

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/264416679>

Structural Evolution of Supercritical CO₂ across the Frenkel Line

ARTICLE *in* JOURNAL OF PHYSICAL CHEMISTRY LETTERS · JULY 2014

Impact Factor: 7.46 · DOI: 10.1021/jz5012127

CITATIONS

8

READS

94

4 AUTHORS, INCLUDING:



[Dima Bolmatov](#)

Brookhaven National Laboratory

29 PUBLICATIONS 241 CITATIONS

SEE PROFILE



[Dmitry Zav'yalov](#)

Volgograd State Technical University

49 PUBLICATIONS 138 CITATIONS

SEE PROFILE



[Mikhail Zhernenkov](#)

Brookhaven National Laboratory

62 PUBLICATIONS 604 CITATIONS

SEE PROFILE

Structural Evolution of Supercritical CO₂ across the Frenkel Line

Dima Bolmatov,^{*,†} D. Zav'yalov,[‡] M. Gao,[¶] and Mikhail Zhernenkov[§]

[†]Baker Laboratory, Cornell University, Ithaca, New York 14853, United States

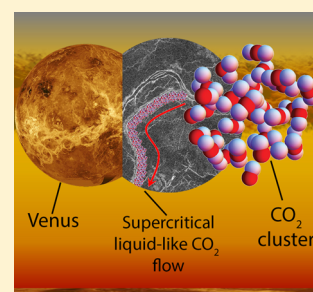
[‡]Volgograd State Technical University, Volgograd, 400005 Russia

[¶]Queen Mary University of London, Mile End Road, London E1 4NS, United Kingdom

[§]Brookhaven National Laboratory, Upton, New York 11973, United States

ABSTRACT: Here, we study structural properties of the supercritical carbon dioxide and discover the existence of persistent medium-range order correlations, which make supercritical carbon dioxide nonuniform and heterogeneous on an intermediate length scale. We report on the CO₂ heterogeneity shell structure where, in the first shell, both carbon and oxygen atoms experience gas-like-type interactions with short-range order correlations while within the second shell, oxygen atoms essentially exhibit a liquid-like type of interactions due to localization of transverse-like phonon packets. Importantly, we highlight a catalytic role of atoms inside of the nearest-neighbor heterogeneity shell in providing a mechanism for diffusion and proving the existence of an additional thermodynamic boundary in the supercritical carbon dioxide on an intermediate length scale. Finally, we discuss important implications for answering the intriguing question whether Venus may have had CO₂ oceans and urge for an experimental detection of this persistent local-order heterogeneity.

SECTION: Liquids; Chemical and Dynamical Processes in Solution



Unlike the long-range order of ideal crystalline structures, local order is an intrinsic characteristic of soft matter materials and often serves as the key to the tuning of materials' properties and to developing their possible applications.^{1–4} Liquid materials often exhibit medium- and/or short-range order, such as nanoscale structural motifs, clustering, and local ordering at the level of the atomic coordination spheres. Describing this local order of soft matter systems and supercritical fluids in particular is crucial for understanding the origins of their material properties.

Theoretical understanding of the supercritical state is lacking and is seen as a bottleneck in the future development of industrial applications of supercritical fluids. Supercritical fluids have started to be employed in several important applications, ranging from the extraction of floral fragrance from flowers to applications in food science such as creating decaffeinated coffee, pharmaceuticals, polymers, cosmetics, functional food ingredients, powders, bio- and functional materials, natural products, nanosystems, biotechnology, fossil and biofuels, microelectronics, the energy, and the environment. The development of new experimental methods and the improvement of existing ones continues to play an important role in this field,^{5–10} with ongoing focus in elucidating and understanding the structure and properties of disordered matter such as glasses and liquids.^{11–18}

Supercritical CO₂ has been extensively studied in neutron, X-ray wide, and small-angle diffraction experiments,^{19,20} but all such experiments have been performed in very limited ranges of pressure and temperature so that any unusual properties of supercritical CO₂ that occur at elevated temperatures and pressures remain unobserved. Here, we focus on the structural properties of the supercritical carbon dioxide within a very wide

temperature range far beyond the critical point. On the basis of molecular dynamics simulations, we calculate partial pair distribution functions (PDFs) and partial static structure factors. We observe fascinating robust medium-range order correlations that make the supercritical CO₂ nonuniform on an intermediate length scale. Therefore, the persistent structural local-order heterogeneity (see Figure 1) challenges the currently held belief that the supercritical state is uniform and homogeneous in terms of physical properties.²¹

Using DL-POLY molecular dynamics (MD) simulations, we have simulated a supercritical Buckingham fluid fitted to CO₂ properties.²² The intermolecular potential was obtained by fitting energies from the MP2 calculations.²³ The MP2 calculation was performed by NWchem code²⁴ and is consistent with experimental data (unpublished results). The potential is similar to the Williams potential.²⁵ The parameters in the Buckingham potential are presented in Table 1. We have simulated the system with 13728 atoms (4576 molecules) using a constant-volume (*NVE*) ensemble in a very wide temperature range (see Figures 2 and 3) extending well into the supercritical region; the system was equilibrated at constant temperature. The temperature range in Figures 2 and 3 is between about *T_c* and 33*T_c*, where *T_c* ≈ 304.1 K is the critical temperature of CO₂. The simulated density, 1195.1 kg/m³, corresponds to approximately three times the critical density of CO₂. A typical MD simulation lasted about 40 ps, and the properties were averaged over the last 20 ps of simulation preceded by 20 ps of equilibration. The

