A discrete model of water with two distinct glassy phases

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Abstract – We investigate a minimal model for non-crystalline water, defined on a Husimi lattice. The peculiar random-regular nature of the lattice is meant to account for the formation of a random 4-coordinated hydrogen-bond network. The model turns out to be consistent with most thermodynamic anomalies observed in liquid and supercooled-liquid water. Furthermore, the model exhibits two glassy phases with different densities, which can coexist at a first-order transition. The onset of a complex free-energy landscape, characterized by an exponentially large number of metastable minima, is pointed out by the cavity method, at the level of 1-step replica symmetry breaking.

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Introduction. – In the last decade, there have been several attempts at describing structural glasses by means of simple lattice models, in the analytical framework of random-regular (Bethe or Husimi) lattices \cite{1–5}. For these models, the cavity method generally predicts a discontinuous replica symmetry breaking, \textit{i.e.}, a sudden emergence of an exponentially large number of metastable free-energy minima. On the other hand, great interest has been attracted by polymorphism (\textit{i.e.}, the existence of different glass forms of the same substance) \cite{6}, both because of the relative novelty of the phenomenon (first discovered for water in 1985 \cite{7}) and because of its relationship with the popular “second critical point” conjecture, put forward by Stanley and coworkers \cite{8} to explain water anomalies \cite{9}.

Lattice models have long been used for investigating water \cite{10–22}. In some recent papers, coauthored by one of us \cite{21,22}, it has been shown that a first-order (quasi-chemical) approximation \cite{23} on a tetrahedral cluster is extremely effective to compute the phase diagram and the thermodynamic properties of a special class of water-like models, derived from the early Bell model \cite{10}. These models, defined on the (regular) body-centered cubic (bcc) lattice, do not contain a mechanism capable of inducing glassy behavior, so that they exhibit only crystalline (ice-like) phases at low temperature.

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The present letter is motivated by the following observations. i) For a generic lattice model, the aforementioned quasi-chemical approximation, with a given choice of the associated cluster, coincides with the exact solution of a corresponding model, defined on a Husimi lattice made up of clusters of the same type \cite{23,24}, under the hypothesis of replica symmetry \cite{25,26}. As a consequence, we can define suitable Husimi lattice models, whose high-temperature behavior turns out to be very similar to that of the original water-like bcc-lattice models. ii) It is known from experiments that directional correlation of hydrogen bonds in real water is almost completely lost after the second consecutive bond (see \cite{27} and references therein). The random nature of a Husimi lattice can roughly describe a similar scenario (this was not possible on a regular lattice). iii) We expect that the resulting frustration might hamper the onset of ice-like order, allowing for the possibility of glassy behavior at low temperature. Such a possibility can be easily investigated by the cavity method \cite{25}.

Concerning point i), let us remark the nontrivial difference between a Husimi \textit{tree} (which is, a system with a boundary) and a Husimi \textit{lattice} (which is, a system without a boundary, in which all sites have the same coordination number). The latter system locally exhibits the same tree-like structure as the former, but contains loops on a larger scale \cite{25}. The two systems may be considered equivalent as long as the frustration arising from the
presence of loops is not strong enough to induce replica symmetry breaking (i.e., glassy behavior).

The main finding of this work is a Husimi lattice model predicting two different glassy phases, which we are led to identify with the low- and high-density amorphous (LDA, HDA) ices, observed experimentally [6,9]. This model provides interesting insights about the controversial nature of water polymorphism and, more in general, the metastable phase diagram of water [9].

The model. – We consider a Husimi lattice made up of oriented plaquettes of 4 sites, as shown in fig. 1. Each site $i$ (characterized by a configuration variable $x_i$) may be empty ($x_i=0$) or occupied by a water molecule, in 2 possible configurations ($x_i=1,2$). Each water molecule possesses four equivalent bonding arms, which can point toward nearest-neighbor sites, and may be either concordant ($x_i=1$) or discordant ($x_i=2$) with edge orientations. An attractive potential energy $-\epsilon < 0$ is assigned to any pair of nearest-neighbor occupied sites. This is the ordinary van der Waals contribution. A hydrogen bond is formed, yielding an extra energy $-\epsilon$ whenever two nearest-neighbor molecules point an arm toward each other, with no distinction between donors and acceptors (more precisely, a bond is formed on an edge oriented from $i$ to $j$ iff $x_i=1$ and $x_j=2$). The hydrogen bond may be weakened by the presence of extra molecules in the same plaquette, namely, each extra molecule gives rise to an energy penalty $\eta c/2$, with $c \in [0,1]$. The Hamiltonian of the system can be written as a sum over plaquettes:

$$H = \sum_{i,j,k,l} h_{x_i,x_j,x_k,x_l}$$

where site indices $i,j,k,l$ are enumerated according to the plaquette orientation. The elementary contribution $h_{x_i,x_j,x_k,x_l}$ ("plaquette energy") can be written as

$$h_{x_i,x_j,x_k,x_z} = a_{x_i,x_j,x_k,x_z},$$

where

$$a_{x_i,x_j,x_k,x_z} = -\mu \frac{n_x}{4} - cn_x n_y - \eta b_{x,y} \left(1 - c \frac{n_x + n_w}{2}\right).$$

