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RESEARCH ARTICLE

A simple one-dimensional lattice model with water-like phase behaviour

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We analyse the phase behaviour of a simple one-dimensional lattice model with two repulsive ranges (a hard core repulsion that covers two sites and a next-to-nearest neighbour repulsive interaction), a long-ranged staggered mean field, and an additional mean field attraction. The model is investigated in terms of its analytic solution. By a suitable choice of the next-to-nearest neighbour repulsive interaction and the mean field attraction, the model displays a phase behaviour closely connected with that of water: a solid phase less dense than its fluid counterpart, a solid that melts upon isothermal compression, and no stable liquid-liquid equilibrium.

1.   Introduction

In recent papers[1, 2], the authors analysed the phase behaviour of a simple one dimensional lattice model with a two-scale repulsive (2SR) interaction and a mean field attraction. The model in question has a nearest-neighbour (NN) hard core exclusion (or an infinitely strong NN antiferromagnetic coupling) and a next-to-nearest neighbour (NNN) antiferromagnetic interaction, whose coupling constant is $K > 0$, together with a long-ranged staggered mean field and a mean field attraction. In a lattice gas the NNN antiferromagnetic interaction term is a NNN repulsion, and in a continuum model it would correspond to a shoulder or the short-range repulsion of a ramp potential[3, 4]. This very simple model was shown to exhibit a liquid-solid transition at moderate densities in which the solid phase melts when pressure is increased along an isotherm. When an attractive mean field term is included, the model also presents a liquid-vapour equilibrium, and in Ref. [2] it was shown that its phase behaviour resembles that of phosphorus[5, 6], in which the molecular liquid P phase transforms upon compression into a base-centred orthorhombic solid, which melts back upon further compression (see Figure 1). As shown in our previous works, this 2SR lattice model is one of the simplest physical models that reproduces the singular phase behaviour found in systems such as P[5, 7], silica[8], or germanium oxide[9]. These substances exhibit temperature-pressure coexistence curves with negative slope, and all have solid phases with relatively low coordination numbers (3-5, that are lower than those of the corresponding liquid phases). However, when one compares the phase diagram of water [see [10] and references therein] with that of our simple model, one notices that the solid-liquid equilibrium line in water starts out with negative slope from the the triple point, so that there is no stable liquid region that solidifies under isothermal compression to melt again at higher pressures, in contrast with the behaviour depicted in Figure 1. The aim of this short paper is to analyse and tune the model Hamiltonian so
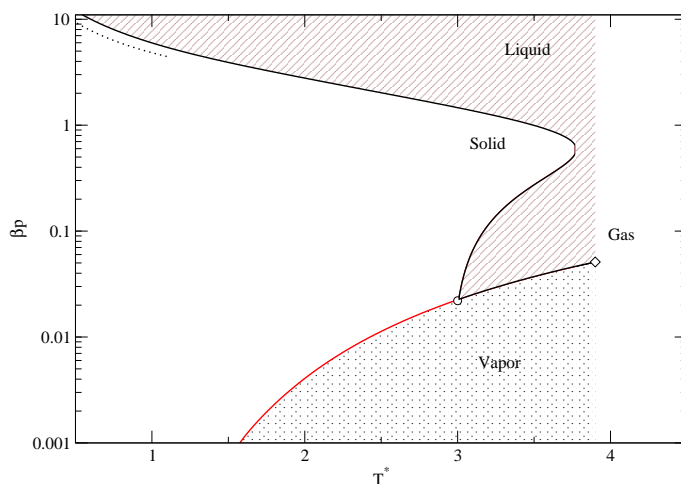
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Figure 1. $p-T^*$ phase diagram of the one-dimensional lattice model with the parameters of Ref. [2] ($\alpha = -8$ and $K^* = 2.5$). The metastable liquid-liquid transition is indicated with a dotted curve **(see Fig. 5 of Ref. [2])**. A circle denotes the triple point, and the vapour-liquid critical point is represented by a diamond.

as to provide a set of parameters that leads to a phase behaviour more alike that of water. To that purpose, in the next section we recall the key features of the lattice model and the equations that describe its phase behaviour. In Sec. 3, in the light of the findings of Ref. [2] and the analysis of how the phase diagram depends upon the model parameters, we find a new set of parameters and discuss the phase behaviour for this new set **in relation with the well known experimental behaviour of various real systems.**