Received: June 12, 2014

Accepted: July 29, 2014

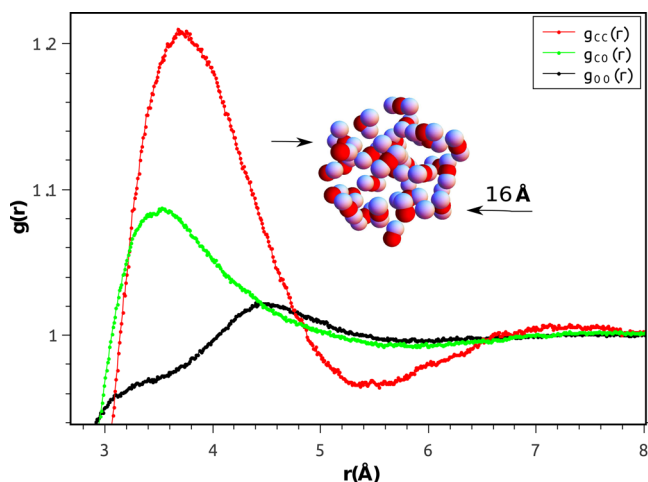


Figure 1. Inter-molecular partial PDFs of supercritical CO₂. Partial PDFs and an inset structure of a heterogeneity generated by molecular dynamics simulations at $T = 10000$ K. The inset heterogeneity, consisting of carbon atoms (red) and oxygen atoms (silver blue), was depicted from a simulated configuration.

Table 1. Buckingham Potential $\Phi(r) = Ae^{-r/\rho} - (C/r^6)^a$

atom	atom	A	ρ	C
C	O	1604.264900	0.265	12.60546
O	O	1918.857694	0.271389	22.275169
C	C	1532.056507	0.2778	0.000000

^aUnits Used: A [eV], ρ [Å], and C [eV·Å⁶].

simulations at different temperatures included 100 temperature points simulated on the 3000 processors of a high-throughput computing cluster. We calculate PDFs $g(r)$ and partial static structure factors $S(q)$, averaging the quantities over the last 20 ps of the simulation, and show the temperature evolution.

Particles in a gas move in almost straight lines until they collide with other particles or container walls and change course. In liquids, particle motion has two components, a solid-like, quasi-harmonic vibrational motion about equilibrium locations and diffusive jumps between neighboring equilibrium positions. As the temperature increases or the pressure decreases, a particle spends less time vibrating and more time diffusing. Eventually, the solid-like oscillating component of motion disappears, and all that remains is the ballistic-collisional motion. This qualitative change in particle dynamics corresponds to the smooth crossover at the Frenkel line and the disappearance of the medium-range order correlations at high temperatures.²⁶ The disappearance of the second peak in the $g(r)$ profile ($g_{CC}(r)$, $g_{CO}(r)$) in the CO₂ simulations, shown in Figure 2c,d, corresponds to such a Frenkel line crossover change in local structure. The same was seen in the one-component Lennard-Jones (LJ) supercritical fluid.²⁶ The distribution function $g_{OO}(r)$ (see Figure 2a,b) exhibits unconventional behavior where medium-range order correlations remain robust and prevail over the short-range order over a very wide temperature range. This effect we attribute to localization of transverse-like phonon modes, which we will discuss in detail below.

In order to explore the microscopic structure of supercritical CO₂, we calculate partial static structure factors $S(q)$ from corresponding PDFs. The total structure factor can be decomposed as a sum of partial contributions. These contributions are functions of the various properties that

characterize the material. Several methods exist to decompose the total $S(q)$. We calculated the partial structure factors using the method developed by Faber and Ziman.²⁷ In this approach, the structure factor is decomposed following the correlations between the different chemical species. To describe the correlation between the α and the β chemical species, the partial structure factor $S_{\alpha\beta}^{\text{FZ}}(q)$ is defined as

$$S_{\alpha\beta}^{\text{FZ}}(q) = 1 + 4\pi\rho \int_0^{R_{\text{max}}} dr r^2 \frac{\sin qr}{qr} (g_{\alpha\beta}(r) - 1) \quad (1)$$

where the $g_{\alpha\beta}(r)$ are the partial PDFs and the parameter $R_{\text{max}} = 20$ Å in our calculations.

In the limiting case of no interactions, the system is an ideal gas, and the structure factor is completely featureless, $S(q) = 1$. There is no correlation between the positions \mathbf{r}_j and \mathbf{r}_k of different particles (they are independent random variables); therefore, the off-diagonal terms in the structure factor

$$S(q) = 1 + \frac{1}{N} \left\langle \sum_{j \neq k} e^{-i\mathbf{q}(\mathbf{r}_j - \mathbf{r}_k)} \right\rangle \quad (2)$$

average to zero, that is

$$\langle \exp[-i\mathbf{q}(\mathbf{r}_j - \mathbf{r}_k)] \rangle = \langle \exp(-i\mathbf{q}\mathbf{r}_j) \rangle \langle \exp(i\mathbf{q}\mathbf{r}_k) \rangle = 0 \quad (3)$$

Even for interacting particles at a high scattering vector, the structure factor goes to 1. This result follows from the equation $S(q) = 1 + \rho \int_V d\mathbf{r} e^{-i\mathbf{q}\mathbf{r}} g(r)$ because $S(q) - 1$ is the Fourier transform of the “regular” function $g(r)$ and thus goes to zero at high values of q . This reasoning does not hold for a perfect crystal where the distribution function exhibits infinitely sharp peaks.

