Phase diagram and critical properties of a two-dimensional associating lattice gas

I. Ibagon,1,4 A. P. Furlan,1,4 T. J. Oliveira,2,4 and R. Dickman3,4

1) Departamento de Física, ICEx, Universidade Federal de Minas Gerais, C. P. 702, 30123-970, Belo Horizonte, Minas Gerais - Brazil
2) Departamento de Física, Universidade Federal de Viçosa, 36570-900, Viçosa, Minas Gerais, Brazil
3) Departamento de Física and National Institute of Science and Technology for Complex Systems, ICEx, Universidade Federal de Minas Gerais, C. P. 702, 30123-970 Belo Horizonte, Minas Gerais - Brazil

(Dated: September 28, 2021)

We revisit the associating lattice gas (ALG) introduced by Henriques et al. [PRE 71, 031504 (2005)] in its symmetric version. In this model, defined on the triangular lattice, interaction between molecules occupying nearest-neighbor sites depends on their relative orientation, mimicking the formation of hydrogen bonds in network-forming fluids. Although all previous studies of this model agree that it has a disordered fluid (DF), a low-density liquid (LDL) and a high-density liquid (HDL) phase, quite different forms have been reported for its phase diagram. Here, we present a thorough investigation of its phase behavior using both transfer matrix calculations and Monte Carlo (MC) simulations, along with finite-size scaling extrapolations. Results in striking agreement are found using these methods. The critical point associated with the DF-HDL transition at full occupancy, identified by Furlan and coworkers [Phys. Rev. E 100, 022109 (2019)] is shown to be one terminus of a critical line separating these phases. In opposition to previous simulation studies, we find that the transition between the DF and LDL phases is always discontinuous, similar to the LDL-HDL transition. The associated coexistence lines meet at the point where the DF-HDL critical line ends, making it critical-end-point. Overall, the form of the phase diagram observed in our simulations is very similar to that found in the exact solution of the model on a Husimi lattice. Our results confirm that, despite the existence of some waterlike anomalies in this model, it is unable to reproduce key features of the phase behavior of liquid water.

PACS numbers: 68.35.Rh

I. INTRODUCTION

The importance water has to life on Earth is perhaps comparable to the degree of unusual behavior this liquid displays. In fact, when compared with other substances, liquid water presents a number of anomalies (such as in density, diffusivity and so on), which are believed to originate in the particular manner in which H2O molecules interact, through hydrogen bonds forming a local, approximately tetrahedral network.

The three main scenarios proposed to understand water, viz. the stability-limic, the singularity-free and liquid-liquid critical point (LLCP) hypotheses, are all consistent with the presence of such a network. The later scenarios are based on the fact that just as ice becomes glassy and can exist in low- and high-density amorphous phases, the continuation of these phases (increasing the temperature T above that of spontaneous crystallization) may give rise to a low-density liquid (LDL) and a high-density liquid (HDL) phase. Although there is some indirect experimental evidence for the existence of the LLCP, including some coming from water in nanopores, a definitive proof is still lacking, mainly because the LLCP would exist in the metastable, deeply supercooled region, which is very difficult to access experimentally in bulk water.

In this context, much of this debate has been based on computational studies, with several realistic models for water confirming the LLCP hypothesis (see for a recent review). A number of simplified associating lattice gas (ALG) models, designed to possess two liquid phases, have also been introduced in two- and three-dimensional. These ALG models usually feature an attractive, orientation-dependent interaction between molecules occupying nearest neighbor (NN) sites — mimicking the hydrogen bonding in network forming fluids —, competing with a repulsive excluded-volume interaction. Phase diagrams displaying a LLCP have been reported for some of these models, though latter works on some these models have demonstrated a phase behavior without a LLCP.

An example of this is the symmetric version of the Besseling and Lyklema model, firstly analyzed by Girardi et al. This model is defined on the body-centered cubic lattice, where each molecule can form up to four hydrogen bonds with NNs, similar to H2O. While these bonds lower their energy, nonbonding molecules at NN
sites experience a repulsive “van der Waals” interaction. Beyond the GAS-liquid coexistence line ending at a critical point, a LDL-HDL coexistence line ending at a second critical point was also reported \(^{33}\), yielding a phase diagram qualitatively similar to the one in Fig. 1(a). (As an aside, we remark that the phase commonly called GAS in the literature related to these models will be regarded as a disordered fluid (DF) here, since it may extend to large chemical potentials and so, high densities.) Subsequent studies of this ALG \(^{35,38}\), notwithstanding, revealed a much more complex phase behavior, with the LLCP \([c_2\text{ in Fig. } 1(a)]\) being actually a tricritical point, while \(c_1\) is displaced as being a critical-end-point \(^{36,37}\) or a bicritical point \(^{38}\). These works also uncovered a critical line separating the HDL and DF phases \(^{40,45}\).

A similar sequence of events marks the history of the ALG model introduced by Henriques and Barbosa (H&B) \(^{21}\) which is a nonsymmetric two-dimensional (2D) version of the 3D model analyzed by Girardi et al. \(^{13}\). The H&B model is defined on the triangular lattice, in which each molecule has four bonding arms (two donors and two acceptors of protons), beyond two inert arms separated by \(180^\circ\). In their original Monte Carlo analysis, H&B \(^{21}\) reported a phase diagram analogous to that in Fig. 1(a), with two coexistence lines and two critical points. Further work on this model indicated, however, a different and richer phase diagram, with two additional continuous transition lines: DF-LDL and DF-HDL \(^{39}\). In this phase diagram, the DF-LDL coexistence line ends at a tricritical point where it meets the DF-LDL continuous line; and the LDL-HDL coexistence line ends at a bicritical point where it meets the continuous DF-LDL and DF-HDL lines \(^{39}\).

Several modifications of the H&B model have been proposed \(^{22,34-36}\). Of particular interest here is the symmetric version introduced by Balladares et al. \(^{22}\) in which no distinction is made between donor and acceptor arms. The literature on this symmetric ALG is also marked by controversy. For example, the original MC simulations of Ref. \(^{22}\) again suggested the phase behavior of Fig. 1(a), consistent with the LLCP hypothesis. The semi-analytical mean-field solution of this simplified version of the H&B model on a Husimi lattice built with hexagonal plaquettes \(^{34}\) revealed a qualitatively different phase diagram, with three coexistence lines (DF-HDL, DF-LDL and LDL-HDL) meeting at a triple point \((tp)\), as shown in Fig. 1(b). Later MC simulation \(^{35}\) supported the phase behavior of Fig. 1(c), with two coexistence lines (DF-LDL and LDL-HDL) ending at two tricritical points \((tc_1\text{ and } tc_2)\), which are linked by a critical DF-LDL line. No transition between the HDL phase and the disordered fluid was reported in Ref. \(^{32}\).

More recently, this symmetric H&B model was investigated in the limit of full occupancy (corresponding to a chemical potential \(\mu \to \infty\)) using MC simulations and semi-analytical solutions on Husimi lattice \(^{11}\). The simulations yielded a continuous transition between the HDL and the DF phase at a (reduced) temperature \(T_c = 0.9525(5)\), with critical exponents and Binder cumulant in good agreement with those of the three-state Potts model in 2D \(^{42}\). On the other hand, the Husimi lattice solutions furnish a discontinuous transition, as a continuation of the DF-HDL coexistence line found for finite \(\mu\) \(^{11}\) to the limit of \(\mu \to \infty\). All these results raise important questions on the phase behavior of this model: i) Does it indeed exhibit a LLCP as in Fig. 1(a)? ii) What is the true nature of the DF-LDL transition? Is it discontinuous as in Fig. 1(b) or does it have a tricritical point and a continuous part like in Fig. 1(c)? iii) Assuming that a transition line does indeed exist separating the DF and HDL phases: Is it always discontinuous but ends at a critical point in the limit \(\mu \to \infty\)? Or does it start discontinuous and change to continuous at some finite \(\mu\)? Or, even, is the entire line continuous?

