

## Liquid polymorphism and density anomaly in a lattice gas model

Vera B. Henriques\*

*Instituto de Física, Universidade de São Paulo, Caixa Postal 66318, 05315970 São Paulo, SP, Brazil*

Marcia C. Barbosa†

*Instituto de Física, Universidade Federal do Rio Grande do Sul, Caixa Postal 15051, 91501-970 Porto Alegre, RS, Brazil*

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We present a simple model for an associating liquid in which polymorphism and density anomaly are connected. Our model combines a two dimensional lattice gas with particles interacting through a soft core potential and orientational degrees of freedom represented through thermal “ice variables.” The competition between the directional attractive forces and the soft core potential leads to a phase diagram in which two liquid phases and a density anomaly are present. The coexistence line between the low density liquid and the high density liquid has a positive slope contradicting the surmise that the presence of a density anomaly implies that the high density liquid is more entropic than the low density liquid.

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Water is one of the most mysterious materials in nature. It exhibits a number of thermodynamic and dynamic anomalous properties [1–3], such as the maximum as a function of temperature both in density and in isothermal compressibility in the liquid phase. It has been proposed some time ago that these anomalies might be associated with a critical point at the terminus of a liquid-liquid line in the unstable supercooled liquid region [4] at high pressures, following the suggestion, based on varied experimental data [5], of a thermodynamic singularity in supercooled water around 228 K and at atmospheric pressure. In spite of the limit of 235 K below which water cannot be found in the liquid phase without crystallization, two amorphous phases were observed at much lower temperatures [6]. There is evidence, although yet under test, that these two amorphous phases are related to fluid water [7,8].

Notwithstanding its confirmation for metastable water, interest in liquid polymorphism arose, and the coexistence of two liquid phases was uncovered as a possibility for a few others, both associating and nonassociating liquids. Notable examples include liquid metals [9], silica [10], phosphorus [11,12], and graphite [13]. The relation between liquid polymorphism and density anomaly has been a subject of debate in recent theoretical literature [14].

From a microscopic point of view, water anomalies have been interpreted qualitatively since [15], in terms of the presence of an extensive hydrogen bond network which persists in the fluid phase [16]. In the case of lattice models, the main strategy has been to associate the hydrogen bond disorder with bond [17,18] or site [19,20] Potts states. In the former case coexistence between two liquid phases may follow from the presence of an order-disorder transition and a density anomaly is introduced *ad hoc* by the addition to the free energy of a volume term proportional to a Potts order param-

eter. In the second case, it may arise from the competition between occupational and Potts variables introduced through a dependency of bond strength on local density states.

We propose a description also based on occupational and orientational degrees of freedom. Inclusion of the orientational part aims at representing the directionality of the hydrogen bonding that favors open structures. For that purpose, we employ a modification of the thermal version [21,22] of the ice model [23], so successful in the description of ice entropy. Competition between the filling up of the lattice and the formation of an open four-bonded orientational structure is naturally introduced in terms of the ice bonding variables and no *ad hoc* introduction of density or bond strength variations is needed. Our approach is similar to that of some continuous models [24–26], but the reduction of phase space imposed by the lattice allows construction of the full phase diagram from simulations, not always possible for continuous models [24].

We thus consider a lattice gas on a triangular lattice with sites which may be full or empty. Besides the occupational variables  $\sigma_i$  associated to each particle  $i$ , there are six other variables  $\tau_i^{ij}$  pointing to neighboring sites  $j$ : four are the usual ice bonding arms, two donor, with  $\tau_i^{ij}=1$ , and two acceptor, with  $\tau_i^{ij}=-1$ , while two additional opposite arms are taken as inert (nonbonding),  $\tau_i^{ij}=0$ , as illustrated in Fig. 1. Therefore each occupied site is allowed to be in one of 18 possible states. Two kinds of interactions are considered: isotropic “van der Waals” and orientational hydrogen bonding. An energy  $-v$  is attributed to each pair of occupied neighboring sites that form a hydrogen bond, while nonbonding pairs have an energy  $-v+2u$  (for  $u > 0$ ), which makes  $-2u$  the energy of a hydrogen bond. The overall model energy is given by

