \leq 1$) of the isotropic models J. Finally, the number 0 is used to emphasize that the corresponding models are the extreme cases of the subclasses I, J, A, and B, respectively.

Model A0 is the one more directly related to the original Kern–Frenkel potential and was the one analyzed in Ref. 12. Also related to that potential is model B0, where only the interaction between the two hydrophilic patches is purely repulsive. On the other hand, in models I0 and J0 (where $\epsilon_{12} = \epsilon_{21}$) the interaction becomes isotropic and the Janus character of the model is blurred. In model I0 the fluid reduces to a binary mixture with attractive interactions between like components and HS repulsions between unlike ones. This model was previously studied by Zaccarelli et al. using integral equation techniques.

In the complementary model J0 attraction exists only between unlike particles. The points A0, B0, I0, and J0 can be reached from the one-component SW fluid along models represented by the lines A, B, I, and J, respectively. Of course, other intermediate models are possible inside the triangle SW-I0-B0-SW or inside the square SW-B0-I0-J0 (where $\gamma = I, II$). Regarding the volume changes, following Ref. 20 we performed a random walk in ln($V^{(I)}/V^{(II)}$), with $V^{(\gamma)}$ the volume of the box $\gamma$, choosing a maximum volume displacement of 1%. The box move is computationally the most expensive one. This is because, after each volume move, it is necessary, in order to determine the next acceptance probability, to perform a full potential energy calculation since all the particle coordinates are rescaled by the factor associated with the enlargement or reduction of the boxes. However, this is not necessary for the other two moves since in those cases only the coordinates of a single particle change.

Both in the condensation and in the demixing problems, the Monte Carlo swap move consisted in moving a particle selected randomly in one box into the other box, so that the number of particles of each species in both boxes ($N_{1}^{(I)}$, $N_{1}^{(II)}$, $N_{2}^{(I)}$, and $N_{2}^{(II)}$) were fluctuating quantities. The only constraint was that the total number of particles was the same for both species, i.e., $N_{1} = N_{1}^{(I)} + N_{1}^{(II)} = N_{2}^{(I)} + N_{2}^{(II)} = N_{2} = N/2$. In the condensation problem we fixed the global density $\rho = N/(V^{(I)} + V^{(II)})$ (in all the cases we took $\rho^* = 0.3$, a value slightly below the expected critical density) and then varied the temperature $T$ (below the critical temperature). The measured output quantities where the partial densities $\rho_{i}^{(I)} = N_{i}^{(I)}/V^{(I)}$ and $\rho_{i}^{(II)} = N_{i}^{(II)}/V^{(II)}$, where $N_{i}^{(\gamma)} = N_{1}^{(\gamma)} + N_{2}^{(\gamma)}$ is the total number of particles in box $\gamma$ = I, II. Note that ($\rho_{i}^{(II)} - \rho_{i}^{(I)})/(\rho - \rho_{i}^{(I)}) = V^{(I)}/V^{(II)}$. In contrast, in the demixing problem we fixed $T$ (above the critical temperature) and varied $\rho$, the output observables being the local mole fractions $x_{\gamma}^{(I)} = N_{\gamma}^{(I)}/N^{(I)}$ and $x_{\gamma}^{(II)} = N_{\gamma}^{(II)}/N^{(II)}$. In this case, the lever rule is $(x_{\gamma}^{(I)} - \frac{1}{2})/(\frac{1}{2} - x_{\gamma}^{(I)}) = N^{(I)}/N^{(II)}$.

The total number of particles of each species was $N_{1} = N_{2} = 250$, what was checked to be sufficient for our

### III. GIBBS ENSEMBLE MONTE CARLO SIMULATIONS

In this paper, we use GEMC techniques to study the gas-liquid condensation process of models SW, A0, B0, I0, and J0 and the demixing transition of models I0 and B0. We have chosen the width of the attractive patch as in the experiment of Hong et al. ($\Delta/\sigma = 0.05$). Given the very small width of the attractive wells, we expect the liquid phase to be metastable with respect to the corresponding solid one. Reduced densities $\rho^* = \rho \sigma^3$ and temperatures $T^* = k_B T / \epsilon$ will be employed throughout.

### A. Technical details

The GEMC method is widely adopted as a standard method for calculating phase equilibria from molecular simulations. According to this method, the simulation is performed in two boxes (I and II) containing the coexisting phases. Equilibration in each phase is guaranteed by moving particles. Equality of pressures is satisfied in a statistical sense by expanding the volume of one of the boxes and contracting the volume of the other one, keeping the total volume constant. Chemical potentials are equalized by transferring particles from one box to the other one.