In this work we address these points through an extensive numerical study of this ALG model using both transfer-matrix analysis and MC simulations in the grand-canonical ensemble. Consistent results are obtained from both methods, demonstrating that the correct topology of the phase diagram is that of Fig. 1(b).
However, in contrast with the mean-field result shown in this figure, we find that the transition between the DF and HDL phases is always continuous and the critical DF-HDL line ends at a critical-end-point, where it meets the DF-LDL and LDL-HDL coexistence lines. The critical properties of the continuous transition line — an interesting problem scarcely tackled in the literature of lattice models for water (see for a discussion) — are also investigated and an intriguing behavior is found, with some quantities presenting a close agreement with the three-state Potts class, while others have a large deviation from it.

The paper is organized as follows. In Sec. II we present the investigated model. The transfer-matrix method and the associated results are discussed in Sec. III. A similar thing is done in Sec. IV for the Monte Carlo simulations. The comparison of the outcomes from both methods and our concluding remarks are presented in Sec. V.

II. MODEL

We study the symmetric version of the Henriques and Barbosa (H&B) associating lattice gas (ALG) model, investigated in Refs. The model is defined on the triangular lattice (co-ordination number $z = 6$), where each site $i$ can be either empty ($\sigma_i = 0$) or occupied by a single molecule ($\sigma_i = 1$). A chemical potential $\mu$ is associated to each particle in the system, since we will work in the grand canonical ensemble. Whenever two molecules occupy nearest-neighbor (NN) sites, they experience a repulsive “van der Walls” interaction, gaining an energy $\varepsilon > 0$. In addition, two NN molecules can form a hydrogen bond, which decreases their energy by a factor $-\gamma < 0$, provided that their bonding arms point toward each other. In fact, a key feature of the model analyzed here (and of other ALGs as well) is the existence of orientational degrees of freedom and related interactions introduced by bonding arms. In our case, each molecule has four bonding arms and two inert (nonbonding) arms, as shown in Fig. 2. The four bonding arms are all equivalent and always interact with those of NN molecules in the same manner, i.e., there is no distinction between donors and acceptors (of protons) here, in opposition to the original (non-symmetric) H&B model. The inert arms of a given molecule are in diametrically opposed lattice edges (forming an angle 180$^\circ$), which results in three orientational states for each molecule (see Fig. 2). Following Ref., we may conveniently define an orientational variable, $\eta_i$, pointing along one of the nonbonding directions of the molecule at site $i$. In this fashion, it is simply given by the generators of the triangular lattice, $\hat{e}_k$ with $k = 1, 2$ and 3, which are also depicted in Fig. 2. Namely, $\eta_i \equiv \hat{e}_k$, where $\hat{e}_1 = \hat{i}$, $\hat{e}_2 = +\frac{1}{2}\hat{i} + \frac{\sqrt{3}}{2}\hat{j}$ and $\hat{e}_3 = -\frac{1}{2}\hat{i} + \frac{\sqrt{3}}{2}\hat{j}$.

With these definitions, we may write the Hamiltonian of this ALG model as,

$$ H(\eta, r) = \sum_{\langle i,j \rangle} \sigma_i \sigma_j [\varepsilon + u_{ij}] - \mu \sum_i \sigma_i, \quad (1) $$

where $r = r_i - r_j$ is a unit vector in the set $\{\pm \hat{e}_1, \pm \hat{e}_2, \pm \hat{e}_3\}$. The second sum gives the total number of particles, $N$, while the first sum runs over all NN pairs $(i, j)$, whose orientational interaction is encoded in variable $u_{ij}$, given by

$$ u_{ij} = -\gamma \left( \frac{4}{3} \right)^2 \left[ 1 - (\eta_i \cdot r)^2 \right] \left[ 1 - (\eta_j \cdot r)^2 \right], \quad (2) $$

Note that whenever $r$ is parallel or antiparallel to $\eta_i$ and/or $\eta_j$, molecules $(i, j)$ do not form a hydrogen bond and $u_{ij} = 0$; otherwise $u_{ij} = -\gamma$. Following most of the previous studies of the ALG model, we will use the parameter $\varepsilon$ as the energy scale and set $\gamma / \varepsilon = 2$. In this way, the net interaction between two NN molecules forming (not forming) a hydrogen bond is attractive (repulsive). We therefore have as free parameters the dimensionless temperature $T = k_B T / \varepsilon$ and chemical potential $\bar{\mu} = \mu / \varepsilon$. We remark that in Ref. the temperature (called $\tau$ there) was defined in units of $\gamma$, so that $\tau = T/2$.

As already discussed in the Introduction [Sec. I], from previous studies of the ALG model, one knows that its phase diagram exhibits three phases: disordered fluid (DF), low-density liquid (LDL) and high-density liquid (HDL). In the ground state ($T = 0$), the DF phase has particle density $\rho = 0$ (the reason it is usually called GAS) and is the most stable phase for $\bar{\mu} < -2$. For
\( \mu \) order to investigate the full-occupancy case (strip of width \( L \)), four different states, we have a total of 4 and a column of \( \sim \) a given row of the strip will be associated with a row (horizontal) direction. As usual, each possible state for final edges, with periodic boundary conditions in the finite

in Fig. 4, we consider square lattice strips with diagonal edges. Working in this way, the “internal” interactions, along the vertical and diagonal directions, are counted once, while each one in the horizontal contribute with 1/2 in each state, since they appear in two states.

It is hard to deal directly with \( \tilde{M}_L \), because all of its elements are non-null. Therefore, in order to save computer RAM memory and speed up the calculations, we replace the procedure of adding an entire row, by the procedure of adding a single elementary cell (formed by squares with a diagonal edge). Working in this way, we have to deal with \( L + 1 \) matrices, \( \tilde{T}^{(s)}_L \), so that

\[
\tilde{M}_L = \tilde{T}^{(L)}_L \cdot \tilde{T}^{(L-1)}_L \cdots \tilde{T}^{(0)}_L.
\]

Here, \( \tilde{T}^{(0)}_L \) creates a new site in row \( n + 1 \) above a complete row \( n \); the matrices \( \tilde{T}^{(s)}_L \), with \( 1 \leq s \leq L - 1 \), add new elementary cells to row \( n + 1 \); and finally \( \tilde{T}^{(L)}_L \) completes the row \( n + 1 \) by imposing the appropriated (periodic here) boundary conditions (see, e.g, Refs. \[33,34\] for more details). The advantage of this method relies on the fact that the matrices \( \tilde{T}^{(s)}_L \) are very sparse. In fact, the total number of non-null terms summing over all matrices \( \tilde{T}^{(s)}_L \) is only \((16L - 8)4^L\).