The whole shape of the nearest-neighbor intermolecular correlations in the supercritical CO₂ changes with temperature, and this change results in the variation of the ratio of peak heights, positions, and widths of the O–O, C–C, and C–O partial static structure factors; see Figure 3a–d. Importantly, $S(q)$ peaks are predicted to change differently with temperature in this picture. Indeed, in the low-temperature regime, $S_{OO}(q)$, $S_{CC}(q)$, and $S_{CO}(q)$ peaks decrease rapidly and undergo the smooth crossover, clearly seen in Figure 3b. On the other hand, in the high-temperature regime, correlations are less sensitive to temperature increase because the dynamics is already randomized by ballistic motions as in a gas. While $S_{OO}(q)$ also exhibits collective excitations at higher q values, it retains the static structure profile as in a liquid.

The unusual behavior of $g_{OO}(r)$ discussed above leads to a very important implication; the system exhibits medium-range order correlations. It has been previously shown^{28–30} that when the liquid relaxation time τ (the average time between two consecutive atomic jumps at one point in space^{31–34}) approaches its minimal value τ_D , the Debye vibration period, the system loses the ability to support propagating high-frequency shear modes with $\omega > (2\pi/\tau)$ and therefore behaves like a gas.³⁵ The inability to support propagating shear modes in the system results in the absence of the second $g_{CC}(r)$ and $g_{CO}(r)$ peaks (see Figure 2c,d), while the presence of the second $g_{OO}(r)$ peak at high temperatures is attributed to robust localized transverse-like phonon excitations, making the supercritical CO₂ nonuniform on an intermediate length scale. The persistent local-order heterogeneity is evidenced by the presence of the structured peaks in $g_{OO}(r)$ and $S_{OO}(r)$ (see Figure 4a,b) over the wide temperature range, the new effect hitherto unanticipated, in view of the currently perceived physical uniformity and homogeneity of the supercritical state.

