Liquid-liquid phase transiton associated with polymerization in a maximal valency model.

Sergey Buldyrev[1] and Nikolay A. Shumovskyi[2]

[1] *Department of Physics, Yeshiva University, New York, NY 10033 USA*

[2] *Department of Physics, Boston University, Boston, MA 02215 USA*

Abstract

We study a model of spherically symmetric particles which attract to each other by a narrow square-well potential with a restriction that at maximum only two particles can populate a well of a given particle. One can assume that the particles inside the well form covalent bonds with each other and the maximum number of bonds a particle may have is two. Such a model polymerizes as temperature decreases by a continuous transformation during which the average chain lengths increases. However, if the particles in addition to covalent bonds may attract to each other by wider range wells the system acquires a liquid gas transition line ending in a gas-liquid critical point. Finally, if the attraction between bivalent particles is stronger than between other particles the system acquired a second liquid-liquid point between monomeric a polymeric liquids ending in second critical point as was recently observed sulfur.

1 Introduction

Liquid-liquid phase transition in a single-component system was proposed to exit in super-cooled water [2] based on molecular dynamic simulations of the ST2 water model. These studies were inspired on a pioneering experimental work of Speedy and Angell[1], who predicted a singularity in the compressibility of deeply supercooled water at -45C. Since than many efforts have been made to experimentally observe this critical point and associated with it polyamorphism and understand it theoretically[?]. However, to this day no definitive confirmation of a liquid-liquid critical point in water have been found. From the theoretical point of view, the liquid-liquid phase transition in water is associated with the tetrahedral network of liquid formed by hydrogen bonds which collapses under pressure into a disordered network of hydrogen bonds with a larger coordination number. Such transition exists also in spherically symmetric potential with a wide attractive well and a repulsive shoulder, in which the particles climb under pressure on a repulsive shoulder. This phenomenon can be understood via a two-state model, in which two species of particles with different local structures may interconvert into each other. Apart from water, a liquid-liquid phase transition was proposed to exist in many single component systems, but most notably in phosphorus and sulfur, where it is associated with polymerization during which a polymeric phase segregates from a monomeric phase. In this paper we propose a minimalistic maximal valence model, [5, 4] which reproduces this phenomenon.

2 Model

We study the system initially consisting of equal number of $N = 1000$ atoms, modeled by a dimer of hard spheres of diameter σ, surrounded by square wells or shoulders of different widths and depths by event driven molecular dynamics[6, 7], in which the velocities of particles after the collision are computed based on conservation of total energy and linear and angular momentum of the colliding particles. We simulate an NVT ensemble in a cubic box of various densities with periodic boundaries and various temperatures, using Berendsen thermostat. We assume that the first member of a dimer, A, represents a nucleus surrounded by inner electron shells, while the second member B represents valence electrons which can form covalent bonds. For simplicity we assume that both members A and B have equal mass m and equal hard core diameter σ and are bonded of short infinite square well bond of maximal length $d = 0.1\sigma$. Particles A interact with each other with an attractive square well of depth ϵ and width $w = 1.4\sigma$. In the absence of interactions between B and B and B and A, such a system has a liquid-gas critical point at $\rho = N/V = 0.350.05$ $T = 1.040.01$, and $P = 0.094005$[8]. We use dimensionless units normalized by appropriate combinations of m, σ and ϵ and Boltzmann constant k_B. This system has a liquid-gas critical point well above equilibrium crystallization line. We assume that particles B do not interact with particles A if they belong to different atoms. Particles B may form