If \( \Lambda_L^{(k)} \) denotes the eigenvalues of \( \tilde{M}_L \), for given values of \( \tilde{\mu} \) and \( \tilde{T} \), with \( \Lambda_L^{(0)} > |\Lambda_L^{(1)}| > |\Lambda_L^{(2)}| > \ldots \), then, the (dimensionless) negative free energy density is

\[
f(L) = \frac{\zeta}{L} \ln \Lambda_L^{(0)},
\]
where \( \zeta \) is a geometric factor given by the thickness of the added row when its circumference is \( L \), which in our case is \( \zeta = 2/\sqrt{3} \). The correlation length \( \xi_k(L) \) associated with the \( k \)th subleading eigenvalue is given by

\[
\xi_k^{-1}(L) = \zeta \ln \left| \frac{\Lambda(0)}{\Lambda_L^{(k)}} \right|.
\]  

(4)

From these correlation lengths, we may define the scaled gaps \( \xi_k(L) = L/[2\pi \xi_k(L)] \). Note that all these quantities obviously depend also on \( \bar{\mu} \) and \( \bar{T} \). Close to a critical point \(( \bar{T}_c \) or \( \bar{\mu}_c \)), from finite-size scaling \cite{15}, we expect that

\[
X_k(L; \bar{T}, \bar{\mu}) = X_k^* + \alpha_1 t L^{y_1} + \alpha_1 t^{b_1} L^{z_1} + \alpha_2 t L^{y_2} + \ldots,
\]  

(5)

where \( y_i > 0 \) is the temperature exponent, \( y_i < 0 \) \((i = 1, 2, \ldots) \) are irrelevant exponents, and \( t = \bar{T} - \bar{T}_c \) if \( \bar{\mu} \) is kept fixed or \( t = \bar{\mu} - \bar{\mu}_c \) when \( \bar{T} \) is the fixed parameter.

In conformally invariant systems, the critical free energy density is expected to follow

\[
f(L) = f_\infty + \frac{\pi c}{6L^2} + p_1 L^{z_1} + \ldots,
\]  

(6)

where \( c \) is the conformal anomaly \cite{20} and \( z_1 \) is a negative exponent.

### B. The full-occupancy limit

Let us start analyzing the limiting case \( \bar{\mu} \to \infty \), where all lattice sites are occupied by molecules. Here, we can work with smaller transfer matrices, as noticed above, what allow us to investigate strip widths up to \( L = 16 \). As recently demonstrated by some of us, in such a limit the system displays only the DF and HDL phases, separated by a critical point in the class of the two-dimensional (2D) 3-state Potts model \cite{11}

If a critical point exists at some critical temperature \( T_c^* \), from Eq. (3) one may expect that curves of the scaled gaps \( X_k(L - \ell; \bar{T}) \) and \( X_k(L + \ell; \bar{T}) \) versus \( \bar{T} \) \((\bar{T} = 0, 1, 2, \ldots) \) and \( \bar{\mu} \) cross at pseudocritical temperatures \( \bar{T}_{c,k}(L) \), which shall converge to \( \bar{T}_c^* \) as \( L \to \infty \). Therefore, \( \bar{T}_{c,k}(L) \) can be determined from the condition \( X_k(L - 1; \bar{T}_{c,k}) = X_k(L + 1; \bar{T}_{c,k}) \equiv X_{c,k}(L) \), from which a pseudocritical estimate \( [X_{c,k}(L)] \) of the asymptotic scaling dimension \( X_k \) is also obtained. The values of these quantities for \( k = 1 \) and \( k = 2 \) are shown in Tab. (1) The first thing to note there is that \( \bar{T}_{c,1} \) has a non-monotonic behavior, initially decreasing and then increasing with \( L \). This prevents any reliable extrapolation of this temperature.

The convergence of \( \bar{T}_{c,2} \), on the other hand, is monotonic and, so, we will focus on it to estimate \( T_c^* \).

In general, from finite-size scaling, one expects that

\[
\bar{T}_{c,k}(L) = \bar{T}_c^* + b_1 L^{-\omega_1} + b_2 L^{-\omega_2} + \ldots,
\]  

(7)

whose exponents are related to those in Eq. (3) as \( \omega_1 = y_i - y_1 \) and \( \omega_2 = y_i - y_2 \). Then, by considering \( b_1 = 0 \) for \( i \geq 2 \) and performing three-point (3-p) extrapolations of the values of \( \bar{T}_{c,2} \) in Tab. (1) with \( T_c^* \), \( b_1 \) and \( \omega_1 \) as unknowns in Eq. (7), we find the temperatures displayed in Tab. (1) Note that for the largest \( L \)’s they are varying at the fifth decimal place. A second round of 3-pt extrapolations \[now of the extrapolated values in Tab. (1)\] yields \( 0.952806 \leq T_c^* \leq 0.952818 \), for the four largest sets of widths, without any clear tendency to increase or decrease. Hence, this gives \( T_c^* = 0.952812(6) \). This value differs by only 0.02% from the one estimated from MC simulations in Ref\[33] \( T_c^* \approx 0.9526 \).

The resulting exponents \( \omega_1 \) from the first 3-pt extrapolations are also displayed in Tab. (1) Three-point extrapolations of them, assuming again a power-law correction, return values close (and converging toward) to \( \omega_1 = 2 \) for the largest sets of widths. We remark that, according to Queiroz\[32], the irrelevant exponents in Eq. (3) are given by \( y_1 = -4/5 \) and \( y_2 = -8/5 \) for the 3-state Potts model.
are shown in Tab. I; and they approximate 4
universality class. The central charge is somewhat consistent with the 3-state Potts model.

| \( L \) | \( T_\star^c \) | \( \omega_1 \) | \( \omega_2 \) |
|-------|-------|-------|-------|
| 4     | 0.9397592 | 1.3793263 | –     |
| 5     | 0.9516285 | 2.6536683 | 0.7857046 |
| 6     | 0.9529237 | 3.2158880 | 0.8086578 |
| 7     | 0.9530776 | 3.3614896 | 0.8119752 |
| 8     | 0.9530316 | 3.2893557 | 0.8121525 |
| 9     | 0.9529681 | 3.1489286 | 0.8117281 |
| 10    | 0.9529211 | 3.0138756 | 0.8119490 |
| 11    | 0.9528904 | 2.9040695 | 0.8109670 |
| 12    | 0.9528705 | 2.8173407 | 0.8107358 |
| 13    | 0.9528570 | 2.7468393 | 0.8105667 |
| 14    | 0.9528474 | 2.6875514 | 0.8104331 |

Table II. Extrapolated temperatures, \( T_\star^c \), and corresponding correction exponents, \( \omega_1 \), from 3-pt extrapolations of the values of \( T_{\nu,2} \) displayed in Tab. I considering Eq. \( \text{[7]} \) and sets of sizes \((L-1, L, L+1)\). The resulting central charges, \( c \), from analogous extrapolations of the values of \( c^{(2)} \) in Tab. I are also shown.

model, whose critical thermal exponent is \( y_L = 6/5 \). This means that \( \omega_1 = 2 \) and \( \omega_2 = 14/5 = 2.8 \) in this case. By assuming that \( \omega_1 = 2 \) and \( b_i = 0 \), for \( i \geq 3 \) in Eq. \( \text{[7]} \), we estimate the exponents \( \omega_2 \) for different \( L \)'s from 4-pt extrapolations; and subsequent 3-pt extrapolations of them yield values close to 14/5 for the largest \( L \)'s. So, the correction exponents of the ALG model in the full lattice regime are consistent with the ones for the 3-state Potts model.

The finite-size amplitudes \( X_{c,1} \) and \( X_{c,2} \) in Tab. I on the other hand, do not agree with the ones expected for the 2D 3-state Potts class. In fact, for conformally invariant models in this class, the asymptotic values of these quantities are \( X_1^\star = 2 - y_L = 2/15 \), and \( X_2^\star = 2 - y_L = 4/5 \). However, our values of \( X_{c,1} \) for the largest \( L \)'s are \( \sim 20\% \) smaller than \( 2/15 \), though they display a non-monotonic convergence and are increasing for large \( L \)'s. So, it may be the case that for very large strip widths they will attain the expected Potts value. For \( X_{c,2} \), our values are smaller than \( 4/5 \) by a factor \( \sim 5 \) and are still decreasing, without any indication of changing in this behavior. Actually, the values in Tab. I extrapolate to \( X_{c,2}^\star \approx 0.15 \), suggesting that \( y_L \approx 1.85 \) and then \( \nu = 1/y_L \approx 0.54 \). Thereby, we can be either dealing with a system displaying very slow convergences in these quantities (what seems strange in the case of \( X_{c,2} \)) or the ALG is not a conformally invariant model or it belongs to a different universality class.