In the GEMC run we have on each step a probability $a_p/(a_p + a_x)$, $a_x/(a_p + a_x)$, and $a_x/(a_p + a_x)$ for a particle random displacement, a volume change, and a particle swap move between both boxes, respectively. We generally chose the relative weights $a_p = 1$, $a_x = 1/10$, and $a_{SW} = 20$. To preserve the up-down fixed patch orientation, rotation of particles was not allowed. The maximum particle displacement was kept equal to $10^{-3}L^3$ where $L^3$ is the side of the (cubic) box $\gamma = I$, II. Regarding the volume changes, following Ref. 20 we performed a random walk in ln($V^{(I)}/V^{(II)}$), with $V^{(\gamma)}$ the volume of the box $\gamma$, choosing a maximum volume displacement of 1%. The volume move is computationally the most expensive one. This is because, after each volume move, it is necessary, in order to determine the next acceptance probability, to perform a full potential energy calculation since all the particle coordinates are rescaled by the factor associated with the enlargement or reduction of the boxes. However, this is not necessary for the other two moves since in those cases only the coordinates of a single particle change.

Both in the condensation and in the demixing problems, the Monte Carlo swap move consisted in moving a particle selected randomly in one box into the other box, so that the number of particles of each species in both boxes ($N_{1}^{(I)}$, $N_{1}^{(II)}$, $N_{2}^{(I)}$, and $N_{2}^{(II)}$) were fluctuating quantities. The only constraint was that the total number of particles was the same for both species, i.e., $N_{1} = N_{1}^{(I)} + N_{1}^{(II)} = N_{2}^{(I)} + N_{2}^{(II)} = N_{2} = N/2$. In the condensation problem we fixed the global density $\rho = N/(V^{(I)} + V^{(II)})$ (in all the cases we took $\rho^* = 0.3$, a value slightly below the expected critical density) and then varied the temperature $T$ (below the critical temperature). The measured output quantities where the partial densities $\rho_{i}^{(I)} = N_{i}^{(I)}/V^{(I)}$ and $\rho_{i}^{(II)} = N_{i}^{(II)}/V^{(II)}$, where $N_{i}^{(\gamma)} = N_{1}^{(\gamma)} + N_{2}^{(\gamma)}$ is the total number of particles in box $\gamma = I, II$. Note that ($\rho_{i}^{(II)} - \rho_{i}^{(I)})/(\rho - \rho_{i}^{(I)}) = V^{(I)}/V^{(II)}$. In contrast, in the demixing problem we fixed $T$ (above the critical temperature) and varied $\rho$, the output observables being the local mole fractions $x_{\gamma}^{(I)} = N_{\gamma}^{(I)}/N^{(I)}$ and $x_{\gamma}^{(II)} = N_{\gamma}^{(II)}/N^{(II)}$. In this case, the lever rule is $(x_{\gamma}^{(I)} - \frac{1}{2})/(\frac{1}{2} - x_{\gamma}^{(I)}) = N^{(I)}/N^{(II)}$.

The total number of particles of each species was $N_{1} = N_{2} = 250$, what was checked to be sufficient for our
purposes. We used 50–100 × 10^6 MC steps for the equili-
branch at slightly larger densities.

In order to determine the critical point (\(T^*_c, \rho^*_c\)) we

emphatically extrapolated the GEMC binodals using the law

of rectilinear “diameters” \[24\] \(1 \times \frac{1}{2} (\rho^*_g + \rho^*_l) = \rho^*_c + A[T^* - T^*_c],\] and the Wegner expansion \[24,25\] for the width of the coex-

istence curve, \(\rho^*_g - \rho^*_l = B[T^* - T^*_c]^\beta_t.\] The criti-

cal coordinates \((T^*_c, \rho^*_c)\) and the coefficients \(A\) and \(B\) are
taken as fitting parameters. The four points corresponding
to the two highest temperatures were used for the extrapolation in each case. We remark that our data do not extend sufficiently close to the critical region to allow for quantitative estimates of critical exponents and non-

universal quantities. However, assuming that the models

belong to the three-dimensional Ising universality class,
we chose \(\beta_t = 0.325.\) The numerical values obtained by this extrapolation procedure will be presented in Table IV below.

The decrease in the critical temperatures and densi-
ties in going from the one-component SW fluid to model B0 and then to model A0 is strongly reminiscent of an analogous trend present in the unconstrained one-patch

Kern–Frenkel model upon decrease of the coverage \[29\].

