Relationship between structural order and water-like anomalies in metastable liquid silicon: *Ab initio* molecular dynamics

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The relationship between structural order and water-like anomalies in tetrahedral liquids is still open. Here, first-principle molecular dynamics are performed to study it in metastable liquid Si. It is found that in *T*-*P* phase diagram, there indeed exists a structural anomaly region, which encloses density anomaly but not diffusivity anomaly. This is consistent with that of SW Si and BKS SiO$_2$ but different from that of SPC/E water. Two-body excess entropy anomaly can neither capture the diffusivity, structural, and density anomalies, as it can in a two-scale potential fluid. In structural anomaly region, tetrahedrality order $q_{tetra}$ (measuring the extent to which an atom and its four nearest neighbours adopt tetrahedral arrangement) and translational order $t_{trans}$ (measuring the tendency of two atoms to adopt preferential separation) are not perfectly correlated, which is different from that in SW Si and renders it impossible to use the isotaxis line to quantify the degree of structural order needed for water-like anomalies to occur. Along the isotherm of critical temperature $T_c$, $t_{trans}/q_{tetra}$ is approximately linear with pressure. With decreasing pressure along the isotherm below $T_c$, $t_{trans}/q_{tetra}$ departs downward from the line, while it is the opposite case above $T_c$.

Tetrahedral liquids, in which the anisotopic bonding gives rise to a three-dimensional, liquid-state network with an energetic bias towards local tetrahedral order, are ubiquitous in everyday life, such as water, SiO$_2$, BeF$_2$, GeO$_2$, C, Si, Ge, Sn. Although the interactions between atoms or molecules are different, including ionic, metallic, covalent and hydrogen bonding, they share a preference for forming tetrahedrally coordinated configurations at the micro level and displaying water-like anomalous behaviour at the macro level, such as the well-known density maximum (density anomaly)\(^1\), the anomalous increase of diffusivity upon pressurising (diffusivity anomaly)\(^2\)–\(^6\), and the first-order liquid-liquid phase transition (LLPT)\(^7\)–\(^18\). Tetrahedral liquids form a large fraction of our world and have fundamental biological and technological relevance. Therefore, a general interpretation of these anomalous behaviours is of wide interest.

In recent years, much effort has been expended to understand the relationship between the atomic level structure and the water-like anomalies. In 2001, Errington and Debenedetti\(^6\) firstly introduced two measures of order, the translational order parameter ($t_{trans}$)\(^19\) and the tetrahedrality order parameter ($q_{tetra}$)\(^20\), to analyse the local structural order in the SPC/E model of water and further to study the relationship between structural order and these anomalies. It was found that, in the region bounded by loci of maximum $q_{tetra}$ at low densities and minimum $t_{trans}$ at high densities along the isotherm, $q_{tetra}$ and $t_{trans}$ decrease on compression, in contrast to what is observed for simple fluids. Therefore, this region was identified by the authors as a structurally anomalous region, which in turn encloses the regions of diffusivity anomaly and density anomaly in the $T$-$

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can not anticipate the occurrence of the diffusivity anomaly and hence can not provide a satisfactory microscopic picture of the anomalous behaviour in liquid silica. The later results of liquid BeF2 with the transferable rigid ion model (TRIM) by Agarwal et al. shows the similar result with BKS SiO2, but that of the Oeffner-Elliot (OE) model of GeO2 by Jabes et al. is similar to SPC/E water. The systematic comparison for different model potentials of water (mTIP3P, TIP4P, TIP4P/2005, TIP5P, SPC/E), ionic liquids (SiO2 and BeF2), and liquids characterised by the Stillinger-Weber (SW) potential (including Si) suggests a strong correlation between q tetra and t trans exists only in rigid-body model potentials for water and SW liquids (in a limited range of tetrahedrality strength), but not in ionic melts. In addition, to obtain a more general picture of the origins of these anomalies, the excess entropy has also been attempted to understand these anomalies and has been tested to be able to predict the regions of anomalies in the phase diagram.

It should be noted that the water-like cascading of anomalous regions in the phase diagram has been observed not only in systems having directional interactions but also in the simulation studies of spherically symmetric potentials. Especially, the study of Jagla model by Yan et al. suggests the water-like relationship between structural order and anomalies is related to the presence of two different length scales in the potential. Moreover, the study of a core-softened model by Fomin et al. shows that the order of the cascading regions of anomaly can be changed by increasing the depth of the attractive part of the potential.