bonds with each other and accordingly acquire different types B0 with zero bonds, B1 with one bond, and B2 with two bonds. All these particles when interact with each other have a hard core diameter σ, which for simplicity coincides with the hard core of particles A. If particles B0 and B0 collide with each other at distance $w_b = 1.02\sigma$ they form a bond with potential energy $\epsilon_b = \epsilon$, and their types become B1 and B1. If particles B0 and B1 collide at distance w_b they form the bond of the same energy ϵ_b and their types become B1 and B2 respectively. the bond between B2 and some other particle remain intact and its energy does to change. However, if the interaction energy between other particles changes due to change of the types of the colliding particles, this energy ΔU is taken into account in the collision equation which computes the new velocities after collision using and conservation of linear and angular momenta of the colliding pairs and energy conservation of the entire system. Finally, if particles B1 and B1 meet at distance w_b they form a bond of the same energy and change their types to B2 and B2 with their other bonds being intact. If particles B0, B1 and B2 interact with particles of type B2 with hard core repulsion at distance σ, such a model would continuously polymerize upon lowering temperature with fraction of B2 particles gradually increasing, and the length of the polymer chains also infinitely increasing. However, if we assume that particles B2 and B2 (not bonded directly with each other by a covalent bond) attract to each other stronger than with particles B_0 and B_1, namely they attract with square well potential of width $w_{22} = 1.3\sigma$ and energy $\epsilon_{22} = 0.5\epsilon$, while B_0 and B_1 do not interact with other particles B other than by hard core repulsion at distance σ, the polymerization transition becomes coupled with a phase segregation transition between polymeric and monomeric phases experimentally observed in sulfur at high pressure and high temperature and the system will acquire a line of liquid-liquid transition ending at a second critical point which is located at much higher pressure $P = 2.28$, and density $\rho = 0.81$ than the liquid-gas critical point but at a comparable temperature $T = 1.187$. Note, that in real sulfur the liquid-gas critical point is located at $T = 1314$ K, $P = 20.7$ MPa, $\rho = 563$kg/m^3 [?] while the liquid-liquid critical point is located at $T = 1035$K and $P = 2.5$GPa and density $\rho \approx 2000$kg/m^3. We note that the model has many free parameters: namely d, w, w_b, ϵ_b, w_{ij} and ϵ_{ij}, where $i,j = 0,1,2$ (measured in units of σ and ϵ) and thus the properties of the liquid-liquid phase transition can change dramatically or it may entirely disappear. However, the detailed study of these dependencies is beyond the scope of this letter, the goal of which is to show how a simple model may reproduce liquid-liquid phase transition caused by polymerization. We detailed a phase diagram only for $w = 1.4$ $w_b = 1.02$, $\epsilon_b = 1$,$w_{22} = 1.3$, $\epsilon_{22} = 0.5$ and $w_{00} = w_{01} = w_{02} = w_{11} = w_{12} = 1$, $\epsilon_{00} = \epsilon_{01} = \epsilon_{02} = \epsilon_{11} = \epsilon_{12} = 0$, while briefly studying the effect of ϵ_b and ϵ_{22}.

3   Results

Figure 1 shows isochores on a P-T plane for three set of Interaction parameters: (a) $\epsilon_{22} = 0.5$, $\epsilon_b = 1.0$, (b) $\epsilon_{22} = 0.4$, $\epsilon_b = 1.0$ and (c) $\epsilon_{22} = 0.5$, $\epsilon_b = 0.05$. The ischores are obtained by slow cooling during which the temperature of the system slowly reduces during 10^5 time units. All three variants have a liquid–liquid critical point indicated by ischores crossing at much higher pressures than liquid gas critical point which practically remains the same as for the square well model without bonds [8]. One can notice that reduction of the ϵ_{22}, reduces the liquid-liquid critical temperature approximately in proportion from $T = 1.187$ to $T = 0.94$. The critical pressure is also significantly reduced from $P = 2.28$ to $P = 0.35$. This tells us that the attraction between B_2 particles is crucial for the existence of the liquid-liquid phase transition, since further decrease is likely to move P_{C2} to negative pressures and eventually below the liquid gas spinodal where it disappears. In contrast, decreasing the bond strength does not have such a strong effect, the critical temperature and density just slightly increase and the critical pressure significantly increases. This shows that the strength of polymer chains is not crucial for the liquid-liquid phase transition: at high densities, long polymer chains would exist due to an entropic effect without any bond energy and even for a negative bond energy.