It is interesting to remark that, even though the influ-

ence of attraction in model A0 is strongly inhibited by the up-

down constrained orientation \((\epsilon_{ij} = \epsilon_{B0} \delta_{ij})\), this model exhibits a gas-liquid transition. This surprising result was preliminarily supported by canonical NVT MC simu-

lations in Ref. [12], but now it is confirmed by the new and more appropriate GEMC simulations presented in this paper. Given the patch geometry and interactions in model A0, one might expect the formation of a lamellar-like liquid phase (approximately) made of alternating layers (up-down-up-down,...) of particles with the same orientation. This scenario is confirmed by snapshots of the liquid-phase box, as illustrated by Fig. 3.

The Kern–Frenkel analogy is not applicable to the

isotropic models I0 and J0. Model J0 presents a criti-

cal point intermediate between those of models B0 and A0, as expected. However, while the decrease in the total average attractive strength is certainly one of the main mechanisms dictating the location of the gas-liquid co-

existence curves, it cannot be the only discriminating factor, as shown by the results for the isotropic model I0, where the critical temperature is higher and the bin-

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odal curve is narrower than that corresponding to the
TABLE II. Gas-liquid coexistence properties for models A0, B0, I0, and J0, as obtained from our GEMC simulations. $T^*$ is the reduced temperature, $\rho^*_g$ is the reduced density of the gas ($\gamma = g$) and liquid ($\gamma = l$) phases, $N^{(g)}$ is the average number of particles in the gas box, and $U^{(g)}_{cc}/N^{(g)}$ is the excess internal energy per particle in box $\gamma$.

| Model | $T^*$ | $\rho^*_g$ | $\rho^*_l$ | $N^{(g)}/N$ | $-U^{(g)}_{cc}/\epsilon N^{(g)}$ | $-U^{(l)}_{cc}/\epsilon N^{(l)}$ |
|-------|-------|------------|------------|-------------|-------------------------------|-------------------------------|
| A0    | 0.075 | 0.1994(6)  | 0.590(1)   | 0.493(2)    | 1.69(1)                       | 1.796(7)                      |
|       | 0.1   | 0.214(2)   | 0.559(5)   | 0.535(4)    | 1.785(4)                      | 1.780(8)                      |
|       | 0.125 | 0.223(1)   | 0.530(6)   | 0.556(3)    | 1.63(9)                       | 1.71(5)                       |
|       | 0.15  | 0.231(1)   | 0.503(4)   | 0.574(4)    | 1.60(1)                       | 1.78(1)                       |
|       | 0.175 | 0.250(2)   | 0.455(8)   | 0.630(6)    | 1.42(1)                       | 1.632(9)                      |
| B0    | 0.3   | 0.112(2)   | 0.887(5)   | 0.284(5)    | 1.6(1)                        | 3.27(1)                       |
|       | 0.325 | 0.128(1)   | 0.839(3)   | 0.324(3)    | 0.761(1)                      | 3.239(7)                      |
|       | 0.328 | 0.145(5)   | 0.771(5)   | 0.363(9)    | 0.88(2)                       | 2.99(1)                       |
|       | 0.33  | 0.15(1)    | 0.73(1)    | 0.380(1)    | 0.95(1)                       | 3.016(9)                      |
|       | 0.335 | 0.18(3)    | 0.65(3)    | 0.45(1)     | 1.0(7)                        | 2.83(2)                       |
|       | 0.337 | 0.23(5)    | 0.54(5)    | 0.59(1)     | 1.273(4)                      | 2.36(4)                       |
| I0    | 0.3   | 0.202(3)   | 0.61(1)    | 0.5146(7)   | 2.48(6)                       | 3.04(1)                       |
|       | 0.325 | 0.211(5)   | 0.58(2)    | 0.5371(6)   | 1.76(4)                       | 2.765(8)                      |
|       | 0.35  | 0.24(1)    | 0.50(3)    | 0.612(3)    | 1.24(3)                       | 2.30(1)                       |
|       | 0.36  | 0.25(2)    | 0.45(4)    | 0.657(5)    | 1.01(1)                       | 1.85(5)                       |
|       | 0.365 | 0.28(3)    | 0.42(5)    | 0.71(1)     | 0.96(2)                       | 1.6(1)                        |
| J0    | 0.2   | 0.10(1)    | 0.93(3)    | 0.249(5)    | 1.67(2)                       | 2.48(3)                       |
|       | 0.25  | 0.14(1)    | 0.83(5)    | 0.34(1)     | 0.82(2)                       | 2.25(3)                       |
|       | 0.255 | 0.17(2)    | 0.70(5)    | 0.433(9)    | 0.90(2)                       | 1.99(2)                       |
|       | 0.257 | 0.19(3)    | 0.60(6)    | 0.62(6)     | 1.10(7)                       | 1.5(2)                        |

TABLE III. Mole fractions in the gas and liquid boxes in model I0 at different temperatures and with a global density $\rho^* = 0.3$. For the gas and liquid densities, see Table II. Because of the symmetry under label exchange $1 \leftrightarrow 2$, we have adopted the criterion $x_1^{(g)} \leq x_2^{(g)}$ without loss of generality.

