A geometric model for cold water and liquid-liquid transitions

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Abstract

Water is an associated liquid in which the main intermolecular interaction is the hydrogen bond (HB) which is limited to four per atom, independently of the number of neighbours. We have considered a hydrogen bond net superposed on Bernal’s geometric model for liquids, which allows for different local environments for the liquid particles. In this study, a mean-field treatment of the two-dimensional version of the model is discussed. Under pressure the model exhibits three phases of different densities and a coexistence line ending in a critical point between low and high density phases. Entropy of the HB network plays an essential role in defining the slope of the coexistence line. The model behaviour might be of interest in describing supercooled water and liquid-liquid transitions of other substances.

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I. INTRODUCTION

Liquid polymorphism has been proposed for different systems, both from experimental evidence, as well as from theoretical arguments [1–10]. The relevant systems must have open molecular coordination environments at low pressures, and may either be liquids associated through a hydrogen-bond net, water being the main example [2], or substances for which the different possibilities for hybridized electronic orbitals imply structures of different densities, as in the case of carbon [3–6].

The anomalous behaviour of water has intrigued physicists and chemists for a long time [11–14]. It is presently accepted that the special properties are related to hydrogen bonds. Because the energy involved in a hydrogen bond is an order of magnitude larger than the typical van der Waals energy [12,15], the fusion and boiling temperatures of water are much higher than those of homologous substances [14]. In fact, liquid water exhibits an extensive random network of hydrogen bonds which continuously reformulates, but presents local tetrahedral symmetry, responsible for the large volume at low temperatures [14,16].

In the last years, interest in supercooled water arose [2,17–19] as a means to explore the behaviour of isothermal compressibility and specific heat which, differently from most substances, rise as one lowers temperature towards the fusion point and beyond [12,20]. Search for an explanation of these two properties led to three different hypotheses: a retracing liquid-gas spinodal [20], a second critical point in the supercooled region [2,17,21], and a “singularity-free” scenario [22–24], in opposition to the first two. Sastry and collaborators [22] have shown that a singularity is not the only explanation for the compressibility or specific heat low temperature behaviour, but molecular dynamics simulations of ST2 water [25] indicate that a divergence of compressibility could occur around 2000 atm, 230 K. Among the several simplified models presented in the literature, some do [26,28], other do not present the second critical point, in some cases depending on model parameters used. From the experimental point of view, the question is very difficult to settle, because in the supercooled region one encounters a nucleation line (−38°C, at 1 atm) beyond which
the system spontaneously crystallizes \[2\].

The second critical point of water would be the end of a coexistence line between two metastable liquids with different densities (HDL and LDL for high and low density liquid) \[2\]. These two liquids would be related to two amorphous solids which exhibit coexistence and are found experimentally beyond the nucleation line \[29\]. The existence of the amorphous phases lends support to the idea of a liquid-liquid transition.

The idea of liquid polymorphism has been applied not only to water, but also to certain molecular liquids, such as I, Se and S, in order to explain an abrupt increase in conductivity, which would be related to a first order phase transition in the supercooled region \[1\]. Experimental evidence of a transition between two distinct thermodynamically stable liquid phases in carbon was found \[3\] some years after a suggestion of its existence appeared in the literature \[4\]. This transition has also been reported from molecular dynamics simulations \[3\] and a scaling formalism \[3\]. Experimental results also report a liquid-liquid transition in phosphorus in the stable phase \[7\].

A few decades ago Bernal proposed a model for liquids which consisted of a close-packed assembly of different regular or quasi-regular polyhedra \[30\]. The typical liquid configuration was expected to be statistically homogeneous and to possess no long-range order, due to the presence of different kinds of polyhedra. Molecules would be located only at the vertices and the edges would represent an average nearest neighbour intermolecular distance. The absence of holes, one of the model hypotheses, reduces the number of allowed polyhedra. Collins studied a mean-field solution for a version of Bernal’s model in two dimensions \[31\], in which case the polygons to be considered are squares and triangles. Collins demonstrated that the model could exhibit a phase transition, at fixed volume, for a specially designed set of interaction constants with no physical motivation. The author was looking for a melting transition, but recognized that the phase change was more analogous to a change of association number from one liquid to another. Interestingly, a recent study \[32\] of a dense system of repulsive Lennard-Jones particles showed that the spatial configurations can be interpreted in terms of random square-triangle tilings, as in Bernal’s proposal. A transition
between two densities was also found.