The central charge is somewhat consistent with the 3-state Potts class, for which \( c = 4/5 \). In fact, the values of \( c \), calculated as \( c(L) = 3[f(L-1) - f(L+1)][L(L-1)]^2/(2\pi L) \) at the pseudocritical temperatures \( T_{\nu,1} \) and \( T_{\nu,2} \), are shown in Tab. I and they approximate \( 4/5 \) as the system size increases. However, 3-pt extrapolations of such estimates (assuming power-law corrections) return \( c \gtrsim 0.81 \) [see Tab. II]. Further 3-pt extrapolations of the extrapolated values in Tab. I considering the largest \( L \)'s available, do not improve this, once they yield \( c \approx 0.809 \), which differs by \( \sim 1\% \) from the Potts value.

| \( L \) | \( f \) | \( X_1 \) | \( X_2 \) | \( c \) |
|-------|-------|-------|-------|-------|
| 2     | 5.029729 | 0.112107 | 0.180682 | –     |
| 3     | 4.960323 | 0.109445 | 0.168819 | 0.944204 |
| 4     | 4.937032 | 0.107661 | 0.161966 | 0.902030 |
| 5     | 4.926737 | 0.106952 | 0.158348 | 0.865111 |
| 6     | 4.921304 | 0.106774 | 0.156322 | 0.838699 |
| 7     | 4.918080 | 0.106823 | 0.155076 | 0.832989 |
| 8     | 4.916008 | 0.106965 | 0.154240 | 0.825738 |
| 9     | 4.914595 | 0.107143 | 0.153641 | 0.817254 |
| 10    | 4.913587 | 0.107334 | 0.153189 | 0.819162 |
| 11    | 4.912844 | 0.107525 | 0.152836 | 0.817377 |
| 12    | 4.912280 | 0.107713 | 0.152551 | 0.816090 |
| 13    | 4.911841 | 0.107895 | 0.152317 | 0.810502 |
| 14    | 4.911494 | 0.108069 | 0.152121 | 0.814293 |
| 15    | 4.911213 | 0.108237 | 0.151953 | 0.813804 |
| 16    | 4.910984 | 0.108397 | 0.151809 | –     |

Table III. Critical free energies, \( f \), and scaled gaps \( X_1 \) and \( X_2 \) calculated at the critical temperature \( T_\star^c = 0.952812 \). The central charges, \( c \), estimated from these free energies are also shown.

\( \omega \)}

C. The DF-HDL transition line

Employing the same analysis from the previous subsection, but for finite \( \bar{\mu} \), we find that the critical DF-HDL transition extends to chemical potentials down to \( \bar{\mu} \sim 2 \), giving rise to a DF-HDL transition line, as found in the mean-field solutions of the model on Husimi lattices.\( ^{5,111} \) Given the non-monotonic convergence observed above in the critical points estimated from \( X_1 \), we will focus here only on those calculated from \( X_2 \). The pseudocritical transition lines obtained from the condition \( X_2(L-1, T_\star^c) = X_2(L+1, T_\star^c) \), for fixed values of \( \bar{\mu} \), are shown in Fig. 5(a), for \( L \leq 11 \). (Here, it is quite hard to go beyond \( L = 12 \), once the TMs have \( 4^L \times 4^L \) terms. Actually, most of our results will be limited to \( L \leq 10 \).) It is important to notice that such lines never cross each other, indicating that the DF-HDL transition is always continuous.

Three-point extrapolations of the pseudocritical lines — assuming the finite-size correction of Eq. 4 for fixed \( \bar{\mu} \), with \( a_i = 0 \) for \( i > 1 \), and considering the sets of widths \((5, 7, 9)\) and \((7, 9, 11)\) — yield lines whose values...
Table IV. Estimates for the critical-end-point from the corner in the DF-HDL transition lines (leftmost values) and from the point where such lines meet the other transition lines (rightmost values).

| $L$ | $T_{cep,1}$ | $\bar{\mu}_{cep,1}$ | $T_{cep,2}$ | $\bar{\mu}_{cep,2}$ |
|-----|-------------|----------------------|-------------|----------------------|
| 3   | 0.884217    | 2.264032             | 0.801210    | 2.010048             |
| 5   | 0.841799    | 2.018722             | 0.812741    | 1.982581             |
| 7   | 0.828528    | 1.981947             | 0.812563    | 1.972774             |
| 9   | 0.823467    | 1.970668             | 0.812692    | 1.968213             |

Figure 5. (Color online) a) Pseudocritical lines separating the DF and HDL phases, obtained from $X_{2}(L-1, T^*_{c}) = X_{2}(L+1, T^*_{c})$ for fixed values of $\bar{\mu}$, for the indicated $L$’s. The outcomes from 3-pt extrapolations of these lines considering the sets (5, 7, 9) [Extrap. 1] and (7, 9, 11) [Extrap. 2] are also shown. b) Detail of the region where the DF-HDL, DF-LDL and LDL-HDL transition lines, for $L = 7$, meet. The green square and the red circle indicate the two estimates for the critical-end-point.

of $T^*_c$ always differ by less than 0.2%. This corresponds to differences (and error bars) at most at the third decimal place, which is accurate enough for our purposes.

Interestingly, the pseudocritical lines have a corner at $\bar{\mu} \approx 2$, which may be seen as their end-point. An example of this is shown in Fig. 5(b), in the line for $L = 7$. As it will be demonstrated below, the critical DF-HDL line ends at a critical end-point (CEP). The coordinates ($T_{cep,1}, \bar{\mu}_{cep,1}$) of the CEP, assuming that it is located at the corner, are depicted in Tab. IV. Since the DF-HDL transition lines continue below these corners and finally meet the DF-LDL and LDL-HDL transition lines [see Fig. 5(b)], one obtains another set of estimates ($T_{cep,2}, \bar{\mu}_{cep,2}$) for the CEP. As shows Tab. IV in this last case the temperatures oscillate around $T_{cep,2} = 0.81266$ (considering the three largest $L$’s). The temperatures of the corners seem to converge toward this value as $L$ increases; though a 3-pt extrapolation of them (following Eq. 2 considering the largest $L$’s) returns a slightly larger value: $T_{cep,1} = 0.81681$. This deviation, of $\sim 0.5\%$, is certainly due to the small widths considered here, so that it is reasonable to regard $T_{cep} = 0.815(3)$ as our estimate for the CEP temperature. This value is close, but a bit smaller than $T_{c}/t_{c} = 0.825$, which was found in previous MC simulations of the ALG model and reported as a critical point in Ref. $^{22}$ and as a tricritical point in Ref. $^{23}$. Our estimate is also smaller than the value found for the triple point ($T_{tp} = 0.835$) in the Husimi lattice solution of the model $^{23}$.