| $T^*$ | $x_1^{(g)}$ | $x_2^{(g)}$ | $x_1^{(l)}$ | $x_2^{(l)}$ |
|-------|-------------|-------------|-------------|-------------|
| 0.3   | 0.03(1)     | 0.992(6)   | 0.98(1)     | 0.02(9)     |
| 0.325 | 0.09(2)     | 0.98(1)    | 0.955(15)   | 0.045(5)    |
| 0.35  | 0.18(3)     | 0.93(3)    | 0.93(3)     | 0.06(1)     |
| 0.36  | 0.26(3)     | 0.89(4)    | 0.93(3)     | 0.06(1)     |

anisotropic model B0. This may be due to the fact that, as said before, the binodal curve in model I0 is not equimolar and this lack of equimolarity is expected to extend to the critical point, as can be guessed from the trends observed in Table III. In other words, two demixed phases can be made to coexist at a higher temperature and with a smaller density difference than two mixed phases.

C. Demixing transition

The bi-component nature of the systems raises the question of a possible demixing transition in which a rich-1 phase coexists with a rich-2 phase at a given temperature $T$, provided the density is larger than a certain critical consolute density $\rho_{cc}(T)$. The points $\rho_{cc}(T)$ or, reciprocally, $T_{cc}(\rho)$ define the so-called A-line. The interplay between the gas-liquid and demixing transitions is a very interesting issue and was discussed in a general framework by Wilding et al.

Since all the spheres have the same size, a neces-
sary condition for demixing in the case of isotropic potentials is that the like attractions must be sufficiently stronger than the unlike attractions.\cite{28,29} Assuming the validity of this condition to anisotropic potentials and making a simple estimate based on the virial expansion, one finds that demixing requires the coefficient of $x_1x_2$ in the second virial coefficient to be positive, i.e., $2ε^{11}/k_BT > ε^{12}/k_BT + ε^{21}/k_BT$. While this demixing criterion is only approximate, it suggests that, out of the five models considered, only models B0 and I0 are expected to display demixing transitions. As a matter of fact, we have already discussed the spontaneous demixing phenomenon taking place in model I0 when a low-density phase and a high-density phase are in mutual equilibrium. In this section, however, we are interested in the segregation of the system, at a given $T$ and for $ρ > ρ_{cc}(T)$, into a rich-2 phase I with $x_1^{(I)} = x_2(ρ) < 1/2$ and a symmetric rich-1 phase II with $x_1^{(II)} = 1 - x_2(ρ) > 1/2$, both phases at the same density.

Our GEMC simulation results are presented in Fig. 5 and Table IV. We observe that, as expected, $x_1^{(I)} = 1 - x_1^{(II)}$ within statistical fluctuations. We have also checked that $ρ^{(I)} \approx ρ^{(II)}$, even though this equality is not artificially enforced in the simulations. Such equality is also equivalent to $ρ^{(I)} \approx ρ^{(II)}$ and we checked that it was satisfied within a standard deviation of 0.02σ−3 in all cases considered in Table IV. To obtain the critical consolute density $ρ_{cc}$ for each temperature, we extrapolated the data again according to the Ising scaling relation $1/2 - x_d(ρ) = C(ρ - ρ_{cc})^{θ_I}$.

It is interesting to note that just the absence of attraction when a particle of species 2 is below a particle of species 1 ($ε_{21} = 0$) in model B0 is sufficient to drive a demixing transition. However, as expected, at a common temperature (see $T^* = 0.4$ in Fig. 5), demixing requires higher densities in model B0 than in model I0.

As said above, the interplay of condensation and demixing is an interesting problem by itself.\cite{28,30} Three alternative scenarios are in principle possible for the in-

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**TABLE IV. Demixing coexistence properties for models I0 and B0, as obtained from our GEMC simulations. $T^*$ is the reduced temperature, $ρ^*$ is the reduced density, and $x_1^{(I)}$ is the mole fraction of species 1 in each one of the two coexisting phases $γ = I, II$.**