$$E = \sum_{(i,j)} \{(-v + 2u)\sigma_i\sigma_j + u\sigma_i\sigma_j\tau_i^{ij}\tau_j^{ji}(1 - \tau_i^{ij}\tau_j^{ji})\}, \quad (1)$$

where  $\sigma_i = 0, 1$  are occupation variables and  $\tau_i^{ij} = 0, \pm 1$  represent the arm states described above. Note that each particle may have six neighbors, but the number of bonds per mol-

\*Electronic address: vhenriques@if.usp.br

†Electronic address: barbosa@if.ufrgs.br; URL: <http://www.if.ufrgs.br/~barbosa>

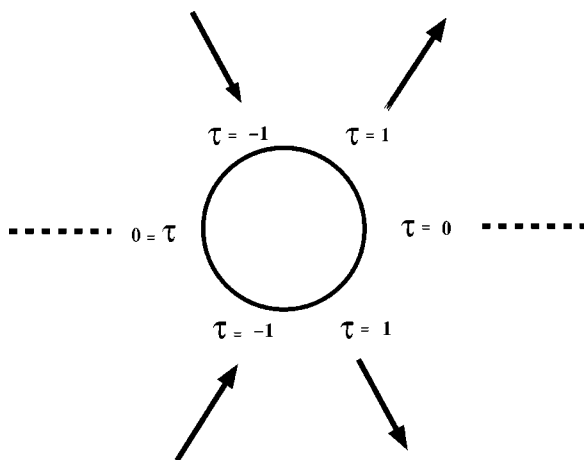


FIG. 1. The model orientational state: four bonding (donor and receptor) and two nonbonding arms.

ecule is limited to 4. For  $u/v > 1/2$ , the van der Waals forces become repulsive. As a result, each molecule attracts four neighbors, if properly oriented, and repels the other two. An interpretation for this “repulsion” would be that the presence of the two extra neighbors distorts the electronic orbitals, thus weakening the hydrogen bonds.

Inspection of the model properties allows the prediction of two ordered states, as shown in Fig. 2. For low chemical potential, the soft core repulsion becomes dominant,  $\rho = 0.75$ , and energy “volume” density is given by  $e = E/V = -3v/2$ , where  $V$  is the number of lattice sites. If the chemical potential is high,  $\rho = 1$ , and energy density  $e = -3v + 2u$ . At zero temperature, the low density liquid (LDL) coexists with the high density liquid (HDL) at chemical potential  $\mu/v = -6 + 8u/v$ , obtained by equating the grand potential density (or pressure) associated with each one of these phases. Similarly the coexistence pressure at zero temperature is given by  $p/v = -3 + 6u/v$ . Besides these two liquid states, a gas phase is also found and it coexists with the low density liquid at chemical potential  $\mu/v = -2$  and pressure  $p = 0$ . The condition for the presence of the two liquid phases is therefore  $u/v > 0.5$ .

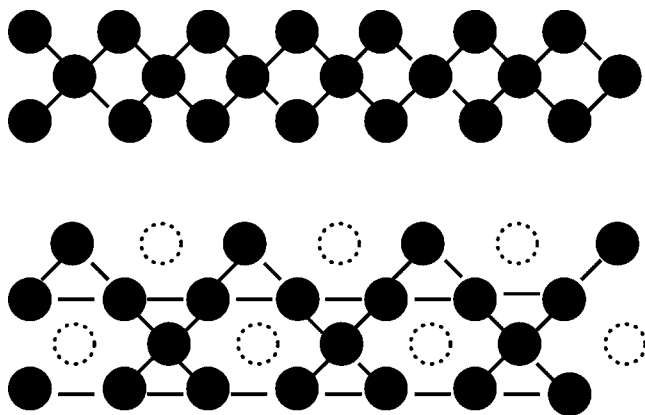


FIG. 2. High density liquid, HDL, with density 1 (top) and low density liquid, LDL, with density 3/4 (bottom) on the triangular lattice.