$n_x$ is an “occupation function” ($n_x = 0$ if $x=0$; $n_x = 1$ otherwise), $b_{x,y}$ is a “bond function” ($b_{x,y} = 1$ if $x=1$ and $y=2$; $b_{x,y} = 0$ otherwise), and $\mu$ is the chemical potential (we study the grand-canonical ensemble). Looking at eq. (2), one immediately realizes that the plaquette energy is invariant under circular permutations of the configuration variables. As a consequence, the full Hamiltonian (1) is unaffected by the choice of the “first site” $i$ in each plaquette.

For the sake of brevity, we have given only a formal description of the model. Indeed, the latter is the Husimi-lattice version of a water-like model similar to that proposed by Roberts and Debenedetti [14]. This can be easily deduced by comparing the original paper [14] with the tetrahedral cluster approximation developed in [18]. The square plaquettes of the Husimi lattice correspond to tetrahedral clusters on the bcc lattice, whereas plaquette orientations are related with the geometric structure of model molecules. Let us remark that, even though the current model neglects some details considered in [14] and [18] (namely, the distinction between donors and acceptors [14], and the presence of extra nonbonding configurations [14,18]), it nonetheless reproduces the typical thermodynamic anomalies observed in real water. Such a result confirms that the physical mechanism underlying the anomalies is mainly based on the “weakening parameter” $c$, which favors states characterized by a positive correlation between higher local entropy (weaker bonds) and higher local density [14,18]. A standard statistical-mechanical argument [9] relates such a positive correlation to a negative thermal expansion coefficient, i.e., to the onset of a density maximum.

The replica-symmetric (RS) solution. – According to the cavity method [25], in the RS assumption, the model can be solved by a recursion equation for so-called “cavity biases” or “messages”. An elementary message $m_{x_i}^{a \rightarrow i}$ represents the probability of the $x$ configuration at the $i$ site, when the latter is detached from all plaquettes except $a$. With reference to fig. 1, denoting by $\hat{m}_{x_i}$ the message from the central plaquette to the bottom site, the recursion equation reads

$$\hat{m}_{x_i} = c^{N-2} \sum_{x_1=0}^{2} \sum_{x_2=0}^{2} \sum_{x_3=0}^{2} e^{-\beta h_{x_1,x_2,x_3}} \prod_{i=1}^{3} m_{x_i}^{a \rightarrow i},$$

where $\beta = 1/k_B T$ is the inverse temperature and $f$ is a normalization constant, ensuring that $\sum_{x=0}^{2} m_{x_i} = 1$.

Let us note that, in our case, since the lattice has no local heterogeneities, the messages do not depend on the position (one can drop the $a \rightarrow i$ superscript). Therefore, eq. (4) eventually simplifies to a set of three equations.
where we have omitted the trivial normalization constant. These equations can be solved numerically by simple iteration. The actual probability \( p_x \) of the \( x \) configuration can then be evaluated by considering the operation of attaching four equivalent branches, like that depicted in fig. 1, to the same “root” site [24]. One obtains \( p_x \propto M_x^2 \), where we have again omitted a normalization constant, needed to ensure \( \sum_{x=0}^2 p_x = 1 \). The RS solution is always characterized by \( p_1 = p_2 \), i.e., no preference between the two molecule configurations. The mass density \( \rho \) is simply related to the occupation probability \( \rho_{occ} = 1 - p_0 = p_1 + p_2 \) as \( \rho = (M/v) \rho_{occ} \), where \( M \approx 18 \text{ g/mol} \) is the molecular mass of water and \( v \) is the volume per site (which is an adjustable parameter of the model).

The grand-canonical free energy per site \( F/N \) (let \( F \) and \( N \) denote, respectively the thermodynamic free-energy times \( \beta \), and the number of lattice sites) can be evaluated as a function of the messages [24]

\[
F = -\ln \frac{2}{N} \sum_{x_0=0}^2 \sum_{x_1=0}^2 \sum_{x_2=0}^2 \sum_{x_3=0}^2 e^{-\beta h_{x_0,x_1,x_2,x_3}} \prod_{i=0}^3 m_{x_i}^3 \prod_{x=0}^2 m_x^4
\]

Pressure can then be computed as \( P = -(k_B T/v)(F/N) \).