We have considered the spatial distribution of particles proposed by Collins and introduced interactions between the molecules which would mimic the HB network. Thus the distribution of energies is a result of the disposibilities of molecules to engage in HBs and favours low-density arrangements at low temperatures and pressures. Also, besides the translational entropy for simple liquids, an entropy term related to the distribution of HBs must be considered. The model does not allow for vacancies, so a gaseous phase is disregarded. A mean-field treatment of the system behaviour as a function of pressure and temperature is undertaken. We have also considered a variant of the model, which could describe non-associated liquids with preference for low density at low pressures (that would be the case of carbon). In the latter case, the HB entropy contribution is absent.

Polymorphism and a critical point are found for both models. However, the slope of the coexistence lines depends on competing entropy contributions. The model for water and the corresponding phase diagram is presented in section II. Liquid-liquid transitions and the phase diagram for non-associated liquids are discussed in section III. Discussion and summary are presented in section IV.

II. THE MODEL FOR WATER

A. The geometric description

In two dimensions, the Bernal liquid consists of a system of adjacent and randomly distributed squares and triangles of equal sides. The particles are localized at the vertices and there are three possibilities for the number of nearest neighbours \( r \), as showed in Fig. 1-a. A 4 and a 6-molecule can never be nearest neighbours by a geometric constraint. We call \( n_r \) the number fraction of molecules with coordination \( r \) (\( r \)-molecule) and \( v_r \) the corresponding specific volume,

\[
v_4 = b^2
\]
\[ v_5 = b^2 (2 + \sqrt{3})/4 \]  

\[ v_6 = b^2 \sqrt{3}/2 \]

for fixed intermolecular length \( b \).

Writing \( v = V/N \) for the volume per molecule, number and volume conservation are written as:

\[ \sum_{r=4,5,6} n_r = 1 \]  

\[ \sum_{r=4,5,6} n_r v_r = v. \]

Interactions must still be specified. In simple liquids, van der Waals interactions depend mainly on interatomic spacings. Hydrogen bonding depends on availability of neighbours to accept or donate hydrogens, thus in liquid water loss of translational order and increased density results in the frustration of some of the HBs for molecules with over four nearest neighbours \[14\]. In order to represent this property we introduce, alongside with the distribution of triangles and squares, a distribution of bonds. We have considered four as the maximum number of bonds per molecule \[13\], thus the HB between a 4 – 5 pair, for instance, may be absent, depending on the distribution of bonds among the neighbours of the 5-molecule (see Fig. 1-b). Note that the energy of the pair depends on the distribution of HBs amongst their neighbours. Because the hydrogen bond is an order of magnitude larger than van der Waals interaction \[12\], in this study we have considered only the HB interaction. The directionality of the hydrogen bond was also ignored.

**B. A mean-field approach for the HB network**

Our approximation for the distribution of HBs is the following: the four possible bonds of an \( r \)-molecule are distributed randomly over the \( r \) possible lines and the average energy of an \( r - s \) pair is calculated as resulting from the two independent distributions (for example: for
5-molecules there are five possible distributions of four bonds on five lines, so the probability of an HB for a 5−5 pair is \( \frac{16}{25} \). In this manner, if the HB energy is \(-\epsilon\), then the average \( r-s \) energy per bond is given by: \( \Phi_{rs} = -\frac{4^2}{r_s} \epsilon \) which makes \( \Phi_{44} \) (the energy of a pair of 4-coordinated particles) the minimum energy. Under this assumption, the energy of the model may be written as: \( E = \sum_{rs} N_{rs} \Phi_{rs} \) where \( N_{rs} \) is the number of \( rs \) pairs.

Standard mean-field conditions may then be implemented by assuming \( N_{rs} = rN_r p_s(r) + sN_s p_r(s) \), where \( N_r = n_r N \) is the total number of \( r \)-molecules and \( p_s(r) \) is the probability that an \( r \)-molecule has an \( s \)-molecule as neighbour. Notice that the geometric restriction must be taken into account, so assuming random distribution of molecules we have:

\[
p_s(r) = \frac{N_s}{N_{tot}(r)},
\]

where \( N_{tot}(r) \) is the maximum number of neighbours for an \( r \)-molecule (\( N_{tot}(4) = N_4 + N_5 \), \( N_{tot}(5) = N_4 + N_5 + N_6 \) and \( N_{tot}(6) = N_5 + N_6 \)).