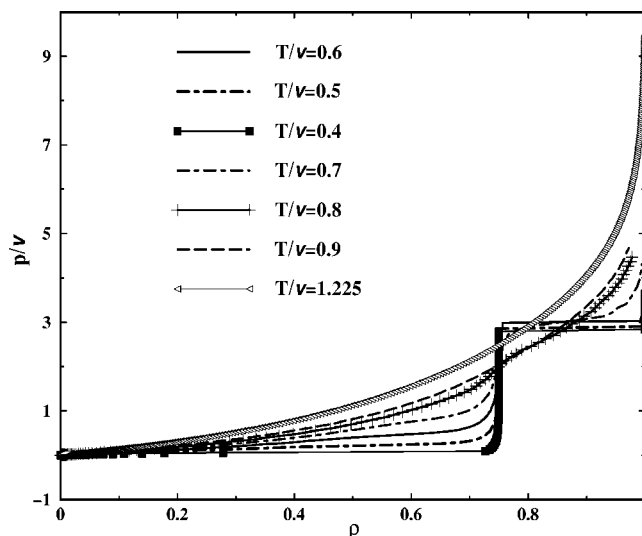


FIG. 3. Pressure vs density isotherms for different temperatures.  $p/v$  and  $\rho$  are given in units of lattice space and the temperature is in units of  $k_B$ .

Our model may be interpreted in terms of some sort of average soft core potential for large hydrogen bond energies. The LD phase implies average interparticle distance  $d_{LD} = \rho_{LD}^{-1/2} = 2/\sqrt{3}$ , whereas for the HD phase we have  $d_{HD} = \rho_{HD}^{-1/2} = 1$ . The corresponding energies per pair of particles is  $-v$  and  $-v + 2u/3$ . The hard core is offered by the lattice. For  $u/v > 3/2$ , the shoulder becomes repulsive, making the potential soft core.

The model properties for finite temperatures were obtained through Monte Carlo simulations in the grand-canonical ensemble using the Metropolis algorithm. Particle insertion and exclusion were tested with transition probabilities given by  $w(\text{insertion}) = \exp(-\Delta\phi)$  and  $w(\text{exclusion}) = 1$  if  $\Delta\phi > 0$  or  $w(\text{insertion}) = 1$  and  $w(\text{exclusion}) = \exp(+\Delta\phi)$  if  $\Delta\phi < 0$  with  $\Delta\phi \equiv \exp\{\beta(e_{\text{particle}} - \mu) - \ln(18)\}$  where  $e_{\text{particle}}$  is the energy of the particle included. Since the empty and full sites are visited randomly, the factor 18 is required in order to guarantee detailed balance.

Simulational data were generated both from fixed temperature and fixed chemical potential simulations. Some test runs were done for  $L = 4, 10, \text{ and } 20$ . A detailed study of the model properties and the full phase diagrams was undertaken for an  $L = 10$  lattice. The relevant parameter range is  $u/v > 1/2$ . For lower values of  $v$ , the LDL disappears. In the present work we consider the case in which bonding and nonbonding interactions are symmetric in strength, thus  $u/v = 1$  [27]. Runs were of the order of  $10^6$  Monte Carlo steps.

The three phases obtained at zero temperature are present for low temperatures, as can be seen in the isotherms of Fig. 3. The model exhibits two first order phase transition lines, gas-LDL and LDL-HDL, respectively.