| Model | $T^*$ | $ρ^*$ | $x_1^{(I)}$ | $x_1^{(II)}$ |
|-------|-------|-------|--------------|--------------|
| I0    | 0.4   | 0.7   | 0.005(5)     | 0.992(5)     |
|       |       | 0.65  | 0.006(6)     | 0.985(6)     |
|       | 0.6   | 0.01(1)| 0.97(1)      |              |
|       | 0.5   | 0.05(3)| 0.93(3)      |              |
|       | 0.4   | 0.19(4)| 0.81(4)      |              |
|       | 0.38  | 0.23(6)| 0.77(6)      |              |
|       | 0.36  | 0.32(9)| 0.68(9)      |              |
|       | 0.34  | 0.4(1) | 0.6(1)       |              |
|       | 0.45  | 0.7    | 0.01(1)      | 0.99(1)      |
|       | 0.6   | 0.05(2)| 0.96(2)      |              |
|       | 0.5   | 0.14(4)| 0.87(4)      |              |
|       | 0.45  | 0.25(7)| 0.74(7)      |              |
|       | 0.43  | 0.4(1) | 0.6(1)       |              |
| B0    | 0.35  | 0.725  | 0.09(2)      | 0.91(2)      |
|       | 0.7   | 0.11(2)| 0.90(2)      |              |
|       | 0.675 | 0.15(3)| 0.87(3)      |              |
|       | 0.66  | 0.18(4)| 0.80(4)      |              |
|       | 0.65  | 0.4(6) | 0.60(6)      |              |
|       | 0.4   | 0.725  | 0.20(3)      | 0.82(3)      |
|       | 0.7   | 0.22(4)| 0.78(4)      |              |
|       | 0.675 | 0.31(5)| 0.69(5)      |              |
|       | 0.665 | 0.45(6)| 0.55(6)      |              |
intersection of the λ-line and the binodal curve: a critical end point, a triple point, or a tricritical point. Elucidation of these scenarios would require grand canonical simulations (rather than GEMC simulations), what is beyond the scope of this paper.

IV. SIMPLE ANALYTICAL THEORIES

Let us now compare the above numerical results with simple theoretical predictions. The solution of integral equation theories for anisotropic interactions and/or multicomponent systems requires formidable numerical efforts, with the absence of explicit expressions often hampering physical insight. Here we want to deal with simple, purely analytical theories that yet include the basic ingredients of the models.

First, we take advantage of the short-range of the attractive well \((\Delta / \sigma = 0.05)\) to map the different SW interactions into SHS interactions parameterized by the "stickiness" parameter\(^2\)

\[
t_{ij} \equiv \frac{1}{12t_{ij}} = \frac{\Delta}{\sigma} \left( 1 + \frac{\Delta^2}{3\sigma^2} \right) \left( e^{\epsilon_{ij}/k_B T} - 1 \right),
\]

which combine the energy and length scales. This mapping preserves the exact second virial coefficient of the genuine SW systems, namely

\[
\frac{B_2}{B_2^{\text{HS}}} = 1 - 3t_{11} + 3x_1x_2(2t_{11} - t_{12} - t_{21}),
\]

where \(B_2^{\text{HS}} = 2\pi\sigma^3 / 3\) is the HS coefficient. The exact expression of the third virial coefficient \(B_3\) in the SHS limit for arbitrary \(t_{ij}\) is\(^12\)

\[
\frac{B_3}{B_3^{\text{HS}}} = 1 - 6t_{11} + \frac{72}{5} t_{11}^2 - \frac{48}{5} t_{11}^3 - \frac{6}{5} x_1x_2 \left( [12t_{11} - 5] 
\times (2t_{11} - t_{12} - t_{21}) - 8t_{11} (t_{11}^2 - t_{12}t_{21}) 
- 2 (4t_{11} - 3) (2t_{11}^2 - t_{12}^2 - t_{21}^2) + 2 \alpha (t_{12} - t_{21})^2 \right),
\]

where \(B_3^{\text{HS}} = 5\pi^2\sigma^4 / 18\) and

\[
\alpha = \frac{3\sqrt{3}}{\pi} - 1.
\]

A. Equations of state

One advantage of the SW \(\to\) SHS mapping is that the Percus–Yevick (PY) integral equation is exactly solvable for SHS mixtures with isotropic interactions \((t_{12} = t_{21})\). In principle, that solution can be applied to the models SW, I0, and J0 represented in Fig. 2. On the other hand, if \(t_{11} \neq 0\) (models SW and I0), the PY solutions are related to algebraic equations of second (SW) or fourth (I0) degrees, what creates the problem of disappearance of the physical solution for large enough densities or stickiness. In particular, we have observed that the breakdown of the solution preempts the existence of a critical point in model I0. However, in the case of model J0 \((t_{11} = 0, t_{12} = t_{21} = t)\), the PY solution reduces to a linear equation whose solution is straightforward. Following the virial \((v)\) and the energy \((u)\) routes, the respective expressions for the compressibility factor \(Z \equiv P / \rho k_B T\) (where \(P\) is the pressure) have the form

\[
Z_v(\eta, t, x_1) = Z_v^{\text{HS}}(\eta) - x_1 x_2 Z_v^{(1)}(\eta, t) - x_1^2 x_2^2 Z_v^{(2)}(\eta, t),
\]