The average energy per molecule is then:

\[
e(\{n_i\}) = \frac{1}{2} \sum_r r n_r \sum_s p_s(r) \Phi_{rs},
\]

where \( \frac{1}{2} \) stands for double counting.

C. Entropy and Gibbs free-energy

The partition function of the system in the Gibbs (constant pressure) ensemble is written as:

\[
Z(T, P) = \sum_{\{n_i\}} \Omega(\{n_i\}) e^{-\frac{[E+PV]}{kT}},
\]

where \( \sum' \) represents the summation over \( n_i \) constrained by particle number conservation (Eq. \( \square \)), and \( \Omega \) is the number of states with volume \( V(\{n_i\}) = N v(\{n_i\}) \) and energy \( E(\{n_i\}) = N e(\{n_i\}) \) (Eqs. \( \heartsuit \) and \( \diamondsuit \)). Two factors contribute to entropy, one related with the spatial distribution of particles, \( \Omega_{part}(\{n_i\}) = \frac{N!}{N_4!N_5!N_6!} \), and the other related with
the distribution of HBs, $\Omega_{HB}(\{n_i\})$. The degeneracy of HBs is taken into account in the simplest way, by considering independent molecules:

$$\Omega_{HB} = \prod_r D_r^{n_r}, \quad (7)$$

where $D_r = \frac{r!}{4!(r-4)!}$ is the number of possible arrangements of four HBs over the vertices of an $r$-molecule. Thus $Z$ (Eq. 6) is rewritten as:

$$Z(T, P) = \sum_{\{n_i\}} e^{-N\gamma(\{n_i\})/kT}, \quad (8)$$

where $N\gamma = E - TS + PV$ and $S = k \ln \Omega_{tot}$ ($\Omega_{tot} = \Omega_{part}\Omega_{HB}$). In the thermodynamic limit the Gibbs free energy per molecule is determined by the equation: $g(T, P) = \gamma(T, P; \{n_i\}_{\text{min}})$, where $\{n_i\}_{\text{min}}$ is the set that minimizes $\gamma$. In order to find it we minimized $\gamma$ with the constraint of Eq. 2, obtaining two transcendental equations, which are solved numerically. Henceforth the temperature and pressure will be written in reduced units $t$ and $p$ ($K_BT/\epsilon$ and $P\beta^2/\epsilon$, respectively).

**D. The phase-diagram**

We find the equilibrium values of $n_i$ as a function of temperature and pressure using a combination of numerical methods. A rough determination of the free energy minima in an extensive search was followed by the Newton method, for more precision.

The phase diagram of the model for liquid water on the pressure-temperature plane is shown in Fig. 2. At lower temperatures, the model presents two coexistence lines between three phases with different densities, with a triple point at an intermediate temperature. At higher temperatures, the coexistence between a high density (HD) and a low density (LD) phase ends at a critical point. The critical temperature is obtained both from the study of the free-energy surface as well from the evolution of the order parameter defined as $\lambda = \rho_{HD} - \rho_{LD}$ where $\rho_{HD,LD}$ are the corresponding densities.

The triple and critical points (in reduced units) are given respectively by: $t_{tp} = 0.0799$, $p_{tp} = 4.0780$, $t_c = 0.0965$ and $p_c = 3.9241$. Curiously, if one assumes 20kJ/mol [11] for the
HB energy ($\epsilon$), a critical temperature of $232K$ is obtained (against $230K$ obtained from MD simulations $[23]$). As for the critical pressure, dimensionality would enter the calculation, rendering it meaningless.

Fig. 3-a illustrates discontinuity of volume on the coexistence lines. The low density phase has more four-coordinated molecules at low temperatures, but on the coexistence line between LD and HD six-coordinated particles predominate in both phases, as can be seen in Fig. 3-b. The three phases differ basically in density.