In fig. 2 we report the RS phase diagram in the temperature-density plane. We obtain a quite good agreement with experimental data for the whole liquid-vapor binodal curve (not fitted). The critical exponent is not correct, due to the mean-field nature of the model, but the critical density \( \rho_c \approx 0.3417 \text{ g/cm}^3 \) is remarkably close to the experimental value \( 0.322 \text{ g/cm}^3 \) [28]. The temperature of maximum density (TMD) locus correctly displays a negative slope, quantitatively similar to the experimental one. Moreover, in the metastable region of the liquid phase at very low densities (negative pressures), the TMD locus exhibits a slight reentrance (i.e., positive slope), which has been predicted by simulations with various intermolecular potentials [31,32]. At odd with such simulations, our TMD line eventually meets the spinodal line. In the pressure-temperature diagram, the two curves meet tangentially at a pressure minimum, as required for thermodynamic consistency [33], but the spinodal is not found to reenter the positive-pressure region. The latter fact contradicts Speedy’s early conjecture [34] about the divergent-like behavior of response functions in the supercooled liquid regime.

A fitting procedure has been performed to fix the model parameters. The hydrogen bond energy \( \eta \) and the volume per site \( v \) are easily computed as a function of the van der Waals energy \( \epsilon \) and the weakening parameter \( c \), by requiring the maximum density at 1 atm to be 1 g/cm\(^3\) and to occur exactly at 3.984°C [28]. We have then fitted only the two parameters \( \epsilon \) and \( c \) by minimizing (in a least-square sense) the difference between a set of experimental density values at 1 atm (fig. 2, inset) and the corresponding theoretical values. The final result is: \( \eta \approx 7.786 \text{ kJ/mol} \), \( \epsilon \approx 3.621 \text{ kJ/mol} \), \( c \approx 0.6450 \), \( v \approx 15.70 \text{ cm}^3/\text{mol} \).

\[1\] We have used the MATLAB routine lsqnonlin.

Fig. 2: Temperature-density phase diagram in the RS assumption. Thick solid lines denote binodals. Thin lines are defined by the following conventions: A solid line denotes the liquid spinodal, a dash-dotted line denotes the TMD locus, a dashed line denotes the stability limit of the RS solution, and a dotted line denotes the zero-entropy locus. Solid and open squares denote experimental results for the liquid-vapor binodal [29] and the TMD locus [30] (the latter data refer indeed to heavy water; pressure values have been converted to density values by [29]). The inset displays the isobar at \( P = 1 \text{ atm} \), along with the experimental values [28] used for parameter fitting.

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Conversely, our model seems to support Stanley’s conjecture, as it predicts, at very low temperature, a “second critical point”, terminating a coexistence region of two different liquid-like phases. Unfortunately, all this coexistence region lies below the stability limit of the RS solution (dashed line in fig. 2), where the latter is no longer valid. The inadequacy of such a solution in this regime is also pointed out by the fact that its entropy becomes negative below a given temperature (dotted line in fig. 2).

Figure 3 displays the isobaric specific heat and the isothermal compressibility as a function of temperature, at
atmospheric pressure. The well-known anomalous behavior of these response functions, related, respectively, to entropy and density fluctuations [9], is reproduced by the model in a qualitatively correct fashion. This result is achieved without the singularity required by Speedy’s conjecture. Indeed, upon decreasing temperature, the theoretical curves do not exhibit any divergence, but only pronounced maxima. Quantitative agreement with experimental results is not so good in this case, so that we report data for the theoretical (experimental) curves. A pronounced maximum occurs at 37.45 °C (36.2 °C) and 85.58 °C (46.5 °C).