Although so many computer simulation studies of tetrahedral liquids have focused on the relationship between structural order and water-like anomalies, they all depended on different model potentials or empirical potentials. To our knowledge, first-principle computer simulations have not been performed to study this question so far. It is well-known that the first-principle force neither makes assumptions such as empirical model nor includes fitting parameter to experimental data, so it is expected to give more realistic results. In the past few decades, first-principle simulations have achieved great success in investigating structural and dynamic properties of liquids. Based on first-principle calculations, we have studied the inherent structures of high-density liquid (HDL) and low-density liquid (LDL) Si and found that the first-order LLPT in metastable liquid Si is a transition between a sp3-hybridization LDL and a white-tin-like HDL. Further, we found that the liquid-liquid critical point (LLCP) is hidden, blended in with the continuous reentrant spinodal of HDL, suggesting that the phase behaviour of metastable liquid Si tends to be a critical-point-free scenario rather than a second-critical-point one based on SW potential. In this work, based on the prior research, we turn our attention to the relationship between structural order and water-like anomalies (including the well-known first-order LLPT) in metastable liquid silicon.

Results
The density anomaly and the first-order LLPT have been shown in our previous work. In the studied pressure range from 27.25 to 6.50 kbar, an obvious maximum can be observed along each p-T isobar line and in T-P phase diagram, the line of density maxima tends to pass through the LLCP, located at Tc ~ 1420 ± 10 K and Pc ~ 30.5 ± 1.0 kbar, which is different from the result in ref. 17 (Tc ~ 1120 K and Pc ~ 0.60 GPa). We speculate that such a difference may be due to the different potentials adopted. Although the LLPT is proved to exist for SW liquid Si, it has been reported that it strongly depends on the parameters of the potential and an arbitrary variation, albeit small, of the parameters may even lead to its disappearance. Here, we begin by presenting our results related to the diffusivity anomaly.

Diffusivity anomaly. In Fig. 1, we show our calculated diffusion coefficient D as a function of pressure along eight different isotherms ranging from 1032 to 1800 K. Along each isotherm, the pressure is gradually decreased to the stability limit of HDL and an obvious maximum can be found in the whole temperature range studied here, which marks the upper bound of diffusivity anomaly region. Along each isotherm below Tc, the
locus of diffusivity minimum, which marks the lower bound of diffusivity anomaly region, can not be found and is expected to be located in LDL, where system’s dynamics is slow and there is considerable error in computing D and locating the diffusivity minima. So we have not attempted to find this locus in our study. Above $T_c$, the diffusivity minimum is expected to be located at the HDL-V spinodal because of the larger D in vapor than that in liquid.

**Structural anomaly.** Figure 2 presents the evolution of structural order ($q_{tetra}$ and $t_{trans}$) with decreasing pressure along the isotherm. From Fig. 2(a), it can be found that $q_{tetra}$ increases with the decrease of pressure in the simulated temperature range from 1032 to 1800 K, which is in contrast to what is observed for simple fluids and so is termed as structural anomaly. Below $T_c$, we do not find a maximum of $q_{tetra}$ in our simulated pressure range, which marks the lower bound of structural anomaly region and is expected to be found in LDL. At temperatures above $T_c$, the maximum of $q_{tetra}$ is expected to be located at the HDL-V spinodal, such as for $T = 1532$ and 1800 K. In Fig. 2(b), in the temperature range from 1032 to 1700 K, $t_{trans}$ decreases with decreasing pressure and goes through a minimum, which marks an onset of structural anomaly.

**Excess entropy anomaly.** The excess entropy $S_e$ is defined as the entropy of the liquid relative to that of the ideal gas at the same temperature and pressure and can be expressed in terms of an expansion of n-body correlation functions. The first term, namely the two-body contribution $S_2$, accounts for a large proportion, such as 80–90% in Lennard-Jones fluids. Because $S_2$ characterizes the reduction in the number of states (relative to an ideal gas) accessible to a system due to translational interparticle correlations, it can also be thought of as a metric for translational order. Errington and co-workers argued that the region in the phase diagram where the excess entropy anomalously increases with decrease in density is also the region where translational order anomaly is observed. Indeed, many studies mentioned above have showed that there also exists a $S_2$ or $S_3$ anomaly region in the T-$ho$ phase diagram, where $S_2$ or $S_3$ anomalously increases with increasing pressure. In this work, we calculated $S_2$ as a function of pressure along eight different isotherms, shown in Fig. 3. In the temperature range from 1032 to 1432 K, along each isotherm a maximum occurs but the minimum can not be found until the HDL spinodal is encountered, which is expected to be found in LDL. From 1532 to 1800 K, the maximum can not be found until the HDL-V spinodal is encountered.