The negative sign of the slope between the HD and LD phases in Fig. 2 indicates, in accordance with Le Chatelier’s principle, that entropy increases while volume decreases, on transition into the high temperature phase (HD), as can be seen in Figs. 3-a and 3-c. The higher density phase has higher entropy than the LD phase. Although it is true that the completely ordered 6-phase has higher entropy than the completely ordered 4-phase, because of entropy of bonds (see Eq. 4), at finite temperatures competition with translational entropy may invert the balance in some regions of the phase diagram, as can be seen in Fig. 2 at very small temperatures. But the overall picture is that the higher density phases also have higher entropy.

Compressibility and specific heat for the model can be obtained numerically. These quantities present maxima whose magnitude increase with decreasing temperature, as expected on approach of the critical point. The line of specific heat and compressibility maxima is shown in Fig. 4. The distance between the two lines grows as pressure is lowered. The specific heat maxima are localized at lower temperatures with respect to the compressibility ones, a feature also found for the model discussed by Sastry and collaborators, which presents no liquid-liquid transition $[22]$.

### III. LIQUID-LIQUID TRANSITIONS

In case one does not consider the HB net entropy (Eq. 4), a different phase diagram is obtained. As seen in Fig. 4, the intermediate density phase disappears and an inversion
occurs with respect to entropy: the higher entropy phase, in this case, is the low density one, as can be guessed from the slope of the coexistence curve. These features might be related to other liquid-liquid transition such as that of carbon.

The different structures of solid carbon, diamond and graphite, are a result of hybridization of the carbon atoms. The diamond structure, stable at higher pressures, is associated to \( sp^3 \) tetrahedral hybridization, while graphite is constituted of planes of \( sp^2 \) hybrids. Graphite is less dense, but of higher entropy. Experimental and theoretical results [3-4] point to the possibility of a liquid-liquid phase transition, between a high density liquid phase (dominated by \( sp^3 \) hybridized atoms) and a low density liquid phase (dominated by \( sp \) hybridized atoms in the case of MD simulations [5] and by \( sp^2 \) hybridized atoms in a scaling formalism model [6]). As in the solid state [34], the slope of the liquid-liquid coexistence line in the pressure versus temperature diagram is positive [5,6] and, according to Le Chatelier’s principle, the lower density phase must present the largest entropy. In the absence of the HB net entropy, the model we propose could be thought of as a mean-field treatment of Brenner’s potential, used to describe carbon, and for which bond energies depend on the local environment in such a way as to produce the correct geometries and energies of the known carbon structures [5,35]. Is is not clear whether it would be necessary to consider additional entropy terms, because of the mean-field treatment. As a curiosity, in our model, from \( t_c = 0.062 \) (Fig. 5), if we consider carbon bond energy of the order of 600 kJ/mol [36], we obtain \( T_c \simeq 5000K \) (against 9000K from MD simulations [7]).

The two cases studied lead to a simple description of potential candidates for liquid polymorphism. We discuss this in terms of an analysis of minimization of the Gibbs free-energy. At small temperatures, at which energy wins out against entropy, pressure may produce a transition between a high and a low density if the low energy phase is the less dense (\( \Delta G \simeq_{smallT} \Delta U - P|\Delta V| < 0 \) at some pressure, where \( \Delta X \) is defined as \( X_{HD} - X_{LD} \)).

Thus liquid-liquid transitions may arise if low lying energy states are low density states (as is the case of water or carbon) and for any model with energy monotonically increasing with density. Of course, in order for the system to present also a gaseous phase, mean field
or van der Waals energy should increase towards very low densities, and thus present an extremum, as pointed out by Tejero and Baus [10] and also implied in Poole and collaborators’ proposal [28]. However, we understand the van der Waals attractive potential would have to present a minimum (as can be inferred from [28]): as density increases from the gas region, the potential decreases, as in usual van der Waals theory, but a minimum is present at some intermediate density, above which the potential slightly increases, destabilizing a very dense liquid phase, as in this model. Once the condition for the liquid-liquid transition is fulfilled, two possibilities arise for the slope of the coexistence line, and these, according to Le Chatelier’s principle, will depend entirely on entropy: if the high density phase is the higher entropy phase, as in water, we encounter a negative slope, whereas if it is a smaller entropy phase, as in carbon, we encounter a positive slope.