Our results below show that the phase diagram of the one dimensional model and the ones of substances like water, Si, and P share some characteristics. The main reason for this is that the model and these substances have common qualitative features on the level of fundamental interactions. A common feature is the relative low density of the solid phase. This is because the energy minimum of the interaction is some distance away from the close packing configuration. Thus in the model the particles have hard cores that cover two lattice sites while the resulting staggered mean field attraction (with the uniform field included) is most attractive on the third neighbor (and each third neighbor further on). Thus the solid or ordered phase, mostly filling each third site, can not be at close packing. So further compression will return the system to the disordered liquid state. Now adding a repulsive shoulder next to the hard core will modify the return to the liquid state at high density. Hence we find that the interplay between the interactions included in the model determines the precise phase diagram including that of water. This is discussed in more detail in the last part of Sec. 3.

2.   The model. Equation of state

The Hamiltonian of our model can be written as

$$\mathcal{H} = J \sum_{i=1}^{N} s_i s_{i+1} + K \sum_{i=1}^{N} s_i s_{i+2} + \sum_{i<j}^{N} \varphi(i-j) s_i s_j - H_0 \sum_i^{N} s_i. \qquad (1)$$

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As in Refs.[2, 11] and [1], the $J > 0$ is the antiferromagnetic nearest neighbour (NN) coupling, and we let $J \to \infty$ with H_0 such that $H_0 + 2J$ remains finite. Thus we redefine H_0 to include the $2J$ term by which it becomes finite in the expressions below. Further, N is the number of spins or lattice sites, $s_i = \pm 1$ are the spin variables, and H_0 is the external field. Additionally we have a long-ranged repulsive staggered interaction

$$\varphi(i - j) = \begin{cases} 3a\gamma \exp[-\gamma|i - j|], & \text{if} \quad i - j = 3n + 1, \ 3n + 2 \\ 0, & \text{if} \quad i - j = 3n \end{cases} \qquad (2)$$

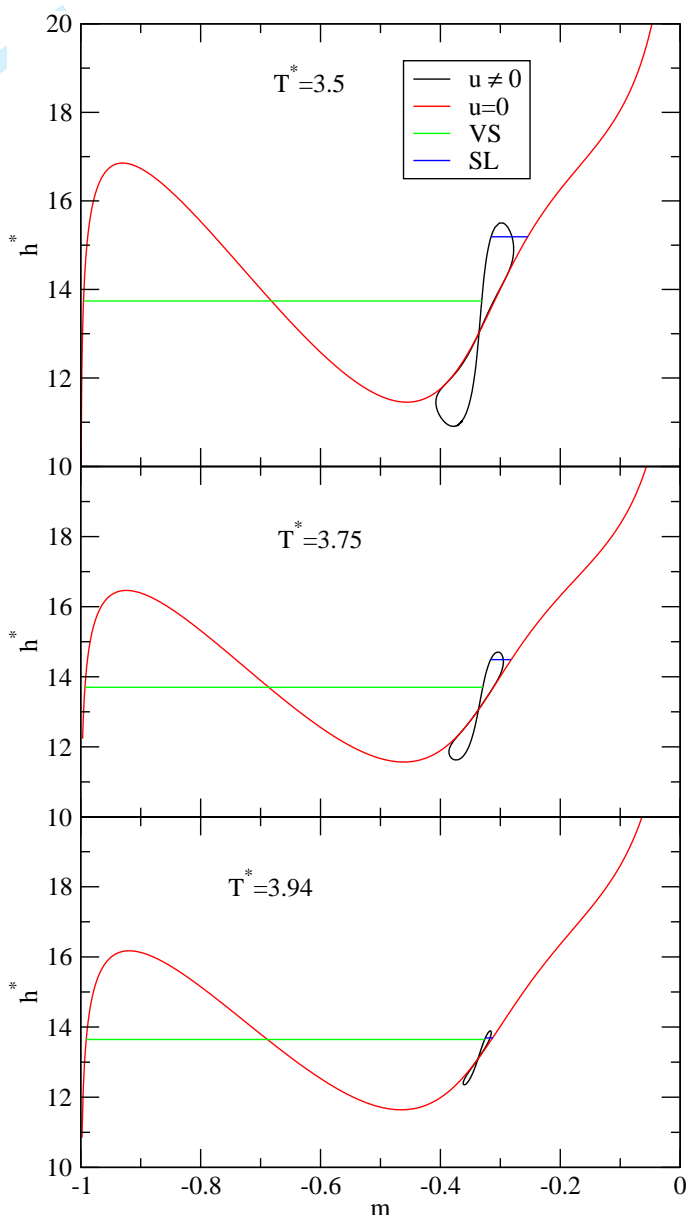where n is integer, the limit $\gamma \to 0$ is considered, and $a > 0$.

