Two types of dynamic crossovers in a network-forming liquid with tetrahedral symmetry

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A B S T R A C T
Liquids with tetrahedral symmetry of the first coordination shell often display anomalous thermodynamic and dynamic behaviors. The main reason for these anomalies is that pressurizing such liquids leads to the disordering of this local symmetry by the particles migrating from the second to the first coordination shell. This in some cases may lead to the increase of entropy upon pressurizing and consequently to the volume increase upon cooling, as well as increase of diffusivity upon pressurizing. Under certain circumstances, pressurizing or cooling these substances may lead to a first-order phase transition between two liquids with different local structures, entropies, energies and densities. The liquid–liquid first-order phase transition can end in a liquid–liquid critical point (LLCP). The Widom line, defined as the line of zero ordering field, emanates from the LLCP into the supercritical region. In the vicinity of the LLCP thermodynamic response functions have extrema along different loci that converge to the LLCP and can approximate the Widom line. In particular, the maxima of the specific heat are associated to continuous structural changes in the liquid and, in general, to dynamic crossovers. Here we present a model of a network-forming liquid with tetrahedral symmetry in which each response function has two loci of maxima as function of temperature at constant pressure. One locus has positive slope in the pressure–temperature (P–T) thermodynamic plane, and the other has negative slope. We show that for each locus there is a dynamic crossover in the diffusivity and that the two crossovers are qualitatively different. For the positively sloped locus, occurring at P above the pressure Pc of the LLCP, the crossover is from low activation energy at high T to high activation energy at low T. For the negatively sloped locus with P < Pc, the crossover is characterized by an increase of activation energy in a certain temperature interval but with similar activation energies at low and high T. Such a behavior has been proposed for water where an apparent glass transition, associated with the increase of the activation energy at high T, could be avoided if the activation energy would decrease in the region where experiments are difficult, the so called “no-man’s-land”.

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1. Introduction
Tetrahedral liquids such as water, silica, beryllium fluoride, silicon and germanium, have a region of thermodynamics and dynamic anomalies in their phase diagrams. Simulations using models with different degrees of tetrahedrality can reproduce these anomalies with various accuracy levels depending on their parameters [1–19]. Some of these models also display a liquid–liquid phase transition (LLPT) ending in a liquid–liquid critical point (LLCP) on the verge of the glass transition or spontaneous crystallization [1,2,9,10,5,17,18]. The Widom line, defined as the line of zero ordering field, emanates from the LLCP into the supercritical region. Near the Widom line the structure, entropy, energy, density and enthalpy of the liquid rapidly change from values typical for the high-temperature phase to the values typical for the low-temperature phase, by decreasing the temperature T. The response functions display maxima near this line approaching the LLCP, while diffusivity and orientational correlation times display rapid change in their behaviors giving rise to dynamic crossovers [20–22], despite the fact that some of these crossovers are associated with maxima in response functions that are not necessarily due to the presence of a LLCP [21].

Here we present a model of a network-forming liquid with tetrahedral symmetry in which each response function has two loci of maxima as function of temperature at constant pressure. One locus has positive slope in the pressure–temperature (P–T) thermodynamic plane, and the other has negative slope. We show that for each locus there is a dynamic crossover in the diffusivity and that the two crossovers are qualitatively different. For the positively sloped locus, occurring at P above the pressure Pc of the LLCP, the crossover is from low activation energy at high T to high activation energy at low T as in BeF2 [23] and SiO2 [2]. For the negatively sloped locus for P < Pc, the crossover is characterized by an...
increase of activation energy near the crossover but with similar activation energies at low and high $T$. Such a behavior has been proposed for water [24] where an apparent glass transition, associated with the increase of the activation energy at high $T$, could be avoided if the activation energy would decrease in the region where experiments are difficult, the so called "no-man’s-land".