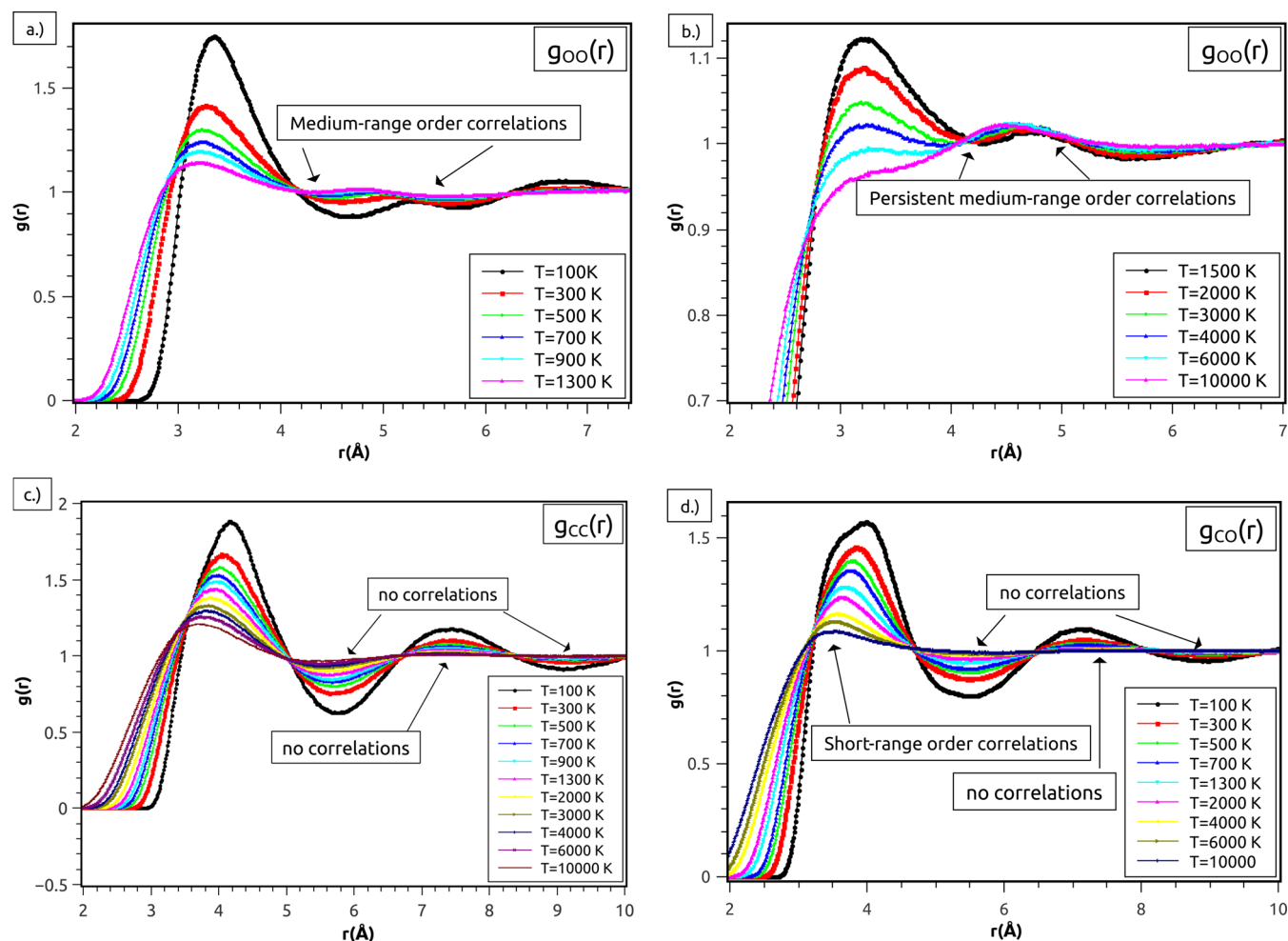


Figure 2. Structural evolution in real space. Evolution of intermolecular partial PDFs. A sharpening of the O–O correlations on an intermediate length scale arising from increased orientational ordering of the supercritical CO₂ fluid.

We emphasize that a strong correlation exists between the atomic structure evolution of first and second coordination shells with oxygen atoms over a wide temperature range (see Figure 2a,b). The positions of both shells consistently change with temperature. The number of oxygen atoms in the second shell (see Figure 4a) is essentially constant at high temperature, while the number of atoms in the first shell constantly reduces due to diffusion. Therefore, atoms inside of the nearest-neighbor heterogeneity shell play a catalytic role in providing a mechanism for diffusion in supercritical carbon dioxide on an intermediate length scale.

The results reported thus far in this work not only provide crucial evidence of an additional thermodynamic boundary in the supercritical regime of CO₂ but lead to very intriguing implications for the field of planetary science, specifically for studies of Venus's atmosphere, which mainly consists of CO₂. The planet Venus, now unbearably hot and dry, may have once been far more like Earth, with oceans and continents. Our knowledge concerning the surface of Venus comes from a limited amount of information, some obtained by the series of landers and probes but primarily from extensive radar imaging of the planet. Venus is a planet that is similar to Earth in terms of some significant planetary parameters (size, mass, presence of atmosphere) and different in terms of other equally important parameters (absence of an intrinsic magnetic field, large atmospheric mass, carbon dioxide composition of the atmos-

phere, lack of water, very high surface pressure and temperature). Also, the surface of Venus has similar geological features found on Earth such as canyons, volcanoes, rift valleys, river-like beds, mountains, craters, and plains.³⁶ Such features are believed to originate from volcanic eruptions and lava flows; however, there is no direct proof of this hypothesis, which does not explain the creation of channels that are 1000 km long in Venusian crust in which lava supposedly selectively flowed.

Presently, the atmosphere of Venus is mostly CO₂, 96.5% by volume. It is believed that in the past, Venus may have had enough water in the atmosphere to cover the entire planet by an ocean 25 m deep. However, even if there was water, it was probably too warm for it to fall as rain and form oceans, and thus, much of the water remained in the atmosphere as well as other constituents including carbon dioxide. Model calculations show that the extensive volcanic activity that occurred during the early era might have also increased the abundance of gases like H₂O and SO₂ in the atmosphere, strengthening the greenhouse effect.³⁸ Although currently the surface pressure on Venus is 9.3 MPa and the surface temperature is 735 K, because of the abundance of CO₂, H₂O, and SO₂, the early surface pressure may have been a few tens of MPa.³⁹ At the same time, these conditions may have been accompanied by significant changes in pressure and temperature (300 K) over a relatively long time duration (100–200 million years), making it possible for liquid CO₂ to be formed in the vicinity of the Venus surface at very early