\[
Z_u(\eta, t, x_1) = Z_u^{\text{HS}}(\eta) - x_1 x_2 Z_u^{(1)}(\eta, t),
\]

where \(\eta = \pi \rho^* / 6\) is the packing fraction,

\[
Z_v^{\text{HS}}(\eta) = \frac{1 + 2\eta + 3\eta^2}{(1 - \eta)^2}
\]

is the HS compressibility factor derived from the PY equation via the virial route, \(Z_v^{\text{HS}}\) is an indeterminate integration constant, and the explicit expressions for \(Z_v^{(1)}, Z_v^{(2)}, \text{ and } Z_v^{(1)}\) are

\[
Z_v^{(1)}(\eta, t) = \frac{24\eta t}{(1 - \eta + 6\eta^2)^2} \left[ 1 + 2\eta + 3\eta t + 2\eta - 5\eta^2 / (1 - \eta)^2 \right],
\]

\[
Z_v^{(2)}(\eta, t) = \frac{288\eta^3 t^2 (2 + \eta)}{(1 - \eta + 6\eta^2)^3} \left[ 1 + t - 2 - 11\eta t - 6\eta^3 t^2 / (1 - \eta)^2 \right],
\]

\[
Z_u^{(1)}(\eta, t) = \frac{6\eta}{(1 - \eta)^2} \left[ 2t(2 + \eta) + \ln (1 - \eta + 6\eta t) \right].
\]

To the best of our knowledge, this extremely simple solution of the PY integral equation for a model of SHS mixtures had not been unveiled before.

As apparent from Fig. 2 model A0 is a close relative of model J0. However, the fact that \(\epsilon_{12} = \epsilon_{21} = 0\) (or \(t_{12} = t_{21} = 0\)) makes the interaction anisotropic and prevents the PY equation from being exactly solvable in this case. On the other hand, we have recently proposed\(^12\) a simple rational-function approximation (RFA) that applies to models with \(t_{12} \neq t_{21}\) and reduces to the PY solution in the case of isotropic models \((t_{12} = t_{21})\). The RFA solution for model A0 yields once more a linear equation. The virial and energy equations of state are again of the forms \((7)\) and \((8)\), respectively, with expressions for \(Z_v^{(1)}, Z_v^{(2)},\) and \(Z_u^{(1)}\) given by

\[
Z_v^{(1)}(\eta, t) = \frac{12\eta t}{1 - \eta + 6\eta t} \left[ 1 + 2\eta t + 2\eta t - 7\eta^2 / (1 - \eta)^3 \right],
\]

\[
Z_u^{(1)}(\eta, t) = \frac{6\eta}{1 - \eta + 6\eta t} \left[ 2\eta t + 7\eta t - 7\eta^2 / (1 - \eta)^3 \right].
\]
\[
Z_v^{(2)}(\eta, t) = \frac{72\eta^3 t^2(2 + \eta)}{(1 - \eta)^3(1 - \eta + 6\eta^2)},
\]
(14)
\[
Z_u^{(1)}(\eta, t) = \frac{3\eta}{(1 - \eta)^2} \left[ \frac{2t(2 + \eta)}{1 - \eta + 6\eta t} + \ln \frac{1 - \eta + 6\eta t}{1 - \eta} \right].
\]
(15)
In the RFA solution for model A0 the exact third virial coefficient \(Z_v^{(3)}\) is recovered by the interpolation formula
\[
Z = Z_{\text{CS}}^{\text{HS}} + \alpha \left( Z_v^{\text{HS}} - Z_v^{\text{CS}} \right) + (1 - \alpha) \left( Z_u^{\text{HS}} - Z_u^{\text{CS}} \right)
\]
\[
= Z_{\text{CS}}^{\text{HS}} - x_1 x_2 \left[ \alpha Z_v^{(1)} + (1 - \alpha) Z_u^{(1)} \right] - x_1^2 x_2^2 \alpha Z_v^{(2)},
\]
(16)
where
\[
Z_{\text{CS}}^{\text{HS}}(\eta) = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}
\]
(17)
is the HS Carnahan–Starling compressibility factor and the interpolation weight \(\alpha\) is given by Eq. (16). By consistency, Eq. (16) will also be employed in the PY solution of model J0.