Figure 2(a) shows detailed isochores equilibrated for 10^6 time units for different temperatures from 1.0 to 1.2 with step 0.02. on a P-T plane for the variant (a) of the model which exhibits two critical points indicated by the largest temperature of crossing isotherms. In contrast with ST2 water, but in agreement with spherically symmetric models, the liquid-liquid coexistence line has positive slope. Figure 2(b) shows isotherms on a $P - \rho$ plane which exhibit two sets of van der Waals loops. Figure 3 shows the liquid-liquid binodal obtained from Fig. 2(b) by Maxwell construction. In addition, it shows the binodal on the $\Phi_2 - T$ plane, where Φ_2 is the mole fraction of particles B_2 among all particles B and the binodal on the $barn - T$ plane, where $\bar{n}$ is the average length of a polymer chain among the chains containing at least 1 particle B_2 i.e. the chains with length n larger than three. One can see a large phase-segregation region separating two liquid phases with dramatically different Φ_2 and $\bar{n}$, which proves that the liquid phase transition is related to polymerization. However, neither Φ_2 , nor $\bar{n}$ show any discontinuity as function of density and temperature, although $\bar{n}$ shows very fast increase with density at constant temperature for densities $\rho > 0.8$, which is the critical density for liquid-liquid phase transition (Fig.3. The life time of the covalent bonds for $T > 1$ is very small, so the polymer chains frequently break and hence the diffusion in both phases is very high (Fig.4

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This is in the marked difference with phase transition in models of water, where the diffusivity of low density liquid is by order of magnitudes smaller than the diffusivity of the high density phase and the liquid-liquid phase transition is submerged below equilibrium crystallization line. In contrast, in our model the diffusivity is very high and the model easily equilibrates without crystallization.

To illustrate structural differences between low and high density liquids We show the density correlation function and the structure factor for several points near binodal and spinodal (Fig.5) computed for particles of type A. The $g(r)$ shows a sharp peak corresponding to the covalent bond length 1.02, while the structure factor $S(q)$ shows the shift of the first peak to larger q, and modification of the second peak related to polymerization, similar to what is observed in experiments with sulfur. Also S(q) shows a dramatic increase for $q \to 0$ for the points within the binodal region indicating the divergence of isothermal compressibility. One of the snapshots corresponding to $\rho = 0.74$, $T = 1.00$ (Fig. 6) shows segregation of polymeric and non-polymeric phases. Red, Green and Blue spheres show B_0, B_1, and B_2 particles, respectively. A particles are not shown.

4   Conclusion

Our results show that the liquid-liquid phase transition in maximal valence model qualitatively reproduces the liquid-liquid phase transition in sulfur at high pressure and temperature. We show that although this transition is associated with polymerization, it is not related to the transitions occurring in polymers, such as theta point which occurs when the length of polymer chains diverges. In our model the length of polymer chains remains finite and the driven force of the transition is interconversion between the particles B_2 with two covalent bonds and B_1, and B_0 with fewer covalent bonds. Particles B_2 attract to each other stronger than particles B_0 and B_1, while the fact that they belong to the polymer chains is irrelevant. The same phenomenon occurs (Fig. 1) for very weak covalent bonds, if their formation increases the overall attraction between the particles. These bonds form at high density just due to the entropic reasons, but if they form, the bonded particles start to attract stronger to each other and the density increases further producing a region of infinite compressibility in which dense phase – formed predominantly by bonded particles – segregate from low density phase formed predominantly by free monomers or dimers. This mechanism is somewhat similar to the mechanism of liquid-liquid phase transition in the core-soften potentials in which the particles with neighbors sitting on top of repulsive shoulders attract stronger to each other since they can accommodate for more neighbors in the attractive well. As in these models, the interaction between particles l depends on their local environment, but in maximal valence model the strength and radius of this interaction is defined explicitly through the parameters ϵ_{ij}, w_{ij}. The local structure of a particle in maximal valence model is quantified simply by the number of particles within a covalent bond range. The experimental question is whether in sulfur at high pressures the particles with 2 covalent bonds interact stronger with each other than monomers and dimer. If the answer to this question is yes, our model provides a good explanation to the liquid-liquid phase transition in sulfur and other elements prone to catenation such as phosphorus as well as in biological polymeric solutions. In any case, our model could be useful in developing a two-state theory of liquid-liquid phase transitions based on interconversion of species[**?**].