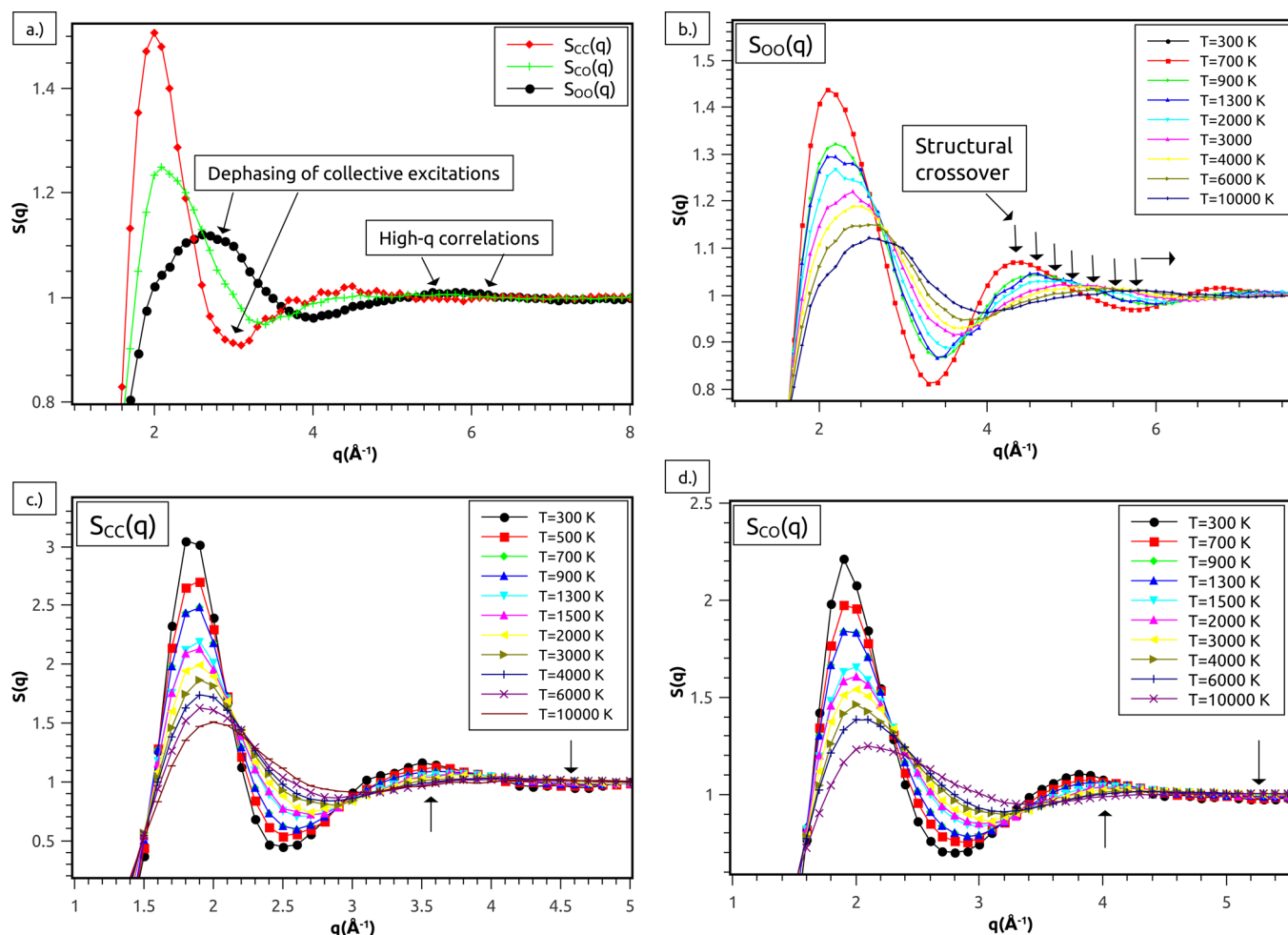


Figure 3. Structural evolution in reciprocal space. Evolution of the partial structure factors. $S_{OO}(q)$ undergoes structural monotonic crossover in reciprocal space across the Frenkel line.

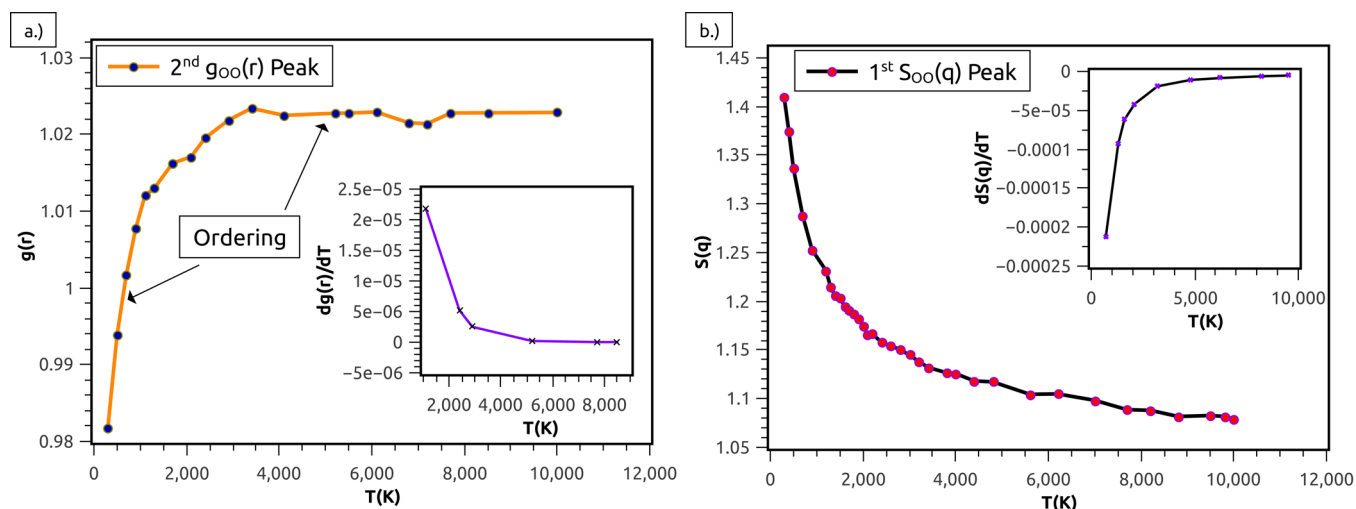


Figure 4. Ordering within disorder. Evolution of $g_{OO}(r)$ and $S_{OO}(r)$ peaks and their derivatives across the Frenkel line.

stages of the greenhouse effect era. To determine the location of the Frenkel line in CO_2 (see Figures 5 and 6) at given pressure and temperature conditions, we apply the same analysis as we used in our previous work for H_2 .⁴⁰ These conditions correspond to CO_2 above the Frenkel line where it exhibits liquid-like behavior. This in turn makes it plausible that such geological

features like rift valleys, river-like beds, and plains are the fingerprints of near-surface activity of liquid-like supercritical CO_2 .