In order to obtain the complete phase diagram, including the two critical points, and to check for density anomalies, pressure was computed by numerical integration of the Gibbs Duhem equation,  $SdT - VdP + Nd\mu = 0$ , at fixed temperature. Integration was carried out from effective zero den-

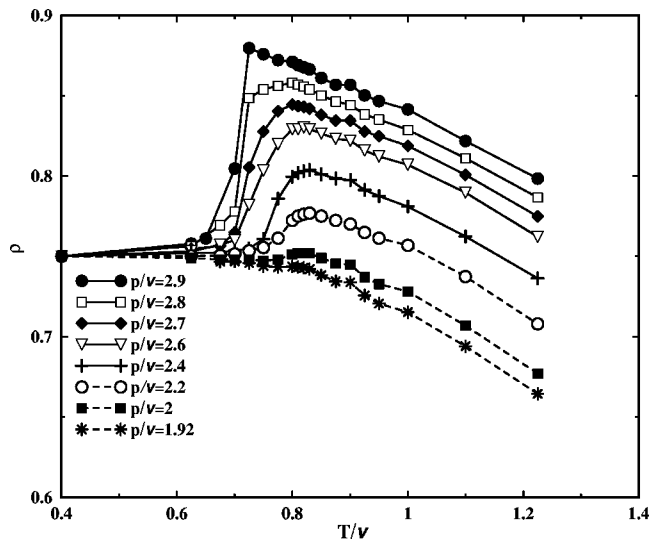


FIG. 4. Density anomaly for different pressures. The units are the same as in Fig. 3.

sity, at which pressure is zero, to obtain  $P(\rho, T)$  isotherms.

The pressure isotherms show that an inversion of the behavior of density as a function of temperature takes place at intermediate pressures, in the LDL phase. At smaller pressures,  $p/v \sim 1$ , density decreases with temperature, whereas at higher pressures,  $p/v \sim 3$ , density increases with temperature. This yields a density anomaly in the higher range of pressures, which we illustrate in Fig. 4.

Finally, from a large set of temperatures, we build up the pressure versus temperature coexistence curves shown in Fig. 5. It shows the gas-LDL and LDL-HDL coexistence lines ending at two critical points  $C$  and  $C'$ , respectively. The presence of the second critical point indicates that the HDL is actually a liquid phase (criticality is not possible between liquid and solid phases). The line of temperature of maximum densities, TMD, is also shown.

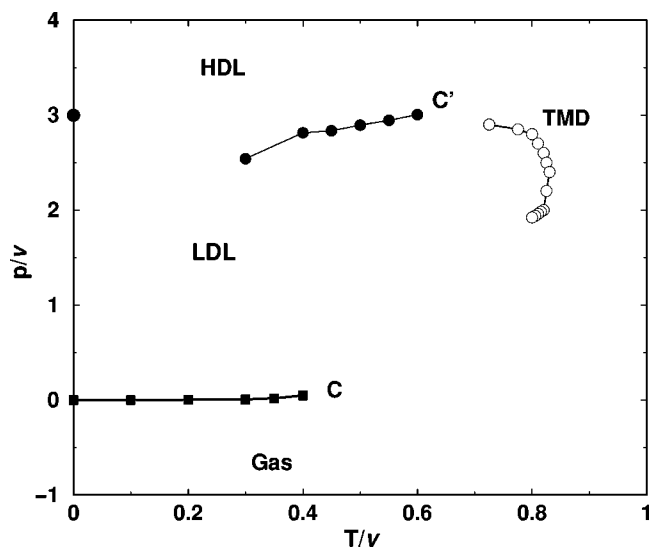


FIG. 5. Phase diagram showing pressure vs temperature. The open circles represent the TMD, the filled circles (squares) are the LDL-HDL (gas-LDL) coexistence lines. The coexistence at zero temperature at  $p/v=3$  is exact.