In the cases of models with \(\epsilon_{11} \neq 0\) (i.e., SW, B0, and I0), the PY and RFA theories fail to have physical solutions in regions of the temperature-density plane overlapping with the gas-liquid transition. In order to circumvent this problem, we adopt here a simple perturbative approach:
\[
Z = Z_{\text{ref}} + (B_2 - B_2^{\text{ref}}) \rho + (B_3 - B_3^{\text{ref}}) \rho^2,
\]
(18)
where \(Z_{\text{ref}}\) is the compressibility factor of a reference model and \(B_2^{\text{ref}}\) and \(B_3^{\text{ref}}\) are the associated virial coefficients. As a natural choice (see Fig. 2), we take the models J0, A0, and HS (which lie on the plane \(\epsilon_{11}/\epsilon = 0\)) as reference systems for the models SW, B0, and I0 (which lie on the plane \(\epsilon_{11}/\epsilon = 1\)), respectively. More specifically,
\[
Z_{\text{SW}} = Z_{\text{J0}} + (B_{2\text{SW}} - B_{2\text{J0}}) \rho + (B_{3\text{SW}} - B_{3\text{J0}}) \rho^2,
\]
(19)
\[
Z_{\text{B0}} = Z_{\text{A0}} + (B_{2\text{B0}} - B_{2\text{A0}}) \rho + (B_{3\text{B0}} - B_{3\text{A0}}) \rho^2,
\]
(20)
\[
Z_{\text{I0}} = Z_{\text{CS}}^{\text{HS}} + (B_{2\text{I0}} - B_{2\text{CS}}^{\text{HS}}) \rho + (B_{3\text{I0}} - B_{3\text{CS}}^{\text{HS}}) \rho^2.
\]
(21)
Here, \(Z_{\text{J0}}\) and \(Z_{\text{A0}}\) are given by Eq. (16) (with the corresponding expressions of \(Z_v^{(1)}, Z_v^{(2)}, \) and \(Z_u^{(1)}\)) and the virial coefficients are obtained in each case from Eqs. (1) and (5) with the appropriate values of \(t_{11}, t_{12},\) and \(t_{21}.)

From the explicit knowledge of \(Z(\eta, t, x_1)\), standard thermodynamic relations allow one to obtain the free energy per particle \(a(\eta, t, x_1)\) and the chemical potentials \(\mu_1(\eta, t, x_1)\) as
\[
\beta a(\eta, t, x_1) = \int_0^\eta d\eta' \frac{Z(\eta', t, x_1) - 1}{\eta'} + x_1 \ln(x_1 \eta)
\]
\[
+ (1 - x_1) \ln(1 - x_1 \eta) + \text{const},
\]
(22)
TABLE V. Comparison between the critical points measured in simulations with those obtained from theoretical approaches.

| Method | SW | B0 | I0 | J0 | A0 |
|--------|----|----|----|----|----|
| Simulation | 0.369^a | 0.338^b | 0.368^b | 0.258^b | 0.193^b |
| Our theory | 0.377 | 0.341 | 0.331 | 0.278 | 0.214 |
| Noro–Frenkel | 0.369 | 0.335 | 0.297 | 0.297 | 0.247 |

^a GCMC results for the one-component SHS fluid From Ref. 23
^b Our GEMC simulation results

\[
\beta \mu_1(\eta, t, x_1) = \beta a(\eta, t, x_1) + Z(\eta, t, x_1)
\]
\[
+ (1 - x_1) \frac{\partial \beta a(\eta, t, x_1)}{\partial x_1},
\]
(23)
\[
\mu_2(\eta, t, x_1) = \mu_1(\eta, t, 1 - x_1),
\]
(24)
where \(\beta \equiv 1/k_B T\).

B. Gas-liquid coexistence

The critical point \((\eta_c, t_c)\) of the gas-liquid transition is obtained from the well-known condition that the critical isotherm in the pressure-density plane presents an inflection point with horizontal slope at the critical density. In terms of the compressibility factor \(Z\), this implies
\[
\partial \left[ \eta Z(\eta, t_c, 1/2) \right] \bigg|_{\eta = \eta_c} = 0,
\]
(25)
where equimolarity \((x_1 = 1/2)\) has been assumed. For temperatures below the critical temperature (i.e., \(t > t_c\)) the packing fractions \(\eta_g\) and \(\eta_l\) of the gas and liquid coexisting phases are obtained from the conditions of equal pressure (mechanical equilibrium) and equal chemical potential (chemical equilibrium) i.e.
\[
\eta_g Z(\eta_g, t, 1/2) = \eta_l Z(\eta_l, t, 1/2),
\]
(26)
\[
\mu_1(\eta, t, 1/2) = \mu_1(\eta, t, 1/2).
\]
(27)

In order to make contact with the GEMC results, the theoretical values of \(t_c\) have been mapped onto those of \(T^*_c\) by inverting Eq. (24), namely
\[
\frac{1}{T^*_c} = \ln \left[ 1 + \frac{t}{(\Delta/\sigma)(1 + \Delta/\sigma + \Delta^2/3\sigma^2)} \right]
\]
(28)
with \(\Delta/\sigma = 0.05\).