References

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Acknowledgements

Author contributions
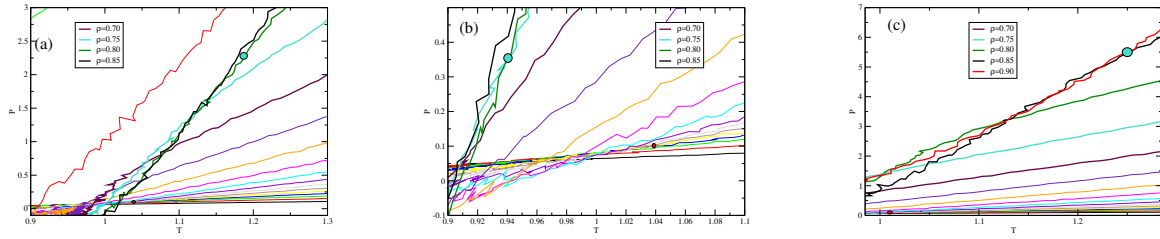
Additional Information

Figure Legends

Figure 1: $P - T$ phase diagrams for the set of parameters (a),(b), and (c) which are obtained by slow cooling for $t = 10^{-5}$ The critical points are shown by ellipses. The locations of the gas-liquid critical point is $(T = 1.023, P = 0.0922, \rho = 0.35)$ and liquid-liquid critical point is $T = 1.187, P = 2.28, \rho = 0.81)$ in panel (a) and $(T = 1.04, P = 0.1, \rho = 0.35)$ (gas-liquid); $(T = 0.94, P = 0.35, \rho = 0.78)$ (liquid-liquid) in panel (b) and $(T = 1.01, P = 0.098, \rho = 0.35)$ (gas-liquid); $(T = 1.25, P = 5.5, \rho = 0.87)$ (liquid-liquid) in panel.
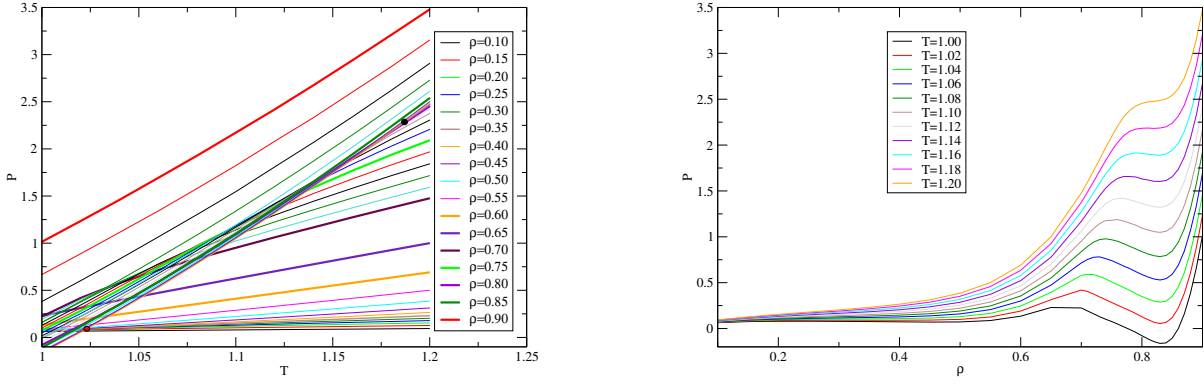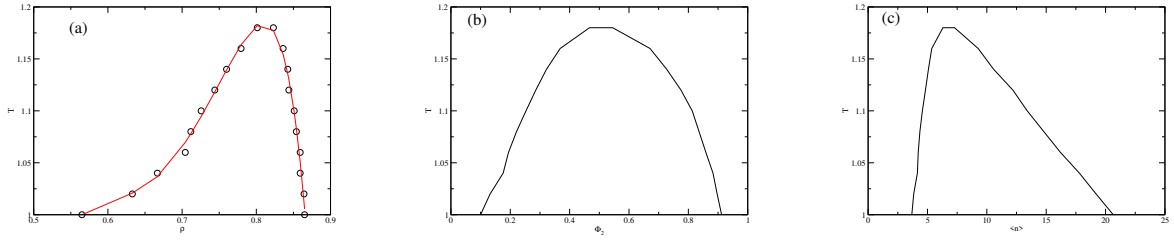
Figure 2: $P-T$ and $P-\rho$ phase diagrams for the parameter set with $\epsilon_{22}=0.5$ which are obtained by long equilibrium runs at NVT ensemble for $t=10^6$. The critical points are shown by ellipses. The locations of the gas-liquid critical point is ($T=1.023, P=0.0922, \rho=0.35$) and liquid-liquid critical point is $T=1.187, P=2.28, \rho=0.81$)