The liquid-liquid coexistence line has a positive inclination, except at very low temperatures, where the result at  $T=0.3$  appears to be below the exact result at  $T=0$ , obtained by equating the enthalpy densities. From the Clapeyron condition,  $(dp/dT)|_{coex} = \Delta s / \Delta v$ , the positive slope implies that within our model and close to the critical point the HDL phase has lower entropy than the LDL phase. The nonmonotonic behavior of the entropic gap between the two phases as the temperature is varied can be discussed in the following terms. There are two “sources” of entropy: particle position and bond distribution. The effect of increasing the temperature starting from  $T=0$  is initially similar for both phases: particles are removed from the HDL phase and added to the LDL phase. However, loss of particles occurs at a higher rate than the addition of particles, while HDL density decreases at a higher rate in the LDL phase than in the HDL phase. The entropy gain for the HDL is bigger than the one for the LDL (the slope of the coexistence line at this low temperature is negative), implying a predominance of the positional entropy contribution. Beyond a threshold temperature the LDL density increase steepens, the hydrogen bonds break at similar rates in both phases and the entropic gain of this phase exceeds that of the HDL. The slope of the coexistence line becomes positive. One may conclude that translational and not orientational entropy commands the sign of the entropy gap.

Inside each phase, the density anomaly can be related to the behavior of entropy as a function of pressure. From thermodynamics, a negative thermal expansion coefficient  $\alpha \equiv (\partial v / \partial T)_p$  implies a positive gradient of entropy with pressure, since  $(\partial v / \partial T)_p = -(\partial s / \partial p)_T$ . This property has been thought [14] to imply that the presence of a density anomaly would lead to a high entropy high density phase, and therefore to a negative slope of the coexistence line, as is true for the ice fusion line. The present model proves that this assumption is misfounded and that this is not a general behavior.

What we have here is the following: on the low density side, the thermal expansion coefficient is negative, whereas on the high density phase it is positive, as can be gathered from the pressure-density isotherms. The positive slope of the coexistence line implies, by Clausius-Clapeyron, that the high density phase is the lower entropy phase. Thus at constant temperature, entropy increases with pressure up to the coexistence line, drops discontinuously across this line, and then decreases with pressure, as in any normal liquid. Therefore the sign of entropy variation across the coexistence line may be either positive, as in this model, or negative, as in the fusion of ice, following, in both cases, the high pressure  $\alpha$  sign.

The model proposed is a truly statistical model which includes orientational and occupational variables, and guarantees the local distribution of hydrogens on molecular bonds, without the need of increasing the volume artificially or introducing artificial orientational variables [29]. In spite of the absence of an orientational order-disorder transition [22], the model presents liquid-liquid coexistence, with positive inclination in the pressure-temperature plane, accompanied by a line of maximum density, on the low density side, a feature expected for water. Besides, this study points to the

fact that the presence of a density anomaly, with  $\alpha < 0$ , on the low temperature side, and as a consequence,  $(\partial S/\partial p)_T > 0$ , does not imply a negative slope of the liquid-liquid line, contrasting with the results for most studies of metastable liquid-liquid coexistence in models for water, which suggest a transition line with negative gradient [28].

The presence of both a density anomaly and two liquid phases in our model begs the question of which features of this potential are responsible for such behavior. Averaged over orientational degrees of freedom, our model can be seen as some kind of shoulder potential, with the liquid-liquid coexistence line being present only for a repulsive van der Waals potential. The same was indeed observed for continuous step pair potentials [14,30], for which, however, the density anomaly is absent. On the other hand, a density anomaly seems to be associated with smooth soft core potentials [31,32], which would be hidden, in our model, in the orientational degrees of freedom.

We have shown that it is possible to incorporate some of the microscopic properties of true water molecules into a very simple minimal model. The model presents some of the expected anomalies (for density, specific heat, and compressibility), but of course studies of its hydration properties and solubility are still needed.

We also address the presence of liquid polymorphism and its relation to the presence of density anomaly. Our model presents both of them and proves the possibility of the presence of both for a high pressure less entropic phase, differently from what was common belief in the literature.

In summary, we have found that a lattice gas with orientational icelike degrees of freedom can generate a density anomaly and a liquid-liquid phase boundary with positive slope.

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