IV. DISCUSSION AND SUMMARY

In liquid water there are two sources of disorder, not really independent: positional disorder of the molecules and disorder of hydrogen bonds. In the case of the latter, molecules may lose HBs either (i) because there are no nearby molecules free to engage in an HB (as in the case of a disfavourable increased local coordination - see Fig. 1-b) or (ii) because of rotations which remove the necessary alignment between neighbouring molecules. In some of the models proposed in the literature only the second feature has been considered [37,38], in terms of ice-like models, while in others [22,23,24] molecular rotations leading to weak bonds are described through Potts variables on cubic lattices, and smaller volume attributed to the disordered bonds in order to account for the first feature (increased non-alignment in dense environments). Interestingly, both kinds of model (except [24]) present only a liquid-gas transition and no low-temperature transition, in support of the “singularity-free” scenario. A low-temperature transition in the ice model would imply a discontinuity in the number of HBs at the transition, a requirement which would also have to be met in the Potts models (except [24]), for which volume is measured directly in terms of bonds.
In the case of the model discussed in this paper, only the first feature, the distortion of
the HB net, leading to rupture of HBs, not due to non-alignment, but to disposibility of
receptor or donor molecules, is taken into account. In this case, liquid-liquid transitions are
present, independently of model parameters, but for specified geometric constraints for local
structure.

In relation to the dispute on the existence of two supercooled waters, the answer could
depend on which of the two mechanisms above, restricted bonding due to varying local
coordination, or weak bonding due to thermally induced non-alignment, is most relevant.

Our study of the Bernal model for liquids on the pressure-temperature plane has shown
the possibility of liquid-liquid coexistence if energy favours low density configurations. Liquid
polymorphism both above and below the fusion line have been suggested in the literature
for associating, as well as for non-associating liquids. Our results point to the role of bond
network entropy. The latter becomes patent if one compares Figs. 2 and 5. The inclination
of the coexistence lines present opposite signs in the critical point region, for the two systems.

The compressibility and specific heat maxima beyond the critical temperature could
relate to the so-called anomalous properties of water. However, as for other models discussed
in the literature, it is senseless to discuss whether the polymorphisms belong to supercooled
or stable liquid phase, since it is unable to describe the solid phase. Also, the model does
not allow for “holes” and is therefore uncapable of describing the liquid-gas transition, but
this is not really a shortcoming, because interest lies really in the dense phases.

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FIG. 1. (a) Three possibilities for the local molecular environment: 4, 5 and 6-molecules (black dots).

(b) The existence of an HB between a 4 and a 5 molecule depends on the distribution of the four molecular bonds (full line) over the respective “neighbouring” lines (dashed lines). In the left figure no HB occurs between the two central molecules because the 5-molecule has engaged its four bonds with the other 4 neighbours.
FIG. 2. Coexistence lines and pressure-temperature phase diagram in reduced variables. Three phases of low, intermediate and high density are identified (LD, ID and HD). The LD phase has $n_4 > n_6 > n_5$ for low temperatures, $n_6 > n_4 > n_5$ for $t > 0.06$ and $n_6 > n_5 > n_4$ above $t = 0.09$. ID and HD have, respectively $n_6 > n_4 > n_5$ and $n_6 > n_5 > n_4$, independently of temperature. The triple and the critical points are indicated. The inset shows the region of interest for supercooled water.
FIG. 3. (a) Volume versus temperature on the coexistence lines. Coexistence regions are indicated by gray lines. LD, ID and HD as in Fig. 2. (b) $n_4$ (full lines), $n_5$ (dashed lines) and $n_6$ (long dashed lines) versus temperature for the LD (circles) and HD (squares) phases on the coexistence line above the triple point. For the region of temperatures shown six-coordinated particles predominate in both phases. (c) Entropy of the HD (squares) and LD (circles) phases versus temperature on the coexistence line.
FIG. 4. Lines of specific heat (squares) and compressibility (circles) maxima and coexistence line (triangles) near the critical point.
FIG. 5. Coexistence line on the pressure-temperature phase diagram in the absence of HB net entropy. The high density phase (HD) has $n_6 > n_4$ and the low density phase (LD) presents $n_4 > n_6$ for low temperatures and $n_6 > n_4$ for $t > 0.06$. The critical point is given by $t_c = 0.0619$ and $p_c = 5.2843$. The inset shows reentrant behaviour at very low temperatures.