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**Figure 2.** The average tetrahedrality order $q_{tetra}$ (a) and translational order $t_{trans}$ (b) as a function of pressure for different temperatures from 1032 to 1800 K obtained from *ab initio* molecular dynamics simulations of liquid Si. $q_{tetra}$ increases with decreasing pressure. From 1032 to 1700 K, $t_{trans}$ decreases with decreasing pressure and goes through a minimum, which marks an onset of structural anomaly.
It is known that there is a strong connection between transport properties of fluids and excess entropy, such as the Rosenfeld scaling relation $D^*_R = a_0 \exp(b_0 S_2)$ and the Dzugutov scaling relation $D^*_z = a_0 \exp(S_2)$, $m$ is the mass of the particle, and $\rho$ is the number density. In the latter, $D^*_z = \Gamma^{1/3} \sigma^{-2}$, $\Gamma$ is the collision frequency and equals $4\pi\sigma^2 g(\sigma) \rho (\pi k_B T/m)^{1/2}$, $\sigma$ is the hard-sphere diameter, and $g(\sigma)$ is the value of radial distribution function at the constant distance. In Fig. 3 (inset), we also test the scaling relation between $D^*_R$ and $S_2$. The relation between $D^*_R$ and $S_2$ is similar to that presented in Fig. 3 (inset) and not shown here. However, it can be seen that the relation between $\ln(D^*_R)$ and $S_2$ is not linear, showing a different behaviour from that of Rosenfeld and Dzugutov. Based on the results in Figs 1 and 3, it is due to the fact that along an isotherm, the change of diffusivity with pressure is out of step with that of $S_2$ versus pressure, which is different from the results in ref. 41 based on a core-softened potential (i.e., a Lennard-Jones potential plus a Gaussian repulsion). Thus we can comment that, based on first-principle calculations, the Rosenfeld and Dzugutov scaling relations are invalid along an isotherm in the anomalous region. This is consistent with that observed in supercooled liquid Si based on SW potential and the systems based on some two-scale potentials.

**Discussion**

Based on the above results, now we turn to discuss the relationship of these anomalies in $T$-$P$ phase diagram, shown in Fig. 4. The spinodals, LLCP, HDL-LDL coexistence line, and density maxima are obtained from our
previous work. The LDL-V and the HDL-V spinodals form a continuous liquid-vapor spinodal, which meets the liquid-vapor critical point at higher temperature and higher pressure (not shown here), and the LLCP seems to just be hidden, blended in with the liquid-vapour spinodal. This is consistent with the critical-point-free scenario suggested by Angell in refs 44 and 45, but is different with the two-critical-point scenario, in which the LLCP occurs above the liquid-vapor spinodal, similar to that presented in Fig. 2 in ref. 46. From Fig. 4, it can be seen that the region of diffusivity anomaly encloses the region of structural anomaly, which in turn encloses the region of density anomaly. This result is consistent with that of SW Si27 and is similar to that of BKS SiO221 but different from that of SPC/E model of water6. In addition, it should be noticed that the two-body excess entropy anomaly region does not enclose the diffusivity anomaly as it does in a fluid interacting through a two-scale potential29.

On the contrary, it is also included in the structural anomaly region determined by the translational order minimum, with the S2 maxima line going across the density maxima line. So S2 anomaly can not be used as a criteria of structural anomaly to capture the region of diffusivity and density anomalies. This may originate in the fact that the relation between ln(DR) and S2 shows an anomalous behaviour, presented in Fig. 3 (inset).