Although the structural order of a fluid is usually enhanced by isothermal compression or isochoric cooling, a few notable systems show the opposite behavior. Specifically, increasing the

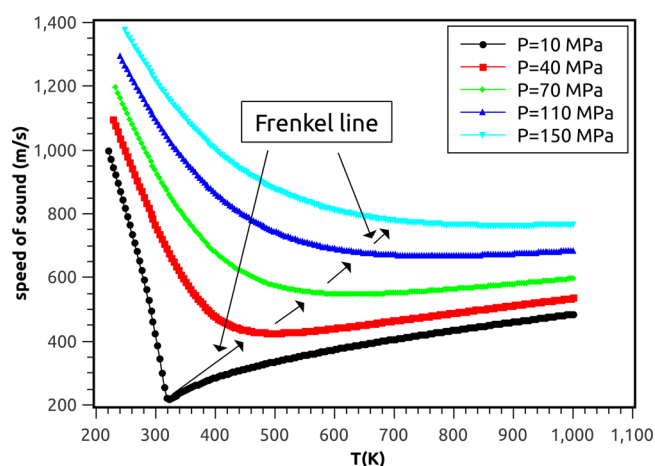


Figure 5. Representative dependencies of the speed of sound as a function of temperature. Supercritical CO₂ at different pressures. The data are from the NIST database.³⁷

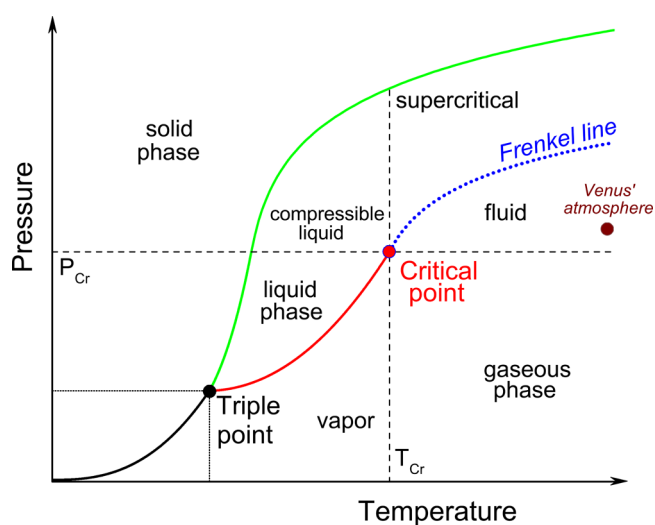


Figure 6. CO₂ pressure–temperature phase diagram. The surface pressure is 9.3 MPa, and the surface temperature is 735 K, above the critical points of both major constituents, making the Venus surface atmosphere a supercritical fluid.

density can disrupt the structure of liquid-like fluids, while lowering the temperature or strengthening of attractive interactions can weaken the correlations of fluids with short-range attractions. The structural order is a particularly insightful quantity to study because its contributions from the various coordination shells of the PDF can be readily determined, and it correlates strongly with self-diffusivity, which allows it to provide insights into the dynamic and structural anomalies of fluids.

In this work, we report on the carbon dioxide heterogeneity shell structure where, in the first shell, both carbon and oxygen atoms experience gas-like-type interactions with short-range order correlations while within the second shell, oxygen atoms essentially exhibit a liquid-like type of interactions with medium-range order correlations due to localization of transverse-like phonon packets. Therefore, the local-order heterogeneity remains in the three-phase-like equilibrium within a very wide temperature range. Atoms inside of the nearest-neighbor heterogeneity shell play a catalytic role due to short-range order interactions, providing a mechanism for diffusion in the supercritical CO₂ on an intermediate length scale. Hence,

persistent local-order heterogeneities in the supercritical carbon dioxide, due to their peculiar structures, might selectively swell particular nanodomains of block copolymers to produce nanocellular and nanoporous structures more efficiently than was seen before.

The emergence of local-order heterogeneities and the existence of localized transverse-like phonon modes are closely inter-related. From the phonon theory of liquid thermodynamics,³² we know that liquids support high-frequency propagating shear phonon modes but lose this ability with temperature increase, even extending well into the supercritical region. Oxygen atoms in the second shell define a boundary between propagating and localized phonon modes in the supercritical CO₂. A 6–8 Å value is estimated as the length scale for highly localized transverse-like phonon modes and also corresponds to the size of the heterogeneities where the phonon packets are localized (see Figures 1 and 2). Similarly, the propagating lengths of the transverse acoustic modes were determined to be 4–10 Å, corresponding to the size of cages formed instantaneously in liquid Ga³⁰ and liquid Sn.⁴¹ Thus, the supercritical state is also universally amenable to supporting fundamental interlinks between fundamental system properties such as structure and dynamics.