The 3-pt extrapolations of the values of $\bar{\mu}_{cep,1}(L)$ and $\bar{\mu}_{cep,2}(L)$ for the largest $L$’s, assuming power-law corrections similarly to Eq. 2, yield $\bar{\mu}_{cep,1} = 1.9589$ and $\bar{\mu}_{cep,2} = 1.9605$, respectively, indicating that $\bar{\mu}_{cep} = 1.9597(8)$. This result agrees with the mean-field value found in Ref. $^{23}$ for the triple point ($\bar{\mu}_{tp} = 1.959$) and differs by $\approx 3\%$ from the critical point reported in Ref. $^{22}$ ($\bar{\mu}_{cep} = 2.02$).

The central charges calculated along the pseudocritical transition lines from Fig. 5(a) are shown in Fig. 6 as a function $\bar{\mu}$. We may note that $c(L)$ is almost independent of the chemical potential for $\bar{\mu} \gtrsim 10$ (similarly to $T_c$), having values very close to those of $c^{(2)}$ in Tab. I for...
When $\bar{\mu}$ approximates $\mu_{\text{cep}}$, however, one sees that $c$ passes to increase and to display stronger finite-size corrections. The large $L$ is the close the approximately constant part of the lines get to $\mu_{\text{cep}}$ before deviating upward. This strongly suggests that for very large $L$’s one must have $c \approx 0.8$ in the entire DF-HDL line, indicating that it belongs to the 3-state Potts class.

## D. The LDL-HDL transition line

The LDL-HDL transition is the only one for which all previous studies of the ALG model agree; the phases are separated by a coexistence line, which exists in a narrow chemical potential interval near $\bar{\mu} = 2.24(18)$. Therefore, in this case, it is convenient to determine the transition lines by varying $\bar{\mu}$ for fixed values of $T$. For the strip widths analyzed here, crossings in the curves of $X_k(L; \bar{\mu})$ versus $\bar{\mu}$ for different $L$’s are only observed for $k \geq 3$. The curves of $X_1(L; \bar{\mu})$ and $X_2(L; \bar{\mu})$ only exhibit a maximum in the coexistence region. The transition lines obtained from the condition $X_3(L - 1, \bar{\mu}_c) = X_3(L + 1, \bar{\mu}_c)$ are depicted in Fig. 7(a). The lines for the smallest widths present maxima in the region close to the CEP, which are absent in those for the largest $L$’s. This turns the extrapolation of these lines unreliable in this region, which is the most important part of such curves, since they are always very close to $\bar{\mu} = 2$ for low temperatures.

Motivated by this and also to confirm the first-order nature of the LDL-HDL transition, we obtain an alternative estimate for the LDL-HDL transition line through the correlation length $\xi_k^{-1}(L)$, defined in Eq. 4, for $k = 6$. We remark that, given the four-fold (three-fold) degeneracy of the ground state of the LDL (HDL) phase, a total of seven possible phases (divided into two sets with three and four equivalent ones) coexist at the LDL-HDL transition line. This means that the seven largest eigenvalues (from $\Lambda_0$ to $\Lambda_6$) of the TMs shall be degenerated in the thermodynamic limit ($L \to \infty$). Hence, curves of $\xi_6^{-1}(L)$ vs $\bar{\mu}$, for a given $T$, are expected to display a minimum at the coexistence$^{29,31}$ As exemplified in Fig. 7(b) for $T = 0.75$, such behavior is indeed found in these curves, confirming that this is a discontinuous transition. The coexistence lines estimated from the loci of these minima are depicted in Fig. 7(c). It is noteworthy that $\bar{\mu}_c(T)$ decreases with $L$ in Fig. 7(a), while for these last estimates an increasing behavior is observed in Fig. 7(c).

In order to extrapolate these lines, we recall that finite-size scaling predicts exponential corrections at the coexistence$^{29,31}$ such that

$$\bar{\mu}_c(L) = \bar{\mu}_c^* + ae^{-bL} + \ldots,$$  \hspace{1cm} (8)

for a given $T$. For a 3-pt extrapolation this gives $\bar{\mu}_c^* = \bar{\mu}_c(L) + \bar{\mu}_c(L+1) - 2\bar{\mu}_c(L)$.

The resulting curve from such an extrapolation, for the three largest $L$’s, is shown in Fig. 7(c).
E. The DF-LDL transition line

The transition lines separating the disordered and LDL phases were estimated following the same procedures from the previous subsection, but varying $\bar{T}$ for fixed values of $\bar{\mu}$. The curves obtained from the condition $X_1(L-1, T_c) = X_1(L+1, T_c)$, for fixed values of $\bar{\mu}$; and b) from the minima in the inverse correlation length $\xi_{\bar{L}}^{-1}$. The respective extrapolated curves [Extrap.], from a 3-pt extrapolation following Eq. 8, are shown in both panels.

Additional evidence of this is obtained from the curves of $\xi_{\bar{L}}^{-1}$ versus $\bar{T}$, for a given $\bar{\mu}$, which have minima hallmarking the coexistence. A behavior analogous to that seen in Fig. 7(b) for $\xi_{\bar{L}}^{-1}$ at the LDL-HDL transition. Note that in the case of the DF phase (one ground state) coexisting with the LDL phase (which has four equivalent ground states), minima are indeed expected in $\xi_{\bar{L}}^{-1}$. From such minima, we estimate the coexistence lines displayed in Fig. 8(b). Interestingly, in this case the values of $T_c(\bar{\mu})$ increases with $L$, in opposition to the behavior seen in Fig. 8(a).

Figures 8(a) and 8(b) present also the asymptotic curves, obtained from 3-pt extrapolations assuming exponential finite-size corrections in $T_c(L)$ similarly to Eq. 8 [i.e., $T_c(\bar{L}) \sim T_c^\ast + a e^{-bL}$]. The difference between the values of $T_c^\ast(\bar{\mu})$ along these lines is always smaller than 0.5% and in the main part of them it is \( \lesssim 0.01\% \). The turning point in the coexistence line (i.e., the point where $T_c^\ast$ is maximum) is located at $T_c^\ast \approx 0.983$ and $\bar{\mu}_c^\ast \approx 0.31$.

The complete phase diagram, presenting all the transition lines found in our MT calculations, will be presented in Sec. 4 where they are compared with the results from the MC simulations discussed in the next section.

IV. MONTE CARLO SIMULATIONS

A. Simulation details and quantities of interest

The thermodynamic properties of the symmetric ALG model were also obtained via extensive Monte Carlo (MC) simulation on the triangular lattice with periodic boundary conditions. We study system sizes $L = 32, 48, 64, 96, 128$ and 192 using the standard Metropolis algorithm in the grand canonical ensemble.

Following references,[22,55] simulations with fixed chemical potential are used to locate the DF-LDL line while simulations along isotherms in the $\bar{\mu}-\bar{T}$ plane are used to locate the DF-LD and LDL-HDL coexistence lines. We study $\bar{\mu} = 1.95, 2.3, 2.4, 2.5, 2.6, 5.0$ and 10 in the HDL region and use a temperature interval $0.50 \leq \bar{T} \leq 0.97$ in the LDL region.

Studies of the HDL region are performed in two steps. First, broad ranges of temperature are studied in order to identify the region of peaks in the response functions. In this step 50 independent realizations are used to compute averages. After identifying the region of interest for each system size, additional simulations are performed in a reduced range of temperatures. The number of points around the maximum depends on the system size; for $L = 64, 128$ we use 60 points while for larger system sizes 30 points are sufficient. In this step 100 independent replicas are used. In all simulations we use $10^6$ MC steps for equilibration, followed by $10^5 - 2 \times 10^6$ MC steps for data production.