Recently, it has been shown for the two-scale potential that different criteria of structural anomaly can lead to completely different results47. It was found that the structural anomaly region determined by the S2 anomaly lies much deeper than that obtained from the approximate S2 anomaly. This means that the structural anomaly calculated from the S2 criterion may be inside the density anomaly shown in Fig. 4, which is in contradiction with the thermodynamically consistent relation that the region of anomalous density is always inside the region of anomalous S2. We think that there are two main reasons accountable for this. The first is that there is a larger error in determining the temperature of density maximum, the higher the pressure, the greater the error (see Fig. 3 in ref. 35). The second is that, although the structural anomaly region determined by S2 anomaly lies much deeper than that obtained from S2 for the two-scale potential47, it is not necessarily the case for other systems. For example, in SW Si the onset pressure of S2 anomaly is the same with that of S2 anomaly and at lower temperatures the former is even slightly larger than the latter (see Fig. 12(a) in ref. 27).

As mentioned above, in the structural anomaly region, a strong correlation between qtetra and ttrans exists in rigid-body model potentials for water and SW liquids (in a limited range of tetrahedrality strength), but not in ionic melts. Here, we also present the correlation between qtetra and ttrans shown in Fig. 5. Similar to water, our Si order parameter map also suggests an inaccessible region in the high-qtetra/low-ttrans quadrant. In other words, for any given value of ttrans, there is a maximum value of qtetra that the system can attain. Likewise, for any given value of qtetra, there is a minimum attainable ttrans. However, in the structural anomaly region, qtetra and ttrans do not collapse onto a single line, as is the case for water, suggesting that qtetra and ttrans are not perfectly correlated.

With the decrease of temperature, the correlation becomes weaker and weaker. These results are different from those observed in SW Si25–27, in which with the decrease of temperature, the correlation becomes weaker and weaker. Inset: The value of ttrans/qtetra against pressure for different isotherms. Along the isotherm of Tc, ttrans/qtetra is approximately linear with pressure, ttrans/qtetra = 0.0015P + 0.494. With decreasing pressure along the isotherm below Tc, ttrans/qtetra departs downward from the line until the LLPT occurs, while it is the opposite case above Tc.

Figure 5. Parametric plot of translational order ttrans against tetrahedral order qtetra for different temperatures from 1032 to 1800 K obtained from ab initio molecular dynamics simulations of liquid Si. qtetra and ttrans are not perfectly correlated in the structural anomaly region and with decreasing temperature, the correlation becomes weaker and weaker. Inset: The value of ttrans/qtetra against pressure for different isotherms.
In summary, first-principle molecular dynamics are performed for the first time to study the relationship between structural order and water-like anomalies in metastable liquid Si. Our results show that in T-P phase diagram, there indeed exists a structural anomaly region, which encloses the density anomaly but not the diffusivity anomaly. This is consistent with that of SW Si and BKS SiO₂ but different from that of SPC/E model of water. Two-body excess entropy anomaly can neither capture the diffusivity, structural, and density anomalies, as it can in a fluid interacting through a two-scale potential. Moreover, in the structural anomaly region, \( q_{\text{tetra}} \) and \( t_{\text{trans}} \) are not perfectly correlated, which is different from that in SW Si and renders it impossible to use the isotaxis line to quantify the degree of structural order needed for water-like anomalies to occur. Along the isotherm of critical temperature \( T_c \), \( t_{\text{trans}}/q_{\text{tetra}} \) is approximately linear with pressure, \( t_{\text{trans}}/q_{\text{tetra}} = 0.0015P + 0.494 \). With decreasing pressure along the isotherm below \( T_c \), \( t_{\text{trans}}/q_{\text{tetra}} \) departs downward from the line until the liquid-liquid phase transition occurs, while it is the opposite case above \( T_c \).

**Methods**

**Ab initio molecular dynamics.** The simulations are performed by the Vienna ab initio simulation package (VASP)\(^{45,49} \) together with projector augmented wave (PAW) potential\(^{50,51} \) in the Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA)\(^{52} \). A system of 216 Si atoms in a cubic supercell with periodical boundary conditions is used. The electronic wave functions are expanded in the plane wave basis set with an energy cutoff of 245 eV and a Pulay stress\(^{39} \) of 1.65 kbar is added to offset the incompleteness of the plane wave basis set. Only Γ-point is used to sample the supercell Brillouin zone. The canonical (NVT) ensemble simulations are performed with a Nosé thermostat for temperature control\(^{54} \). Newton’s equations of motion are integrated using Verlet’s algorithm in the velocity form with a time step of 2 fs.