The glassy phases. – Let us now investigate what happens when the RS ansatz does not hold. We make use of the cavity method at the level equivalent to 1-step replica symmetry breaking (RSB) [25]. For a given free-energy landscape, the complexity function \( \Sigma(F) \) is defined as the log-number of minima (“pure states”, or simply “states”) with free energy in the range \([F, F + dF]\). If the number of states is exponentially large, then \( \Sigma \) is an extensive quantity. One can define a pseudo free-energy (“replicated” free-energy) as [35]

\[
\Phi(\psi) = -\ln \sum_{\alpha} e^{-\psi F_{\alpha}},
\]

where \( F_{\alpha} \) is the free energy of the \( \alpha \) state, the sum runs over all states, and \( \psi \) is a pseudo inverse-temperature (Parisi parameter). A saddle-point calculation shows that \( \Phi(\psi) \) is the Legendre transform of \( \Sigma(F) \), so that \( \Phi(\psi) \) allows one to reconstruct \( \Sigma(F) \) via the parametric representation

\[
F(\psi) = \frac{d\Phi}{d\psi}(\psi), \quad \Sigma(\psi) = \psi \frac{d\Phi}{d\psi}(\psi) - \Phi(\psi).
\]

The replicated free-energy (and all the thermodynamic quantities) can be computed, as a function of \( \psi \), by solving an integral equation for the message distribution \( P(m) \) over the states

\[
P(m) = e^{\Phi} \int \delta(m - \hat{m}) e^{-\psi f \int_{i=1}^{3} \int_{a=1}^{3} P(m^{a \rightarrow i}) \, dm^{a \rightarrow i}},
\]

where both \( \hat{m} \) and \( f \) are defined by eq. (4) as functions of the set of incoming messages \( \{m^{a \rightarrow i}\} \), and \( \phi \) ensures the normalization condition \( \int P(m) \, dm = 1 \). Equation (9) can be solved numerically by a population dynamics technique [25].

In the RS phase, \( P(m) \) is a delta function and eq. (4) is recovered. The stability limit of the RS phase, displayed in fig. 2, can be determined by assuming that \( P(m) \) has only a slight variance around the RS value. One obtains a linearized “propagation equation” for the covariance matrix of \( P(m) \)

\[
\langle \delta m_{x} \delta m_{y} \rangle = \sum_{x'}^{2} \sum_{y'}^{2} K_{x,y;x',y'} \langle \delta m_{x'} \delta m_{y'} \rangle,
\]

where the \((9 \times 9)\) “transfer matrix” is

\[
K_{x,y;x',y'} = \sum_{i=1}^{3} \sum_{a=1}^{3} \frac{\partial \hat{m}_{x}}{\partial m_{x}^{a \rightarrow i}} \frac{\partial \hat{m}_{y}}{\partial m_{y}^{a \rightarrow i}},
\]

and the Jacobians \( \partial \hat{m}_{x}/\partial m_{x}^{a \rightarrow i} \) can be evaluated from eq. (4). The RS solution becomes unstable when the maximum eigenvalue of the transfer matrix (11) becomes larger than 1.

In the RSB phase, the thermodynamically relevant states are identified by a minimum (with respect to \( \psi \)) of the function \( F - \Sigma \), which properly takes into account that the probability measure may be split over a large number of states with free energy around \( F \). We report the typical behavior of \( F/N \) and \( (F - \Sigma)/N \) in fig. 4. The leftmost part of the curves \( (\psi < \psi_{c}) \) is unphysical, because \( dF/d\psi = d^{2}\Phi/d\psi^{2} < 0 \), which is inconsistent with eq. (7). The rightmost part \( (\psi > \psi_{0}) \) is also unphysical, because \( \Sigma < 0 \). Therefore, the physical minimum of \( F - \Sigma \) is attained at the crossing point \( \psi_{0} \), such that \( \Sigma(\psi_{0}) = 0 \). In the jargon of replica theory, this is called a “condensed” glass phase. The number of thermodynamically relevant states is sub-exponential, but there exists an exponentially large number of metastable states. Figure 5 shows that the former states exhibit the
The corresponding complexity is $\Sigma = 0$; $\psi$ values other than 0 result in a negative complexity.

A discrete model of water
The glassy behavior originates in the competition between the tendency of the model to form regular hydrogen-bond networks, driven by the energy term $-\eta b_{x,y}$ of eq. (3), and the topological disorder of the Husimi lattice, which induces frustration. In other words, the lattice randomness plays a relevant role in the model behavior, as it is responsible for suppressing the ice-like phases that appear in the corresponding regular lattice models. Even though the latter feature might be considered a weakness of the model, we believe that it roughly illustrates the physical mechanism underlying glassy behavior in a hydrogen-bonded (network-forming) fluid. In this framework, the onset of polyamorphism is related to the fact that, due to the weakening term $+\eta b_{x,y}(n_x+n_w)/2$, the original model predicts a low-density network structure (stable at low pressure), besides the “ordinary” crystal-like ground state. The glass-glass transition may thus be viewed as a “frustrated” reminiscence of the coexistence between these two phases.

In the future, it might be interesting to investigate whether a similar mechanism could give rise to glass-glass transitions even for lattice models predicting a dynamical transition scenario [1–5]. A more technical issue, still deserving investigation, is the stability of the current picture with respect to further RSB steps.