The transition between the HDL and the DF phases can be analyzed using the order parameters,

$$
\theta(T, \bar{\mu}; L) \equiv \frac{3}{2} \left( \max(n_1, n_2, n_3) - \frac{1}{3} \right),
$$

where $n_1, n_2, n_3$ are the number of particles in each of the three sites of the triangular lattice, respectively.
and

$$Q(\bar{T}, \bar{\mu}; L) \equiv \frac{1}{N} \sqrt{\frac{1}{n_1^2 + n_2^2 + n_3^2 - n_1n_2 - n_1n_3 - n_2n_3}}$$

(10)

where \(n_k\) denotes the number of molecules in orientational state \(k\) and \(N = \sum_{k=1}^{3} n_k\) is the total number of molecules. In the DF phase, one has \(n_1 \approx n_2 \approx n_3\), so that \(\theta \to 0\) and \(Q \to 0\). On the other hand, \(\theta \to 1\) and \(Q \to 1\) in the HDL phase, where, e.g., \(n_1 \approx N\) and \(n_2 \approx n_3 \approx 0\).

To analyze the transitions we also use the susceptibilities related to the order parameters:

$$\chi_X(\bar{T}; L) = \frac{L^2}{T} \left[ \langle X^2 \rangle - \langle X \rangle^2 \right]$$

(11)

with \(X = \theta\) or \(Q\); the specific heat at constant volume

$$c_V(\bar{T}; L) = \frac{1}{VT^2} \left[ \langle E^2 \rangle - \langle E \rangle^2 \right] - \frac{\langle EN \rangle - \langle E \rangle \langle N \rangle}{\langle N^2 \rangle - \langle N \rangle^2}$$

(12)

and the isothermal compressibility

$$\kappa(\bar{T}; L) = \frac{V}{k_BT} \left( \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle^2} \right).$$

(13)

In Eqs. (11)-(13) \(\langle \cdot \rangle\) denotes grand canonical averages.

### B. Discontinuous transitions

In this subsection we present the results for DF-LDL and LDL-HDL transitions. As reported in the Refs. [22,25] the density plays the role of an order parameter for the referred transitions. Figures (a) and (b) show the density as a function of chemical potential for the DF-LDL transition and the LDL-HDL transition, respectively. The density histograms for each transition are shown in the insets of Figs. (a) and (b). In both cases, the histograms are bimodal indicating a discontinuous transition and confirming the results from the transfer matrix (TM) calculations (see Subsec. III D and III E). For each temperature, we plotted the histogram for the chemical potential that was closest to the coexistence value within our resolution (\(\Delta \bar{\mu} = 10^{-4}\) or larger). We take the coexistence chemical potential as that for which the heights of the two peaks are equal.

The coexistence chemical potential is estimated as follows: First we identify the values of the maxima of the probability distributions, \(\max[P(\rho_{DF})]\) and \(\max[P(\rho_{LDL})]\), for each chemical potential studied (see blue crosses and red pluses in Fig. [10]). Subsequently, we plot the \(\max[P(\rho_{LDL,DF})]\) as function of chemical potential as shown in Fig. [10] for \(\bar{T} = 0.55\). The crossing point of the curves is estimated through a polynomial fit in the vicinity of the intersection, using the reciprocals of the variance \(1/\sigma_i^2\) of the averages computed over the replicas as weights for the polynomial fit of the points. In most cases, 7 points around the intersection region are enough to obtain a satisfactory region of crossing. The order of the polynomial is chosen as the lowest order that yields random behavior of residuals; a 3rd-order polynomial fit was sufficient in most cases. Subsequently, the error of the fit was computed through the root mean square error (RMSE) over the points used in the fit. Finally, the uncertainty in the crossing-point estimate is computed as the square root of the RMSE resulting from each polynomial. This procedure yields the dots in the phase diagram of Fig. [15].

In the region around \(\bar{\mu} = 0\), \(\bar{T} > 0.95\) the densities \(\rho_{LDL}\) and \(\rho_{DF}\) are very similar and the coexistence temperature and chemical potential cannot been obtained using the density histogram (see Fig. [15] b)).

For the LDL-HDL transition, the data for the density are very noisy for \(\bar{T} \leq 0.75\) (see Fig. 9 b)) and it is not possible to use the procedure described above to determine the coexistence chemical potential. For these cases, we adopted the following procedure: for each point on the curve \(\max[P(\rho_i)] \times \bar{\mu}\) (see inset of Fig. [10]) we sum a Gaussian random variable proportional to the error bar of that point. We then fit the curves and estimate the crossing point. An average is computed over \(10^3\) real-
The specific heat at constant volume $\chi$ and isothermal compressibility $\kappa$ are parameters, $Q_1$, and $Q_2$, and isothermal compressibility (Eq. 13).

transition. In all cases the peaks increase systematically with system size. Similar results are obtained for $\mu = 2.4, 2.5, 2.6, 5.0$ and 10. The set of pseudocritical temperatures appear to converge as $L \to \infty$ for all the studied values of $\mu$. The global estimate of $T_c^\ast$ was obtained through a weighted average with weight $1/\sigma^2$, where $\sigma$ represents the uncertainty of each quantity. The final estimates of $T_c^\ast$ are the squares in the phase diagram Fig. 15.

D. Critical exponents

For $\mu = 2.3$ and 10, we estimate the critical exponents ratios $\beta/\nu$ and $\gamma/\nu$ from fits to the data for $Q(T_c)$, $\theta(T_c)$, $\chi(T_c)$, and $\kappa(T_c)$ versus system size (see Fig. 3). From the linear fits, and including the effect of the uncertainty in $T_c^\ast$, we obtained the estimates in Table V. The values for these ratios for the two-dimensional three-state Potts model are $\beta_{\text{Potts}}/\nu_{\text{Potts}} = 0.1333 \ldots$ and $\gamma_{\text{Potts}}/\nu_{\text{Potts}} = 0.17333 \ldots$. In the worst cases, the discrepancy is about 6% for $\mu = 2.3$ and 8% for $\mu = 10$.

Figure 14 shows the linear fit for $\ln c_\nu(T_c)$ for $\mu = 10.0$, yielding the estimate $\alpha/\nu = 0.44(1)$, i.e., a discrepancy with the ratio for the two-dimensional, three-state Potts model $\alpha/\nu_{\text{Potts}} = 0.4$ of 10%. For $\mu = 2.3$, the discrepancy in this ratio is 73%. We believe this huge difference is likely due to finite-size corrections that are more important close to the CEP ($\bar{\mu}_{\text{cep}} = 1.9498$) where the DF-HDL line encounters the LDL-HDL and DF-LDL lines.

| $\mu$ | $\beta_Q/\nu$ | $\beta_\theta/\nu$ | $\gamma_Q/\nu$ | $\gamma_\theta/\nu$ | $\alpha/\nu$ |
|-------|---------------|------------------|----------------|----------------|------------|
| 2.3   | 0.126(7)      | 0.136(8)         | 0.166(4)       | 0.133(4)       | 0.11(1)    |
| 10.0  | 0.126(7)      | 0.122(7)         | 1.75(5)        | 1.754(4)       | 0.44(1)    |

Table V. Estimates of the ratios $\beta/\nu$, $\gamma/\nu$ and $\alpha/\nu$ for chemical potentials $\bar{\mu} = 2.3$ and 10.

V. DISCUSSION

Figure 15(a) shows the phase diagram of the symmetric ALG model in the $T - \bar{\mu}$ plane, summarizing the results reported above. The predictions of the TM analysis are in very good quantitative agreement with MC simulation. In fact, the maximum difference between the
estimates from each method is smaller than 2% along the LDL-HDL coexistence line and, notably, is at most 0.1% for the DF-HDL and DF-LDL lines. The natures of the transitions are also the same in both cases. This remarkable agreement confirms that we are accessing the correct thermodynamic behavior of the model.