In summary, the results of this study support the emerging view that the supercritical state is nonuniform and heterogeneous, which can generally be attributed to quantifiable structural changes in the first and higher coordination shells of the partial PDFs and their corresponding static structure factors. Away from the critical point, the structure of the PDFs typically persists for distances comparable to a few particle diameters, reflecting the short range of the interparticle correlations. The existence of persistent medium-range order correlations in the supercritical CO₂ has not been hitherto anticipated and is contrary to how the supercritical state has been viewed until now.

Our results call for experimental observation of the persistent local-order heterogeneities. This observation would not only prove the existence of an additional thermodynamic boundary in the supercritical state, it would provide compelling evidence that supercritical liquid-like carbon dioxide may have influenced the formation of the current geological map of Venus.

AUTHOR INFORMATION

Corresponding Author

*E-mail: d.bolmatov@gmail.com or db663@cornell.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

D.B. thanks Ben Widom and Cornell University for support. M.G. thanks Martin Dove for intermolecular potential modelling assistance. Brookhaven National Laboratory is supported under U.S. D.O.E. Grant No. DE-AC02-98CH10886. We are grateful to Ben Widom, Neil Ashcroft, Martin Dove, Zeb Kramer, and Colin Wilson for fruitful discussions. We acknowledge the use of data products or imagery from the Magellan Venus Explorer system operated by the NASA with funding provided by NASA/HQ.

REFERENCES

- (1) Ziman, J. M. *Models of Disorder: The Theoretical Physics of Homogeneously Disordered Systems*; Cambridge University: Cambridge, U.K., 1979.