REFERENCES

[1] Franz S., Mézard M., Ricci-Tersenghi F., Weigt M. and Zecchina R., Europhys. Lett., 55 (2001) 465.
[2] Biroli G. and Mézard M., Phys. Rev. Lett., 88 (2002) 025501.
[3] Pica Ciamarra M., Tarzia M., de Candia A. and Coniglio A., Phys. Rev. E, 67 (2003) 057105.
[4] Weigt M. and Hartmann A. K., Europhys. Lett., 62 (2003) 533.
[5] Krzakala F., Tarzia M. and Zdeborová L., Phys. Rev. Lett., 101 (2008) 165702.
[6] Loerting T. and Giovambattista N., J. Phys.: Condens. Matter, 18 (2006) R919.
[7] Mishima O., Calvert L. D. and Whalley E., Nature, 314 (1985) 76.
[8] Poole P. H., Sciortino F., Essmann U. and Stanley H. E., Nature, 360 (1992) 324.
[9] Debenedetti P. G., J. Phys.: Condens. Matter, 15 (2003) R1669.
[10] Bell G. M., J. Phys. C, 5 (1972) 889.
[11] Lavis D. A. and Southern B. W., J. Stat. Phys., 35 (1984) 489.
[12] Sastry S., Sciortino F. and Stanley H. E., J. Chem. Phys., 98 (1993) 9863.
[13] Besseling N. A. M. and Lyklema J., J. Phys. Chem., 98 (1994) 11610.
[14] Roberts C. J. and Debenedetti P. G., J. Chem. Phys., 105 (1996) 658.
[15] Sastry S., Debenedetti P. G., Sciortino F. and Stanley H. E., Phys. Rev. E, 53 (1996) 6144.
[16] Franzese G. and Stanley H. E., J. Phys.: Condens. Matter, 14 (2002) 2201.
[17] Franzese G., Marquès M. I. and Stanley H. E., Phys. Rev. E, 67 (2003) 011103.
[18] Buzano C. and Pretti M., J. Chem. Phys., 121 (2004) 11856.
[19] Henriques V. B., Guisoni N., Barbosa M. A. A., Thieio M. and Barbosa M. C., Mol. Phys., 103 (2005) 3001.
[20] Hoye J. S. and Lomba E., Mol. Phys., 108 (2010) 51.
[21] Buzano C., De Stefani E. and Pretti M., J. Chem. Phys., 129 (2008) 024506.
[22] Pretti M., Buzano C. and De Stefani E., J. Chem. Phys., 131 (2009) 224508.
[23] Lavis D. A. and Bell G. M., Statistical Mechanics of Lattice Systems, Vol. 1 (Springer, Berlin) 1999, p. 173.
[24] Pretti M., J. Stat. Phys., 111 (2003) 993.
[25] Mézard M. and Parisi G., Eur. Phys. J. B, 20 (2001) 217.
[26] Mézard M. and Montanari A., J. Stat. Phys., 124 (2006) 1317.
[27] Cabane B. and Vullleumier R., C. R. Geosci., 337 (2005) 159.
[28] Chaplin M., http://www1.lsbu.ac.uk/water/.
[29] Linstrom P. J., Mallard W. G. (Editors), NIST Chemistry WebBook, NIST Standard Reference Database Number 69 (National Institute of Standards and Technology, Gaithersburg, Md.) http://webbook.nist.gov/, retrieved November 21, 2008.
[30] Angell C. A. and Kanno H., Science, 193 (1976) 1121.
[31] Netz P. A., Starr F. W., Stanley H. E. and Barbosa M. C., J. Chem. Phys., 115 (2001) 344.
[32] Yamada M., Mossa S., Stanley H. E. and Sciortino F., Phys. Rev. Lett., 88 (2002) 195701.
[33] Poole P. H., Sciortino F., Essmann U. and Stanley H. E., Phys. Rev. E, 48 (1993) 3799.
[34] SpeeRy R. J., J. Phys. Chem., 86 (1982) 982.
[35] Monasson R., Phys. Rev. Lett., 75 (1995) 2847.
[36] Angell C. A., Science, 319 (2008) 582.
[37] Yue Y. and Angell C. A., Nature, 427 (2004) 717; 435 (2005) E1.
[38] Kohl I., Bachmann L., Mayer E., Hallbrucker A. and Loerting T., Nature, 435 (2005) E1.
[39] Tulk C. A. et al., Science, 297 (2002) 1320.
[40] Mishima O., J. Chem. Phys., 100 (1994) 5910.