Our results demonstrate that the DF-LDL transition is always discontinuous, without any critical or multicritical point. This is confirmed by the absence of a crossing in the pseudocritical transition lines from the TM analysis, by the bimodal histograms in MC simulations and also in the phase diagram of temperature versus total density ($T - \rho$), depicted in Fig. 15(b). This diagram makes it clear that the densities are discontinuous at the DF-LDL transition line up to temperatures very close to the turning point (in the $\bar{T} - \bar{\rho}$ diagram), which is located at $\bar{T} \approx 0.983$. It is, however, difficult to estimate the densities accurately very near this point, since $\rho_{DF}$ becomes very similar to $\rho_{LDL}$. An analogous behavior was found in the Husimi lattice solution of this model and indeed our $T - \rho$ diagram is very similar to the one found there (see Fig. 4(a) of Ref). Importantly, these

Figure 11. (a) Order parameters $Q$ and $\theta$, (b) susceptibilities $\chi_Q$ and $\chi_\theta$, (c) specific heat $c_V$, and (d) isothermal compressibility for $\bar{\mu} = 2.3$. Blue, red, magenta, black, cyan, and yellow correspond to system sizes $L = 32, 48, 64, 96, 128$ and 192. The order parameter $Q$ and its susceptibility $\chi_Q$ are represented by solid lines, $\theta$ and $\chi_\theta$ by symbols.

Figure 12. Pseudocritical temperatures associated with, $c_v$, $\chi_Q$, $\chi_\theta$ and $\kappa$, with symbols as indicated, versus $1/L$ for $\bar{\mu} = 2.3$. Dash lines are linear fits to the data and the filled black dot indicates the global estimate for the critical temperature $T_c$.

Figure 13. (a) Order parameter $Q(\theta)$ versus system size for $\bar{\mu} = 2.3$. The circles (squares) are the simulation data; dashed lines are least-squares linear fits of the data. Inset shows the residuals of the fits. (b) Analogous plots for the susceptibilities $\chi_Q(\chi_\theta)$.

Figure 14. Specific heat $c_V$ versus system size at critical temperature for $\bar{\mu} = 10.0$. The circles are the simulation data; the dashed lines is a least-squares linear fit of the data. Inset shows the residuals of the fit.
results provide compelling evidence that the entire DF-LDL transition line is discontinuous, ruling out a critical point at $T \approx 0.55$ or a tricritical point at $T \approx 0.65$, as claimed in previous MC analyses in references\cite{22,23}, respectively.

Also in contrast with earlier simulations, we find a critical line separating the DF and HDL phases. This line meets the LDL-HDL and DF-LDL coexistence lines at a critical end point (CEP). This shows that the point where the LDL-HDL coexistence line ends — reported in literature as critical\cite{23} and tricritical\cite{35} — is actually a CEP. Therefore, although this ALG model has an interesting phase behavior, beyond displaying some thermodynamic anomalies, it is not a good model for liquid water, as initially suggested, because it has neither a liquid-gas coexistence line ending at a critical point, nor a LLCP. In light of the discussion in the Introduction, it seems that absence of a LLCP is a general feature of lattice models with attractive orientational interactions competing with "van der Waals" repulsion between first neighbor molecules.

Although determining the universality class of the continuous transitions displayed by models for water is key to establish a full connection with the actual behavior of water, this has not been widely investigated, perhaps because the very nature of these transitions are the subject of controversy. A recent account of these critical properties for realistic models can be found in Ref.\cite{55}. For lattice models, some examples include the debate in the literature on the critical exponents of the liquid-liquid transition in the classic Bell-Lavis model\cite{34,35}, and our previous study of the present ALG model in the fully occupied limit, where the DF-HDL transition was found to be in the 3-state Potts class. The central charge obtained here, deviating by $\sim 1\%$ from the Potts value, gives additional evidence of this. The scaled gaps, on the other hand, present a large deviation from those of the 3-state Potts class. The analysis of the central charge for finite chemical potentials indicates that it converges to the same value along the entire DF-HDL critical line. Nevertheless, finite-size corrections become very strong as $\bar{\mu}$ approaches $\bar{\mu}_{\text{CEP}} = 1.9597(8)$. This certainly explains why some critical exponent ratios estimated in simulations for $\bar{\mu} = 2.3$ exhibit considerable deviations from the Potts values, while for $\bar{\mu} = 10$ the deviations are much smaller. Despite this, the overall picture suggests that this order-disorder transition is always in the 3-state Potts class, as is expected from its three-fold ($S_3$) symmetry breaking.

ACKNOWLEDGMENTS

Authors acknowledge financial support from CAPES Brazil and the National Institute of Science and Technology for Complex Systems of Brazil.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

\cite{1} H. E. Stanley, ed., *Liquid Polymorphism: Advances in Chemical Physics* Vol. 152 (Wiley, NY, 2013).
2 R. J. Speedy and C. A. Angell, “Isothermal compressibility of supercooled water and evidence of a singularity at \(-45^\circ\)C,” J. Chem. Phys. 65, 851 (1976)

3 S. Sastry, P. G. Debenedetti, F. Sciortino, and H. E. Stanley, “Singularity-free interpretation of the thermodynamics of supercooled water,” Phys. Rev. Lett. 53, 6144 (1984)

4 P. H. Poole, F. Sciortino, U. Essmann, and H. E. Stanley, “Phase behavior of metastable water,” Nature 360, 324 (1992)

5 O. Mishima, L. D. Calvert, and E. Whalley, “An apparently 1st-order transition between 2 amorphous phases of ice induced by pressure,” Nature 314, 76 (1985)

6 M. Lynden-Bell, S. C. Morris, J. D. Barrow, J. L. Finney, and C. L. Harper Jr., eds., \textit{Water and life: The unique properties of \text{H}_2\text{O}} (CRC Press, Boca Raton, FL, 2010).

7 A. Te Sopper and M. A. Ricci, “Structures of high-density and low-density water,” Phys. Rev. Lett. 84, 2881 (2000)

8 O. Mishima and H. E. Stanley, “Decompression-induced melting of ice IV and the liquid–liquid transition in water,” Nature 392, 164 (1998)

9 S. Woutersen, B. Ensing, M. Hilbers, Z. Zhao, and C. A. Angell, “A liquid-liquid transition in supercooled aqueous solution related to the HDA-LDA transition,” Science 359, 1127 (2018)

10 L. Liu, S.-H. Chen, A. Faraone, C.-W. Yen, and C.-Y. Mou, “First-order dependence of fragile-to-strong transition and a possible second critical point in supercooled confined water,” Phys. Rev. Lett. 95, 117802 (2005)

11 S.-H. Chen, F. Mallamace, C.-Y. Mou, M. Broccio, C. Corsaro, A. Faraone, and L. Liu, “Violation of the Stokes-Einstein relation in supercooled water,” Proc. Natl. Acad. Sci. USA 103, 12974 (2006)

12 F. Mallamace, M. Broccio, C. Corsaro, A. Faraone, D. Majolino, V. Venuti, L. Liu, C.-Y. Mou, and S.-H. Chen, “Evidence of the existence of the low-density liquid phase in supercooled, confined water,” Proc. Natl. Acad. Sci. USA 104, 421 (2007)

13 F. Mallamace, “The liquid water polymorphism,” Proc. Natl. Acad. Sci. USA 106, 15997 (2009)

14 A. K. Soper, “Is water one liquid or two?” J. Chem. Phys. 150, 234503 (2019)

15 J. C. Palmer, P. H. Poole, F. Sciortino, and P. G. Debenedetti, “Advances in computational studies of the liquid-liquid transition in water and water-like models,” Chem. Rev. 118, 9120 (2018)