Figure 2.   (Colour online) $h^* - m$ isotherms of the one-dimensional lattice model with NNN interaction and staggered field ($\alpha = -15$ and $K^* = 2.75$) in the neighbourhood of the triple point temperature

An attractive mean field interaction similar to (2) but acting on all sites is

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introduced *ad hoc* in the free energy expressions below in order to give rise to the usual vapour-liquid transition. The strength of this mean field attraction is related to the strength of interaction (2) by means of a parameter α.

The analytical solution of the model was presented in full in Ref. [2], so here we recall only the key equations needed to describe its thermodynamics.

The lattice can be split into groups of cells made up of three sublattices consistent with the staggered interaction (2). One has a magnetization per particle m_i on sublattice i. It is then possible to define $m_1 = m + 2u$ and $m_2 = m_3 = m - u$, where m is the average magnetization and u represents the periodic ordering (staggered magnetization) of the sublattices.

The free energy G per spin [1, 2] is given by

$$-\beta G = \ln \lambda + \beta \alpha a m^2 - \beta a u^2. \tag{3}$$

where λ is the partition function per spin or lattice site with effective magnetic fields, a is the strength of the staggered mean field, and α tunes the mean field attractive term relative to the staggered one. The effective fields are $H_1 = H_e + H_{s_e}$, $H_2 = H_3 = H_e - \frac{1}{2}H_{s_e}$ with H_e and H_{s_e} given by Eqs. (7) and (8) below. The partition function is obtained from the eigenvalue equation of the transfer matrix (Eqs. (23)-(25) in Ref. [2]), namely

$$\Lambda^3 + a_2 \Lambda^2 + a_1 \Lambda + a_0 = 0 \tag{4}$$

where $\Lambda = \lambda^3$, and

$$a_2 = -[D^3 p^{-3} + D(2e^{-v} + e^{2v})p]$$
$$a_1 = -[D^2(e^{-2v} + 2e^v)(p^{-2} - p^2) + p^{-6}]$$
$$a_0 = D^3 p^{-3}(p^{-2} - p^2)^3, \tag{5}$$

with

$$D = CB^{2/3} = \exp(-\beta H_e)$$
$$e^{-v} = B^{4/3} \; ; \; v = \beta H_{s_e}. \tag{6}$$

The effective staggered and average fields are given by

$$H_{s_e} = 2au \tag{7}$$
$$H_e = H_0 - 2\alpha a m. \tag{8}$$

The α is the coupling term that can switch from uniform mean field attraction ($\alpha < 0$) to repulsion ($\alpha > 0$).

Once λ is obtained by solution of (4), the magnetization m and staggered magnetization u can be obtained by differentiation of the eigenvalue equation by the method used in Ref.[11]. Starting from

$$m = \frac{\partial \ln \lambda}{\partial \beta H_e}$$
$$u = \frac{\partial \ln \lambda}{\partial(\beta H_{s_e})} \tag{9}$$

one gets

$$m = -\frac{1}{3}\sum_{n=0}^{3} a'_n \Lambda^n / N \tag{10}$$

$$u = -\frac{1}{3}\sum_{n=1}^{3} a'_{s_n} \Lambda^n / N, \quad N = \sum_{n=1}^{3} n a_n \Lambda^n. \tag{11}$$

Here

$$a'_n = \frac{\partial a_n}{\partial(\beta H_e)}$$

$$a'_{s_n} = \frac{\partial a_n}{\partial(\beta H_{s_e})}, \tag{12}$$

whose explicit expressions can be found in Ref. [2]. We have thus all the ingredients to study the phase behaviour of our model.

3.   Phase behaviour

Explicit calculations are carried out in terms of reduced quantities. In the present instance, the corresponding reduced field and the NNN coupling constant will be $h^* = H_0/a$ and $K^* = K/a$. Phase equilibrium conditions determine that the field,
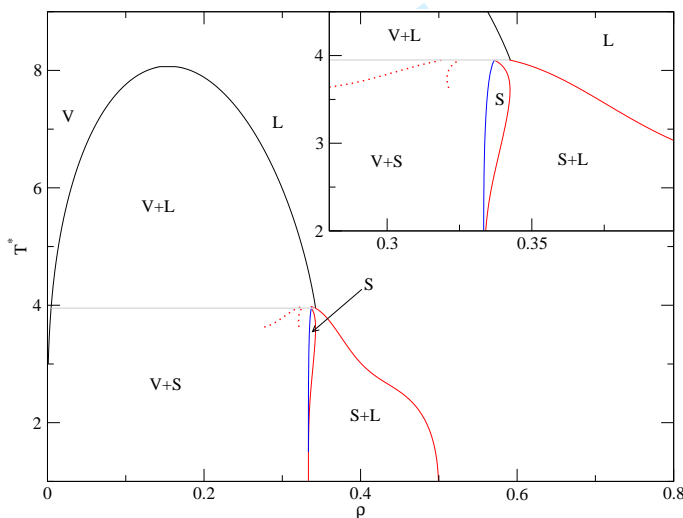