The initial configuration, a diamond cubic crystal structure with the volume of 17.2 Å\(^3\)/atom, is heated up to 2000 K. After a run of 20 ps with constant temperature 2000 K, the system arrives at an equilibrium liquid state. The temperature is then gradually reduced to the desired temperature with a cooling rate of 0.5 \( \times 10^{15} \) K/s and a subsequent run of 15–20 ps is performed at this temperature. Then, the simulations are performed with a series of successively larger volumes along the isotherm up to the stability limit of HDL. At each simulation point, we performed a simulation about 15–30 ps. It is found that for HDL 5 ps is enough to equilibrate and the statistical averages are collected for the rest of the simulation. Along each isotherm, the end point of the previous simulation is scaled to obtain the initial conditions for the next.

**Calculation of self-diffusion coefficient \( D \).** The self-diffusion coefficient \( D \) in liquids was obtained by fitting the long time mean square displacement (MSD). MSD is defined as

\[
\Delta r^2 = \frac{1}{N} \sum_{i=1}^{N} (\mathbf{r}_i(t) - \mathbf{r}_i(t_0))^2
\]

where \( \mathbf{r}_i \) is the coordinates of atom \( i \), \( t_0 \) is an arbitrary origin of time. The diffusion coefficient \( D \) can be calculated by

\[
D = \lim_{t \to \infty} \frac{\Delta r^2}{t}
\]

**Structural order parameters.** The translational order parameter \( t_{\text{trans}} \) is defined as

\[
t_{\text{trans}} = \int_{0}^{\xi_c} |g(\xi) - 1| d\xi
\]

where \( \xi = r \rho^{1/3} \) is the distance \( r \) between two Si atoms divided by the mean separation between a pair of atoms at the given number density \( \rho \). \( g(\xi) \) is the pair correlation function, and \( \xi_c \) is a cutoff distance beyond which the system’s pair correlation function cannot be distinguished from its asymptotic value of 1. In this work, \( \xi_c \) is chosen to be 9.0 \( \times 10^{12} \). Scaled coordinates are used so that the above integral sums over an equivalent number of coordinate shells at each density. For an ideal gas, since \( g(\xi) = 1.0 \), \( t_{\text{trans}} \) is zero and for a crystal, it has a finite value depending on the cutoff distance. In the liquid phase, \( t_{\text{trans}} \) will have a value in between that of the ideal gas and a crystal. The tetrahedrality order parameter \( q_{\text{tetra}} \) is defined as

\[
q_{\text{tetra}} = 1 - \frac{3}{8} \sum_{i=1}^{N} \sum_{j=1}^{N} \left( \cos \psi_{jk} + \frac{1}{3} \right)^2
\]

where \( \psi_{jk} \) is the angle formed by the lines joining a reference atom \( i \) and its nearest neighbours \( j \) and \( k \). The average \( q_{\text{tetra}} \) varies between 0 (in the case of an ideal gas) and 1 (in the case of a cubic diamond crystal).

**Excess entropy.** Excess entropy \( S_E \) is defined as \( S_E = S - S_{id} \) where \( S \) is the total entropy of the system and \( S_{id} \) is the entropy of an ideal gas system. In present work, we calculate the two body approximation (\( S_2 \)) to \( S_E \) from the pair correlation function, and is given by

\[
S_2/Nk_B = -2\pi \rho \int_{0}^{\infty} [g(r) \ln(g(r)) - [g(r) - 1]r^2] dr
\]

where \( g(r) \) is the pair correlation function, and \( \rho \) is the number density.
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**Acknowledgements**

This work is supported by Natural Science Foundation of Shandong Province of China (Grant Nos ZR2012AQ014 and ZR2014AP014) and National Natural Science Foundation of China (Grant No. 11504154).

**Author Contributions**

G.Z., Y.J.Y., M.C.D. and X.G.Z. conducted MD simulations at School of Physics and Optoelectronic Engineering in Ludong University; G.Z., J.L.Y. and H.Y.W. analysed the data; G.Z. wrote the paper and J.L.Y. revised it.

**Additional Information**

**Competing financial interests:** The authors declare no competing financial interests.

**How to cite this article:** Zhao, G. \textit{et al.} Relationship between structural order and water-like anomalies in metastable liquid silicon: \textit{Ab initio} molecular dynamics. \textit{Sci. Rep.} \textbf{7}, 39952; doi: 10.1038/srep39952 (2017).

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