16 G. M. Bell and D. A. Lavis, “Two-dimensional bonded lattice fluids. I. Interstitial model,” J. Phys. A 3, 427 (1970)

17 G. M. Bell and D. A. Lavis, “Two-dimensional bonded lattice fluids. II. Orientable molecule model,” J. Phys. A 3, 568 (1970)

18 D. A. Huckaby and R. S. Hanna, “A two-dimensional lattice gas model for water,” J. Phys. A 20, 5311 (1987)

19 A. Patrykiejew, O. Pizio, and S. Sokolowski, “Novel phase behavior in a two-dimensional network-forming lattice fluid,” Phys. Rev. Lett. 83, 3442 (1999)

20 C. Buzzano, E. D. Stefani, A. Pelizzola, and M. Pretti, “Two-dimensional lattice-fluid model with water-like anomalies,” Phys. Rev. E 69, 061502 (2004)

21 V. B. Henriques and M. C. Barbosa, “Liquid polymorphism and density anomaly in a lattice gas model,” Phys. Rev. E 71, 031504 (2005)

22 J. C. Barbadoes, V. B. Henriques, and M. C. Barbosa, “Liquid polymorphism, density anomaly and H-bond disruption in associating lattice gases,” J. Phys.: Condens. Matter 19, 116105 (2007)

23 G. M. Bell, “Statistical mechanics of water: lattice model with directed bonding,” J. Phys. C 5, 889 (1972)

24 H. E. Meijer, R. Kikuchi, and E. V. Royen, “Phase diagram of water based on a lattice model,” Physica A 115, 124 (1982)

25 D. A. Lavis and B. W. Southern, “Renormalization group study of a three-dimensional lattice model with directional bonding,” J. Stat. Phys. 35, 489 (1984)

26 N. A. M. Besseling and J. Lyklema, “Equilibrium properties of water and its liquid-vapor interface,” J. Phys. Chem. 98, 11610 (1994)

27 C. J. Roberts and P. G. Debenedetti, “Polyamorphism and density anomalies in network-forming fluids: Zeroth- and first-order approximations,” J. Chem. Phys. 105, 658 (1996)

28 C. J. Roberts, A. Z. Panagiotopoulos, and P. G. Debenedetti, “Liquid-liquid immiscibility in pure fluids: Polymorphism in simulations of a network-forming fluid,” Phys. Rev. Lett. 77, 4386 (1996)

29 M. Pretti and C. Buzzano, “Thermodynamic anomalies in a lattice model of water,” J. Chem. Phys. 121, 11856 (2004)

30 M. Pretti and C. Buzzano, “Thermodynamic anomalies in a lattice model of water: Solution properties,” J. Chem. Phys. 123, 024506 (2005)

31 S. Sastry, F. Sciortino, and H. E. Stanley, “Limits of stability of the liquid phase in a lattice model with water-like properties,” J. Chem. Phys. 98, 9863 (1993)

32 S. Borick, P. G. Debenedetti, and S. Sastry, “A lattice model of network-forming fluids with orientation-dependent bonding: Equilibrium, stability, and implications for the phase behavior of supercooled water,” J. Chem. Phys. 99, 3781 (1993)

33 M. Girardi, A. L. Ballaikes, V. B. Henriques, and M. C. Barbosa, “Liquid polymorphism and density anomaly in a three-dimensional associating lattice gas,” J. Chem. Phys. 126, 064509 (2007)

34 J. Oliveira, J. F. Stilck, and M. A. A. Barbosa, “Solution of an associating lattice-gas model with density anomaly on a husimi lattice,” Phys. Rev. E 82, 051131 (2010)

35 A. P. Furlan, C. E. Fiore, and M. C. Barbosa, “Influence of disordered porous media on the anomalous properties of a simple water model,” Phys. Rev. E 92, 032404 (2015)

36 C. Buzzano, E. De Stefani, and M. Pretti, “Cluster-variation approximation for a network-forming lattice-fluid model,” J. Chem. Phys. 129, 024506 (2008)

37 M. Pretti, C. Buzzano, and E. De Stefani, “Revisiting waterlike network-forming lattice models,” J. Chem. Phys. 131, 224508 (2009)

38 M. M. Szortyka, M. Girardi, V. B. Henriques, and M. C. Barbosa, “Dynamic transitions in a three dimensional associating lattice gas model,” J. Chem. Phys. 132, 134904 (2010)

39 M. M. Szortyka, V. B. Henriques, M. Girardi, and M. C. Barbosa, “Dynamic transitions in a two dimensional associating lattice gas model,” J. Chem. Phys. 130, 184902 (2009)

40 A. P. Furlan, N. G. Almarza, and M. C. Barbosa, “Lattice model for water-solute mixtures,” J. Chem. Phys. 145, 144501 (2016)

41 A. P. Furlan, T. J. Oliveira, J. F. Stilck, and R. Dickman, “Order-disorder transition in a two-dimensional associating lattice gas,” Phys. Rev. E 100, 022109 (2019)

42 F. Y. Wu, “The Potts model,” Rev. Mod. Phys. 54, 235–268 (1982)

43 W. Guo and H. W. J. Blöte, “Finite-size analysis of the hard-sphere lattice gas,” Phys. Rev. E 66, 046140 (2002)

44 J. T. Oliveira and J. F. Stilck, “Transfer-matrix study of a hard-square lattice gas with two kinds of particles and density anomaly,” Phys. Rev. E 92, 032101 (2015)

45 M. E. Fisher, in \textit{Proceedings of International School of Physics \textit{\textit{Enrico Fermi}},} edited by M. S. Green (Academic, New York, 1971)

46 H. W. J. Blöte, J. L. Cardy, and M. P. Nightingale, Phys. Rev. Lett. 56, 742 (1986); I. Affleck, ibid. 56, 746 (1986)

47 S. A. de Queiroz, “Finite-size scaling corrections in two-dimensional Ising and Potts ferromagnets,” J. Phys. A: Math. Gen. 33, 721 (2000)

48 P. A. Rikvold, W. Kinzel, J. D. Gunton, and K. Kaski, “Finite-size-scaling study of a two-dimensional lattice-gas model with a tricritical point,” Phys. Rev. B 28, 2686 (1983)

49 N. C. Bartelt, T. L. Einstein, and L. D. Roselofs, “Transfer-matrix approach to estimating coverage discontinuities and multicritical-point positions in two-dimensional lattice-gas phase diagrams,” Phys. Rev. B 34, 1616 (1986)
50 J. C. Xavier, F. C. Alcaraz, D. P. Lara, and J. A. Plascak, “Critical behavior of the spin-3/2 Blume-Capel model in two dimensions,” Phys. Rev. B 57, 11575 (1998).
51 M. Jung and D.-H. Kim, “First-order transitions and thermodynamic properties in the 2D Blume-Capel model: the transfer-matrix method revisited,” Eur. Phys. J. B 90, 245 (2017).
52 M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids*, Oxford Science Publ (Clarendon Press, 1989).
53 P. G. Debenedetti, F. Sciortino, and G. H. Zerzel, “Second critical point in two realistic models of water,” Science 369, 280 (2020).
54 C. E. Fiore, M. M. Szortyka, M. C. Barbosa, and V. B. Henriques, “Liquid polymorphism, order-disorder transitions and anomalous behavior: A monte carlo study of the Bell-Lavis model for water,” J. Chem. Phys. 131, 164506 (2009).
55 M. Simenas, A. Ibenskas, and E. E. Tornau, “Phase transition properties of the Bell-Lavis model,” Phys. Rev. E 90, 042124 (2014).