2. The model

We study a model similar to a patchy model of Kern–Frenkel [25–29], by means of the Discrete Molecular Dynamics (DMD) algorithm designed for spherically symmetric potentials [30,31]. In order to simulate the anisotropic patchy molecules by this algorithm we represent them in the following way. Each molecule consists of a hard sphere of diameter $a$, which plays the role of unit of length, and four point particles attached to the center of the hard sphere by an infinite square well of radius $c < a/2$ (Fig. 1a). To make sure that these particles are forming an almost perfect tetrahedron they repel each other as hard spheres of diameter $d = \sqrt{8/3}c$ where $0 < f < 1$ is a parameter which must be close to unity. If $f < \sqrt{3}/2$, then all four point particles can be placed in the same plane and the tetrahedrality is completely lost. Each of these point particles attract to the analogous particles in different molecules with a square well potential of range $b > a - 2c$ and attractive energy $\epsilon$. To guarantee that the network of molecules at low $T$ is tetrahedral, we avoid cases with large $b$, for which a point particle may interact with more than one point particle belonging to other molecules (See Fig. 1b,c). In this study we select $c = 0.4a$, $b = 0.28a$, $d = 0.62a$, then $f = 0.949$.

We will show in the next section, that the model displays a LLCP if we add a short-range square-well attractive interaction of energy $\epsilon = -0.15\epsilon$ and with a range $R_b = 1.1a$ between the centers of the hard spheres. We find that without this isotropic attraction the model has no LLCP, although it has a wide region of density anomaly.

To prevent the crystallization into a body centered cubic structure, made of two interpenetrating diamond lattices, we add to the attractive well a square shoulder of diameter $R_s = 1.05a$ and repulsive energy $\epsilon_s = 0.075\epsilon$. The resulting isotropic potential (Fig. 1d) between the centers of the hard spheres is

$$U_s(r) = \begin{cases} 
-0.075\epsilon & a \leq r < 1.05a \\
-0.15\epsilon & 1.05a \leq r < 1.1a \\
0 & r \geq 1.1a 
\end{cases}$$

Such square-shoulder–square-well potentials with much wider shoulders and wells are known to have a LLCP even without tetrahedral interactions [32–34]. However, the potential in Eq. (1) without tetrahedral interactions have no LLCP. Its gas–liquid critical point is located at approximately $T = 0.06/\kappa_b$ [33], where $\kappa_b$ is a Boltzmann constant, i.e. at $T$ much lower than the LLCP temperature for the tetrahedral model studied here.

Each molecule has mass $m$, equally distributed among the four point particles forming the tetrahedron and the hard sphere to which they are linked. In the following we express the time in units of $a N \sqrt{\epsilon/m}$, the length in units of $a$, the (number) density $\rho$ in units of $1/a^3$, the pressure $P$ in units of $\epsilon/a^3$, the temperature $T$ in units of $\epsilon/k_b$, and the diffusion coefficient

$$D = \lim_{\Delta t \to \infty} \langle \Delta \mathbf{r}^2(\Delta t) / 6 \Delta t \rangle$$

in units of $a \sqrt{\epsilon/m}$. The quantity $\langle \Delta \mathbf{r}^2(\Delta t) \rangle$ appearing in the Einstein relation Eq. (2) is the mean square displacement of the center of mass of the molecule during time $\Delta t$. In the following, for sake of simplicity of notation, we omit the explicit indication of the units, having in mind that each quantity has its own proper unit as indicated above.

We perform DMD simulations at constant NVT, with $N = 512$ number of molecules, $V$ volume of a cubic box with periodic boundary conditions such that $\rho = 0.60, 0.62, ..., 0.88$ and $T = 0.105, 0.110, 0.115, ..., 0.140$. We use the Berendsen thermostat to keep the temperature constant. To ensure good equilibration and enough statistics at the lowest temperature we have studied, $T = 0.105$, we simulate for each state point $N_t = 5$ independent runs of $t_{\text{sim}} = 2.4 \times 10^6$ time units.