- (2) Giordano, V. M.; Monaco, G. Fingerprints of order and disorder on the high-frequency dynamics of liquids. *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 21985–21989.
- (3) Widmer-Cooper, A.; Perry, H.; Harrowell, P.; Reichman, D. R. Irreversible reorganization in a supercooled liquid originates from localized soft modes. *Nat. Phys.* **2008**, *4*, 711–715.
- (4) Hedges, L. O.; Jack, R. L.; Garrahan, J. P.; Chandler, D. Dynamic order–disorder in atomistic models of structural glass formers. *Science* **2009**, *323*, 1309–1313.
- (5) Kolesov, B. A. Experimental determination of vibrational anharmonic contributions. *J. Raman Spectrosc.* **2003**, *44*, 1786–1787.
- (6) Wikfeldt, K. T.; Huang, C.; Nilsson, A.; Pettersson, L. G. M. Enhanced small-angle scattering connected to the Widom line in simulations of supercooled water. *J. Chem. Phys.* **2011**, *134*, 214506.
- (7) Cunsolo, A.; Kodituwakku, C. N.; Bencivenga, F.; Said, A. H. Shear propagation in the terahertz dynamics of water-glycerol mixtures. *J. Chem. Phys.* **2013**, *139*, 184507.
- (8) Heo, Y.; Bratescu, M. A.; Aburaya, D.; Saito, N. A phonon thermodynamics approach of gold nanofluids synthesized in solution plasma. *Appl. Phys. Lett.* **2014**, *104*, 111902.
- (9) Bolmatov, D.; Musaev, E. T.; Trachenko, K. Symmetry breaking gives rise to energy spectra of three states of matter. *Sci. Rep.* **2013**, *3*, 2794.
- (10) Bolmatov, D. Equations of state for simple liquids from the gaussian equivalent representation method. *J. Stat. Phys.* **2009**, *137*, 765–773.
- (11) Tröster, P.; Tavan, P. The microscopic physical cause for the density maximum of liquid water. *J. Phys. Chem. Lett.* **2014**, *5*, 138–142.
- (12) Orr-Ewing, A. J.; Glowacki, D. R.; Greaves, S. J.; Rose, R. A. Chemical reaction dynamics in liquid solutions. *J. Phys. Chem. Lett.* **2011**, *2*, 1139–1144.
- (13) Caplan, M. E.; Giri, A.; Hopkins, P. E. Analytical model for the effects of wetting on thermal boundary conductance across solid/classical liquid interfaces. *J. Chem. Phys.* **2014**, *140*, 154701.
- (14) Giri, A.; Hopkins, P. E. Spectral analysis of thermal boundary conductance across solid/classical liquid interfaces: a molecular dynamics study. *Appl. Phys. Lett.* **2014**, *105*, 033106.
- (15) Hecksher, T.; Nielsen, A. I.; Olsen, N. B.; Dyre, J. C. Little evidence for dynamic divergences in ultraviscous molecular liquids. *Nat. Phys.* **2008**, *4*, 737–741.
- (16) Patel, A. B.; Bhatt, N. K.; Thakore, B. Y.; Vyas, P. R.; Jani, A. R. Temperature dependent atomic transport properties of liquid Sn. *Eur. Phys. J. B* **2014**, *87*, 39.
- (17) Holten, V.; Anisimov, M. A. Entropy driven liquid–liquid separation in supercooled water. *Sci. Rep.* **2012**, *2*, 713.
- (18) Shintani, H.; Tanaka, H. Universal link between the boson peak and transverse phonons in glass. *Nat. Mater.* **2008**, *7*, 870–877.
- (19) Ishii, R.; Okazaki, S.; Okada, I.; Furusaka, M.; Watanabe, N.; Misawa, M.; Fukunaga, T. Density dependence of structure of supercritical carbon dioxide along an isotherm. *J. Chem. Phys.* **1996**, *105*, 7011.
- (20) Blanchard, L. A.; Hancu, D.; Beckman, E. J.; Brennecke, J. F. Green processing using ionic liquids and CO₂. *Nature* **1999**, *399*, 28–29.
- (21) Kiran, E.; Debenedetti, P. G.; Peters, C. J. *Supercritical Fluids: Fundamentals and Applications*, NATO Science Series E: Applied Sciences 366; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2000.
- (22) Dove, M. T. *Structure and Dynamics: An Atomic View of Materials*; Oxford Master Series in Condensed Matter Physics; Oxford, U.K., 2003.
- (23) Möller, C.; Plesset, M. S. Note on an approximation treatment for many-electron systems. *Phys. Rev.* **1934**, *46*, 618–622.
- (24) Valiev, M.; Bylaska, E. J.; Govind, N.; Kowalski, K.; Straatsma, T. P.; van Dam, H. J. J.; Wang, D.; Nieplocha, J.; Apra, E.; Windus, T. L.; de Jong, W. A. NWChem: a comprehensive and scalable open-source solution for large scale molecular simulations. *Comput. Phys. Commun.* **2010**, *181*, 1477–1489.
- (25) Williams, D. E. Improved intermolecular force field for molecules containing H, C, N, and O atoms, with application to nucleoside and peptide crystals. *J. Comput. Chem.* **2001**, *22*, 1154–1166.
- (26) Bolmatov, D.; Brazhkin, V. V.; Fomin, Y. D.; Ryzhov, V. N.; Trachenko, K. Evidence for structural crossover in the supercritical state. *J. Chem. Phys.* **2013**, *139*, 234501.
- (27) Faber, T. E.; Ziman, J. M. A theory of the electrical properties of liquid metals. *Phil. Mag.* **1965**, *11*, 153–173.
- (28) Pilgrim, W. C.; Morkel, C. State dependent particle dynamics in liquid alkali metals. *J. Phys.: Condens. Matter* **2006**, *18*, R585.
- (29) Sette, F.; Krisch, M. H.; Masciovecchio, C.; Ruocco, G.; Monaco, G. Dynamics of glasses and glass-forming liquids studied by inelastic X-ray scattering. *Science* **1998**, *280*, 1550–1555.
- (30) Hosokawa, S.; Inui, M.; Kajihara, Y.; Matsuda, K.; Ichitsubo, T.; Pilgrim, W. C.; Sinn, H.; Gonzales, L. E.; Gonbzaes, D. J.; Tsutsui, S.; et al. Transverse acoustic excitations in liquid Ga. *Phys. Rev. Lett.* **2009**, *102*, 105502.
- (31) Frenkel, J. In *Kinetic Theory of Liquids*; Fowler, R. H., Kapitza, P., Mott, N. F., Eds.; Oxford University Press: Oxford, U.K., 1947.
- (32) Bolmatov, D.; Brazhkin, V.; Trachenko, K. The phonon theory of liquid thermodynamics. *Sci. Rep.* **2012**, *2*, 421.
- (33) Bolmatov, D.; Trachenko, K. Liquid heat capacity in the approach from the solid state: anharmonic theory. *Phys. Rev. B* **2011**, *84*, 054106.
- (34) Bolmatov, D.; Brazhkin, V.; Trachenko, K. Helium at elevated pressures: quantum liquid with non-static shear rigidity. *J. Appl. Phys.* **2013**, *113*, 103514.
- (35) Bolmatov, D.; Brazhkin, V.; Trachenko, K. Thermodynamic behavior of supercritical matter. *Nat. Commun.* **2013**, *4*, 2331.
- (36) Bray, V. J.; Bussey, D. B. J.; Ghail, R. C.; Jones, A. P.; Pickering, K. T. Meander geometry of Venusian canali: constraints on flow regime and formation time. *J. Geophys. Res.* **2007**, *112*, E04S05.
- (37) Lemmon, E. W.; McLinden, M. O.; Friend, D. G. Thermophysical Properties of Fluid Systems, In *NIST Chemistry WebBook*; Linstrom, P. J., Mallard, W. G., Eds.; NIST Standard Reference Database Number 69; National Institute of Standards and Technology: Gaithersburg, MD; <http://webbook.nist.gov> (retrieved January 25, 2014).
- (38) Hashimoto, G. L.; Roos-Serote, M.; Sugita, S.; Gilmore, M. S.; Kamp, L. W.; Carlson, R. W.; Baines, K. H. Felsic highland crust on Venus suggested by Galileo near-infrared mapping spectrometer data. *J. Geophys. Res.* **2008**, *113*, E00B24.
- (39) Urey, H. C. *The Planets, Their Origin and Development*; Yale Univ. Press: New Haven, CT, 1952.
- (40) Trachenko, K.; Brazhkin, V. V.; Bolmatov, D. Dynamic transition of supercritical hydrogen: defining the boundary between interior and atmosphere in gas giants. *Phys. Rev. E* **2014**, *89*, 032126.
- (41) Hosokawa, S.; Munejiri, S.; Inui, M.; Kajihara, Y.; Pilgrim, W. C.; Ohmasa, Y.; Tsutsui, S.; Baron, A. Q. R.; Shimojo, F.; Hoshino, K. Transverse excitations in liquid Sn. *J. Phys.: Condens. Matter* **2013**, *25*, 112101.