Figure 3.   Phase diagram of the one-dimensional lattice model with NNN interaction and staggered field calculated using a mean field coupling $\alpha = -15$ and $K^* = 2.75$. The liquid-solid metastable transition is shown with dotted curves. **When extended to temperatures above the triple point these latter curves smoothly join the solid-liquid equilibrium curves inside the metastable region, so as to form again the previous liquid-solid-liquid equilibrium curve studied in Refs.[1] and [2].**

h^*, and the spin free energy, βG, stay the same in both phases at equilibrium. Thus one has to solve,

$$\beta G(u = 0, m_d; T^*) = \beta G(u_o, m_o; T^*) \tag{13}$$

$$h^*(u = 0, m_d; T^*) = h^*(u_o, m_o; T^*) \tag{14}$$

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where the subscripts $_d$ and $_o$ denote the disordered and ordered phases respectively. Additionally, m_d and h^*, and m_o, u_o and h^* are connected via Eqs.(10) and (11). Details as to the explicit numerical solution of these equations can be found in Refs. [1] and [2].
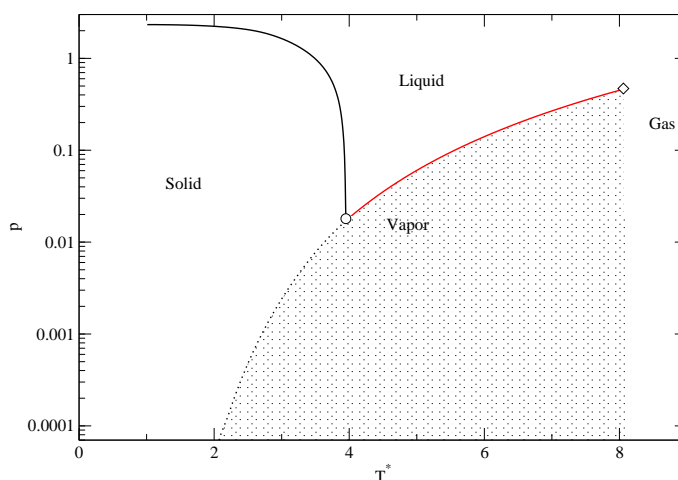

Figure 4. $p - T^*$ phase diagram of the one-dimensional lattice model with NNN interactions and staggered field calculated using a mean field coupling $\alpha = -15$ and $K^* = 2.75$. A circle denotes the triple point, and the vapour-liquid critical point is represented by a diamond.

Now let us focus on the phase diagram depicted in Fig. 1. In contrast to the well known phase diagram of water, we observe here that the solid-liquid equilibrium curve starts out from the triple point with positive slope, and then bends backwards at a point of maximum temperature. This feature, present in systems such as phosphorus, selenium and tellurium[7] is clearly absent from water[10] and other tetrahedrally coordinated substances, such as Si and Ge[7]. After a careful examination of Fig. 1 and the corresponding $\rho - T$ diagram (see Fig. 5 of Ref. [2]), it became evident to us that the weight of the attractive mean field term in the Hamiltonian must be increased, so as to raise the vapour-liquid critical temperature, which in realistic water models is well above the triple point temperature in contrast with the situation of Fig. 1. Increasing the mean field attraction will also widen the liquid-vapour coexistence curve, and thus by tuning the α parameter, the undesired liquid-solid equilibrium can be made metastable with respect to the gas-solid (or vapour-solid) transition and thus somehow be "'squeezed" into the vapour-liquid equilibrium. Additionally, increasing the repulsive parameter K^* shifts the liquid-solid-equilibrium to higher densities. Thus changes in α had to be accompanied by a fine tuning of the K^* parameter. After some trials, we found that the combination $\alpha = -15$ (which doubles the magnitude of the α parameter in Fig.1 and Ref. [2]) and $K^* = 2.75$ (just a minor change with respect to Fig. 1) reproduced the sought for features. In Figure 2 we present various isotherms calculated using these parameters for temperatures in the vicinity of the triple point. In the figure the fields corresponding to the various phase equilibria found for each temperature are shown with straight lines connecting coexisting magnetizations or densities, as determined from Maxwell's equal area rule. One immediately sees how the solid-liquid transition shrinks, but remains finite as the triple point is approached.