![Fig. 1. (a) The schematic representation of the model. Thin large circle shows the hard sphere particle of diameter $a$. Four small solid circles represent point particles which can run within the sphere of radius $c$ with the same center as the hard sphere. The distance between the point particles from the same molecule cannot be smaller than $d$. If $d < \sqrt{8/3}c$, the point particles must locate at the corners of the perfect tetrahedron. For smaller $d$ the degree of tetrahedrality decreases. The point particles from the different molecules attract to each other if their distance is less than $b$ (dashed circle). A minimal distance that a point particle of the second molecule can have from the center of the first molecule is $a-c$, shown by the bold arc. The attractive region of a point particle is the region between the two bold arcs bounded by these two distances. (b) A situation in which two point particles from two different molecules can be within the attractive range of the third point particle from a third molecule. (c) A situation in which two point particles from the same molecule can be within the attractive range of the third point particle in a different molecule. (d) Interaction potential $U_s(r)$ between the hard spheres.](image-url)
each. We confirm that this simulation time is sufficient to allow the root mean square displacement to reach at least 2a for any of the state points with \( T = 0.105 \) simulated in this work. At larger temperatures where equilibration is much faster, we use fewer independent runs and shorter \( T_{\text{sim}} \) sufficient to achieve the same level of accuracy over the entire temperature range. We estimate the error bars by the fluctuation analysis of the potential energy time series. We exclude from the simulation time \( T_{\text{sim}} \), the equilibration time \( \tau_e \) during which the potential energy markedly changes with time. For the rest of the trajectory we compute the standard deviation \( \sigma \), measured for the time series averaged over intervals of duration \( t \). If \( t \) is less than the correlation time \( \tau \), the averages over nonoverlapping windows of duration \( t \) are not statistically independent and hence we expect \( \sqrt{\sigma t} \) to grow with \( t \). For \( t > \tau \), \( \sqrt{\sigma t} \) must saturate, due to the central limit theorem. We analyze \( \sqrt{\sigma t} \) for each independent run and define \( \tau \) as its maximal point. If \( \tau > T_{\text{sim}}/4 \), it may indicate the existence of the global trend in potential energy, i.e. poor equilibration. Accordingly, we increase the simulation time twice and measure \( \tau \) again for the increased time series. If the preliminary determined \( \tau \) appears to be shorter than \( \tau \), we exclude \( \tau = \tau \) from the beginning of the simulation. Eventually we define the error bar as \( \sigma t / \sqrt{N T_{\text{sim}}/t - 1} \), because \( N T_{\text{sim}}/\tau \), can be regarded as the number of statistically independent measurements. Similarly, we define the error bars for the pressure, using \( \tau \) found for potential energy, which usually appears to be longer than the analogous quantity for pressure.

3. Results

3.1. The density anomaly and the LLCP

We find that for \( T < 0.125 \) the isotherms intersect at \( \rho = 0.74 \) indicating a region of density anomaly (Fig. 2). We observe that \( \partial P / \partial \rho = 0 \) along the isotherm at \( T = 0.110 \) at \( \rho = 0.1487 \), consistent with the divergence of the compressibility along this isotherm. Furthermore, at \( T = 0.105 \) we find that from \( \rho = 0.72 \) to \( \rho = 0.76 \), \( \partial P / \partial \rho < 0 \), i.e. the compressibility is negative, as expected at the coexistence between two fluid phases in the NVT ensemble (Fig. 2). The analysis of these two isotherms suggests the occurrence of a LLCP at \( \rho = 0.74 \pm 0.02 \).

The Maxwell construction in the \( P-V \) plane gives equilibrium pressure \( P_e = 0.1485 \) at \( T = 0.105 \), which is slightly less than the pressure of the inflection point at \( T = 0.110 \), suggesting that the liquid–liquid coexistence line has a slope that approaches zero from positive values in the \( P-T \) plane. Visual inspection of configurations at the coexistence near the critical density at \( T = 0.105 \) shows the segregation of the system into high density liquid (HDL) in which molecules have five or more first neighbors and low density liquid (LDL) in which molecules have four or less first neighbors and are tetrahedrally coordinated (Fig. 3).