Table V compares the critical points obtained in simulations for the one-component SW fluid (in the SHS limit) and for models B0, I0, J0, and A0 (see Fig. 2).
C. Demixing transition

In the case of the demixing transition, the critical consolute density $\eta_{cc}$ at a given temperature is obtained from

$$\left. \frac{\partial^2 a(\eta_{cc}, t, x_1)}{\partial x_1^2} \right|_{x_1=\frac{1}{2}} = 0.$$  \hfill (29)

For $\eta > \eta_{cc}$, the demixing mole fraction $x_1 = x_d(\eta)$ is the solution to

$$\mu_1(\eta, t, x_d) = \mu_1(\eta, t, 1 - x_d).$$  \hfill (30)

In terms of the compressibility factor $Z$, Eqs. (29) and (30) can be rewritten as

$$\int_0^{\eta_{cc}} \frac{\partial^2 Z(\eta, t, x_1)}{\partial x_1^2} \bigg|_{x_1=\frac{1}{2}} \frac{d \eta}{\eta} = -4,$$  \hfill (31)

$$\int_0^{\eta_{cc}} \frac{\partial Z(\eta', t, x_d)}{\partial x_d} \frac{d \eta'}{\eta'} = \ln \frac{1 - x_d}{x_d},$$  \hfill (32)

respectively.

The perturbative approximations for models I0 and B0 succeed in predicting demixing transitions, even though their respective reference systems (HS and A0) do not demix. In the case of model I0, the critical consolute densities are $\rho_{cc}(T^* = 0.4) = 0.306$ and $\rho_{cc}(T^* = 0.45) = 0.390$, which are about 9% lower than the values obtained in our GEMC simulations. In the case of model B0, our simple theory predicts a critical consolute point only if $t > 0.7667$, i.e., if $T^* < 0.364$, so no demixing is predicted at $T^* = 0.4$, in contrast to the results of the simulations. At $T^* = 0.35$ the theoretical prediction is $\rho_{cc} = 0.406$, a value about 39% smaller than the GEMC one. The theoretical demixing curves at $T^* = 0.4$ and $T^* = 0.45$ for model I0 and at $T^* = 0.35$ for model B0 are compared with the GEMC results in Fig. 5. We can observe a fairly good agreement in the case of model I0, but not for model B0. In the latter case, the theoretical curve spans a density range comparable to that of model I0, while simulations show a much flatter demixing curve.

V. CONCLUDING REMARKS

In conclusion, we have proposed a novel class of binary-mixture Janus fluids with up-down constrained orientations. The class encompasses, as particular cases, the conventional one-component SW fluid, mixtures with isotropic attractive interactions only between like particles (model I0) or unlike particles (model J0), and genuine Janus fluids with anisotropic interactions and different patch-patch affinities (models A0 and B0). Both GEMC numerical simulations and simple theoretical approximations have been employed to analyze the gas-liquid transition under global equimolar conditions for the five models and the demixing transition for the two models (I0 and B0) where the attraction between like particles is stronger than between unlike ones. The theoretical analysis employed a mapping onto SHS interactions, that were then studied by means of the PY theory (model J0), the RFA (model A0), and low-density virial corrections (models SW, I0, and B0), with semi-quantitative agreement with numerical simulations.

Interestingly, the presence of attraction in only one out of the four possible patch-patch interactions (model A0) turns out to be enough to make the gas-liquid transition possible. Reciprocally, the lack of attraction in only one of the two possible patch-patch interactions between unlike particles (model B0) is enough to produce a demixing
transition. Except in model I0, the coexisting gas and liquid phases have an equimolar composition. As the average attraction is gradually decreased, the gas-liquid critical point shifts to lower temperatures (except for an interesting inversion of tendency observed when going from the isotropic model I0 to the anisotropic model B0) and lower densities. Moreover, the coexistence region progressively shrinks, in analogy with what is observed in the unconstrained one-component Janus fluid and in the empty liquid scenario. On the other hand, the imposed constraint in the orientation of the attractive patches does not allow for the formation of those inert clusters which in the original Janus fluid are responsible for a re-entrant gas branch. A.S. has been supported by the Spanish government (contract 2010LKE4CC). The research of M.A.G.M. and A.G. acknowledges funding from PRIN-COFIN2010-2011 (contract 2010LKE4CC). The research of M.A.G.M. and A.S. has been supported by the Spanish government through Grant No. GR101583, partially financed by FEDER funds. M.A.G.M is also grateful to the Junta de Extremadura (Spain) through Grant No. FIS2010-16587 and by the Junta de Extremadura (Spain) for the predoctoral fellowship PD1010.

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