Now, one can construct the complete $\rho - T$ phase diagram for the new parameter set, which is displayed in Fig. 3. One observes now a vapour-liquid critical point well above the triple point. Below the triple point, the vapour freezes into a low

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density solid, that is in equilibrium with a higher density liquid. Right at the triple point, the liquid density is one percent higher that that of the solid. The liquid-solid equilibrium has turned metastable (plotted in dotted curves in the figure), as desired. When the phase diagram is plotted in terms of $p - T$ variables (see Fig. 4) and compared with Fig. 1 we observe that the maximum temperature for the liquid-solid transition has disappeared, and the liquid-solid equilibrium curve starts out at the triple point with a slightly negative slope, in a fashion similar to that of water.

We might ask ourselves what is the relevance of these simple model results for real systems. If we think in terms of tetrahedrally coordinated systems, such as water, Si or Ge, the complex nature of their atomic or molecular interactions can be reduced by means of a simple Boltzmann weighted angular average of their intermolecular potentials. In the case of water the angular dependence stems from the anisotropic nature of their molecular pair interactions, but in Si and in Ge it arises from the strong directional character of the covalent bonding, that can be expressed in terms of three and four body correlations. Such an average would immediately evidence the presence of a very short range hard core like repulsion due to Pauli's principle (from O atoms in the case of water), and an additional longer range repulsion arising from the angular average of the tetrahedral-like bonding that stabilizes the low density solid structures. These two repulsive ranges explain the presence of a high density solid phase and a low density one, separated by a liquid phase somewhat denser that the low-density solid. Thus, the negative slope of the $P - T$ solid-equilibrium curve in real systems has its origin in the presence of the two repulsive ranges, which is a key feature of our model. Now, obviously, our averaged interaction also includes an attractive term resulting from the presence of dispersion forces and hydrogen bonding (in water) or from the average attractive nature of covalent bonding (or the partial metallic character of bonding in liquid Ge and Si). This interplay between attractive forces and the medium range repulsion that stabilizes the open solid structures smoothly switches from the phase diagram of Figure 1 (phosphorus-like) to that of Figure 4 (water or Si-like). Let us focus on the difference between P and Si, since the nature of their bonding is similar (covalent and strongly directional). In the case of P, we are dealing with a molecular-like system composed of P_4 units (in the liquid) where the P-P distance is around $2.2 \pm 0.1\text{\AA}$. Upon compression it transforms into a laminar solid (rombohedral black P) where the threefold coordination and the bond distance are more or less preserved. Its melting temperature is **879K**[12]. When compared with Si, its diamond-like form is composed of tetrahedral units with a Si-Si distance of **2.43Å** and its melting temperature is **2693K**. Larger differences are found in their boiling temperatures. This is telling us two things, first, one should expect the second repulsive range in P to be somewhat shorter than that of Si. Secondly, the attractive forces in Si must be much larger than those in P. This is in fact in agreement with the details of our model, in Figure 1 (P-like) we have **K=2.5** vs **2.75** in Figure 4 (Si-like). In our model we do not modify the range of the second repulsive shoulder but we increase its intensity. Then, regarding dispersive (attractive forces), in our P-like model $\alpha = -8$ and in our Si-like model $\alpha = -15$, thus one should expect attractive forces to be substantially more intense in this case, by which the transition from

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low density liquid to solid upon compression becomes metastable with respect to the condensation of the vapour into a solid, as seen in Figure 4. In this way a P-like phase diagram transforms into a Si (or water)-like diagram. Our simple model thus stresses those elements that are key to shape the phase diagram of rather complex materials.

In summary, we have seen, how tuning the ratio between the mean field attraction and the NNN repulsion reshapes the phase behaviour of the simple model considered leading from a phosporous-like to that of a water-like phase diagram, **and we have provided qualitative arguments as to the correspondence to the behaviour found in real systems**. On the other hand, it is also well known that water is endowed with a large amount of solid phases (and multiple triple points are found). More complex models are obviously needed to possibly account for some of these additional features.

Acknowledgement(s)

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