3.2. Structural analysis near the LLCP

To further verify the nature of the liquid–liquid phase transition, we construct histograms of the structural bond order parameter \( d_s \) defined in Ref. [17], for different densities at \( T = 0.105 \) (Fig. 4a). For the positive-compressibility part of the isotherm at low density (\( \rho < 0.66 \)), we find the characteristic bimodal distribution observed for the LDL in the ST2 model [17]. For the positive-compressibility part of the isotherm at high density (\( \rho > 0.76 \)) we find the characteristic unimodal distribution observed for the HDL in ST2 [17]. For the densities with negative compressibility, where the two phases coexist, we find a fast transformation of the LDL-like distribution to the HDL-like distribution (Fig. 4a).

This analysis is corroborated by the analysis of the average number of neighbors of a hard sphere on its shoulder, \( n_w \), in its square well \( n_w \), and in the number of neighbors \( n_i \) linked by the tetrahedral bonds created by the point particles of each molecule (Fig. 4b). One can see that the number of tetrahedral bonds decreases with density indicating the collapse of the tetrahedral order, while the number of particles in the first coordination shell experiences an almost two-fold increase with density. These results demonstrate that the anomalous behavior and the LLCP of the tetrahedral liquids are both linked to the migration of the particles from the second coordination shell to the first associated with the collapse of the tetrahedral order.

3.3. Two loci of maxima for each response function near the LLCP

From the crossing of the isochores we estimate the LLCP at \( T = 0.108 \pm 0.001 \) (Fig. 5). The accuracy of the data near the LLCP is sufficient to find the maxima of the isothermal compressibility, \( K_T \), of the constant pressure thermal expansion coefficient, \( \alpha_p \), and of the constant pressure specific heat, \( C_p \).
We find two distinct lines of $K_T$ maxima. One emanating from the LLCP with slightly negative slope, another emanating from the minimum of the LDL spindal, which is located very close to the LLCP. Unfortunately, the accuracy of our results is not sufficient to verify whether these two points are distinct or coincide as should be in the case of the LLPT with zero slope. We also find two lines of extrema for $\alpha$ and $C_p$. Interestingly the lines of extrema of $\alpha$ and $C_p$ closely follow the lines of $K_T$ maxima. Again the accuracy of our results is not sufficient to verify the behavior of these lines in the close vicinity of the critical point, which would be interesting to do in light of the predictions of the linear scaling theory\[35\].

As we will discuss later, these results on the one hand remind us of those for a many-body tetrahedral water model\[19\], with the difference that in the water model studied by Bianco et al. the LLPT has a negative slope in the $P$–$T$ plane and all the loci of the extrema near the LLCP have negative slope as well. On the other hand, the present results remind those for an isotropic model for anomalous liquids and with a LLPT many-body tetrahedral water model near the two lines of maxima of $\alpha$ and $C_p$ closely follow the lines of $K_T$ maxima. This result reminds us the crossovers observed for the many-body tetrahedral water model near the two lines of maxima of $\alpha$ and $C_p$\[22,36\]. However, there is an important difference between the present case and the one studied by Mazza et al.\[22,36\]. In the many-body tetrahedral water model both lines of maxima have a negative slope in the $P$–$T$ plane. Hence, by decreasing $P$ the system experiences two dynamic crossovers along isobars.

Here, instead, the two lines of maxima of $C_p$ have slope of different signs in the $P$–$T$ plane. Hence, at any $P$ there is only one single dynamic crossover as function of $T$.

The two crossovers in Fig. 7 are qualitatively different. For the crossover at $P < P_c$, we find that $\partial \ln (D_c)/\partial (1/T)$ decreases upon cooling near the $C_p$ maxima, but increases upon further cooling, and slightly overcoming, the slope at higher $T$. This behavior is consistent with the one discussed in Ref. [24] for water. In their work Starr et al. consider that the apparent glass transition of water at 240 K could be avoided if the activation energy of the dynamics would decrease in the region where it is difficult to perform experiments, the "no-man’s-land," and then would increase upon further cooling toward a glass transition temperature at 138 K.