Figure 3: Binodal lines on (a) $\rho-T$ plane, (b) Φ_2-T plane and (c) $\langle n \rangle$–T planes.
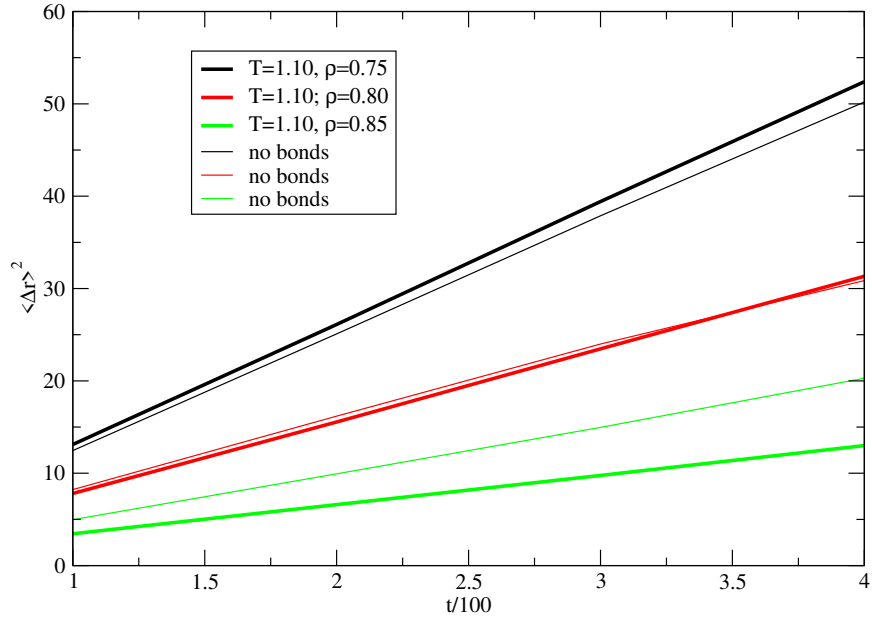
Figure 4: Mean square displacement of particles A as function of time across the phase transition at T=1.10 in comparison for the model without bonds. One can see that the bonds play role only in the dense phase but their effect is small because the bonds constantly brea and form.
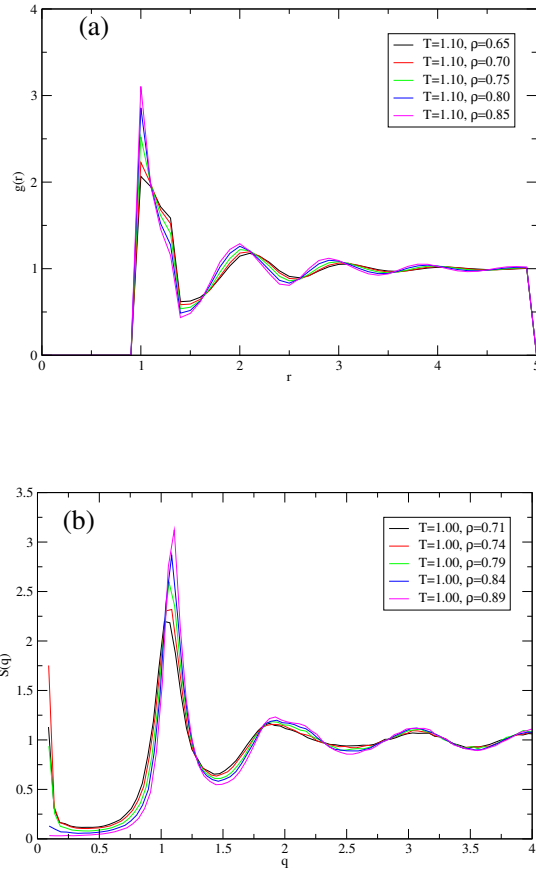
Figure 5: Density correlation function $g(r)$ (a) and Structure factor S(q)(b) across for various densities across the line of liquid-liquid phase transition
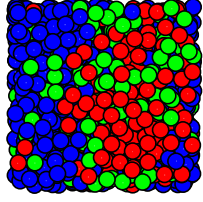
Figure 6: The snapshot of the system exhibiting phase segregation at $T = 1.00$ and $\rho = 0.74$ in the binodal region. Red, Green, and Blue spheres indicate particles B_1, B_2 and $B3$, respectively. Particles A are not shown.