For the crossover at $P > P_c$, instead, we observe that $\partial \ln (D_c)/\partial (1/T)$ decreases upon crossing the line of $C_p$ maxima, without increasing at lower $T$. We observe in this case a dramatic slowdown in diffusivity.

### 3.4. The diffusion coefficient

We find that the diffusion coefficient $D_c$ also drastically decreases by decreasing $T$. It drops by four orders of magnitude within our simulation range, from $10^{-7}$ to $10^{-3}$ at $T = 0.140$, to $10^{-6}$–$10^{-7}$ at $T = 0.105$ (Fig. 6a). At the lowest temperature and highest density state point ($\rho = 0.88, T = 0.105$), we find that $D_c = 2.9 \cdot 10^{-7}$, which requires $\Delta t \approx 6 \cdot 10^6$ simulation time steps to allow the root mean square displacement to reach one hard square diameter.

Furthermore, $D_c$ has a water-like anomalous behavior. At low-enough $T (T \leq 0.120$) it has a non-monotonic behavior with respect to $P$, with an anomalous increase of diffusivity upon pressurizing for $P \leq 0.15$ (Fig. 6b). At higher $P$ the normal behavior is restored, with $D_c$ decreasing for increasing $P$ along isotherms.

To study the behavior of the diffusivity near the two branches of the maxima of $C_p$, we consider the Arrhenius plot of the $D_c$ along different isobars (Fig. 7). We find two dynamic crossovers near the two lines of $C_p$ maxima. This result reminds us the crossovers observed for the many-body tetrahedral water model near the two lines of maxima of $C_p$\[22,36\]. However, there is an important difference between the present case and the one studied by Mazza et al.\[22,36\]. In the many-body tetrahedral water model both lines of maxima have a negative slope in the $P$–$T$ plane. Hence, by decreasing $T$ the system experiences two dynamic crossovers along isobars.

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### 3.5. Crystallization near the LLCP

We test if the system spontaneously crystallizes near the LLCP. We observe no spontaneous crystallization for $T = 0.110$ and $T = 0.105$. For $T = 0.115, 0.116, \ldots, 0.119$ we perform two independent runs,
of $4 \times 10^5$ time units each, for $\rho = 0.60, 0.62, \ldots, 0.88$, i.e. we perform 150 independent simulations. We never observe spontaneous crystallization for $\rho < 0.8$, while for $0.8 \leq \rho \leq 0.88$ we observe 11 crystallization events out of 150 independent runs. In these 11 events we find that the system always crystallizes as a body centered cubic (BCC) lattice and we estimate that a crystal critical nucleus size in this range of temperatures is at least five molecules (Fig. 8a).

We never observe spontaneous crystallization into a low density diamond or hexagonal crystals (Fig. 8b). The largest crystal we observed consists of 17 molecules and occurs at $\rho = 0.68$ and $T = 0.117$. All such crystallites melt within our simulation time. However, we observe three crystallization events in which the system first spontaneously crystallizes into a BCC crystal, and then nucleates the low density diamond crystal. This is a consequence of the fact that in NVT simulations the nucleation of the high-density BCC crystal forces the density of the remaining liquid to drop drastically. Then, this low-density liquid heterogeneously crystallizes into a diamond crystal, which starts to grow using the existing BCC crystal as a template (Fig. 9).

4. Discussion

In this work we present a behavior of a tetrahedral model of a liquid with short range interactions which has density and diffusivity anomalies as well as liquid–liquid phase transition with almost horizontal coexistence line. We find a LLCP from which two lines of maxima emanate for each response function, one toward positive pressures and one toward negative pressures. We find that the lines for different response functions with the same $P$-dependence overlap within the accuracy of our simulations.

For each of the two lines of extrema we expect a dynamic crossover based on general considerations. Indeed, the loci of $C_P$-maxima mark the maximal structural changes in the one-phase fluid, suggesting the possibility of a change in the dynamic behavior of the structural relaxation. Our results regarding the diffusivity confirm the existence of the two crossovers and show that they are qualitatively different. In particular, the crossover for $P < P_c$ reproduces a scenario that has been discussed in Ref. [24] for water. At $P > P_c$ the crossover resembles the behavior discussed for silica [37].

The presence of two lines of extrema for each response function and two associated dynamic crossovers reminds the recent results for the many-body tetrahedral water model studied in Refs. [22,36,19,38] where it is clear that the Widom line corresponds to the loci of maxima at lower $T$ and with a large negative slope in the $P$-$T$ plane.

Here the two lines of maxima have $P$-dependencies with different signs. Hence, the comparison of the present results with those from Refs. [22,36,19,38] is not straightforward. An intriguing possibility is that in the present case the Widom line would coincide with the loci of maxima with a large negative slope in the $P$-$T$ plane. This would make the present results consistent with the prediction about the Widom line made by Bertrand and Anisimov based on experimental water data [39].

It is also interesting to observe that this model apparently violates the recently published prediction of the linear scaling theory [35]. In the spherically symmetric core softened models of liquids with density anomaly and liquid–liquid phase transition [40–51] there are two branches of compressibility and thermal expansivity maxima, but only one line of the specific heat maxima. The line of $C_P$ maxima disappears when the slope of the coexistence line approaches zero. In these models, the dynamic crossover is observed near the line of heat capacity maxima which emanates from the critical point with a positive slope. In particular, the slope of the Arrhenius plot of diffusivity increases upon cooling below the $C_P$ maxima [51]. However, this slope is still much more negative than the slope in the high temperature phase above the $C_P$ maxima.

Here, the heat capacity maxima lines are present above and below the critical pressure. According to the linear scaling theory, in the vicinity of the critical point at the end of a phase transition line with horizontal slope, the loci of maxima of the specific heat must approach the critical point from the low temperature side along the coexistence line, while the loci of maximal compressibility and thermal expansivity must approach the critical point from the high temperature side along the Widom line. However, this prediction does not rule out that the background entropy fluctuations produce the maxima of the specific
heat in the supercritical region. Apparently our model represents this interesting novel case. The existence of the two branches of the \( C_p \) maxima suggests that both low density and high density liquids in our model significantly differ in their structure from the supercritical fluid at the correspondent pressures. In particular, the high density phase appears to have a very high compressibility at low temperatures, because the system we study is prone to collapse at high pressure into two interwoven tetrahedral networks almost doubling its density. That is why our system easily crystallizes into BCC at high pressures. We find that in our system the LLCP is metastable with respect to spontaneous crystallization into BCC and never crystallizes into a low density diamond or hexagonal crystals, as reported recently for another system of tetrahedral particles [52].

An intriguing possibility exists that the line of the heat capacity with the positive slope is a precursor of another hidden critical point associated with the transition to a very high density liquid held by the attractive square well interactions. The existence of the multiple critical points in the systems characterized by a large free space between the particles at low pressures was observed in the SSSW systems with multiple steps [53] and in the interpenetrating networks, where the phase transition is observed between the non-interpenetrating and interpenetrated networks [54]. In our system we expect that this transition is between the diamond-like network at low densities and the two interpenetrating diamond-like networks similar to the BCC crystal observed in our simulations at high pressures. This transition is facilitated by the attractive square well. Accordingly, at high densities we observe an almost two-fold increase of the number of neighbors in the square well (Fig. 4b). In contrast, at low densities we observe the increase in number of the neighbors linked by the tetrahedral bonds, indicating the transition to a low density liquid. The high density transition may be hidden by the crystallization to the BCC, or by the glass transition as in water where a smooth transition between the high density and a very high density glass has been observed [55]. On the other hand, the \( C_p \) maxima with the positive slope may represent a pseudo Widom line which does not lead to any critical point, observed in the patchy system [28] and the WAC silica model by [56]. At present, investigation of these interesting scenarios is beyond our computational reach.

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