SVI-6

超臨界流体プラズマの基礎と応用
－自然界が創る気液ナノ混相場でのプラズマ－
Basics and Applications of Supercritical Fluid Plasmas
- Presents from the Nature ; Plasmas in the multiphase field of gas and liquid on the nanoscale -

寺嶋和夫、シュタウス スベン、宗岡　均
Kazuo Terashima, Sven Stauss, and Hitoshi Muneoka

東京大学　大学院新領域創成科学研究科
The Univ Tokyo, Graduate School of Frontier Sciences

Supercritical fluids (SCFs) (Fig. 1) are media in a state of temperature and pressure above their respective critical values, *T; T*$_{crit}$, *p; p*$_{crit}$. From a macroscopic point of view, SCFs are in an intermediate state between liquid and gas. SCFs possess high density, high diffusivity, high solubility, and they have been used in a wide range of applications. These excellent reaction process characteristics derive from the microscopic fluid structure in SCFs —molecular clustering. In the vicinity of the critical point, because of balancing of van der Waals' forces and thermal motion, molecules aggregate and disperse in the order of pico-seconds, so that the density fluctuates greatly. Around the critical point, the compressibility is greatly enhanced. This compressibility region is not limited to the region where $T > T_{crit}$ and $p > p_{crit}$, but reaches also in the liquid domain. In addition, it has been found that passed the critical point, the supercritical phase above show either gas-like or liquid-like behaviour. In the case of the isothermal compressibility, this line is called Widom line and it has been shown that clusters above or below the Widom line show either liquid-like or gas- like behavior and structure. Clusters in SCF solutions are different from those in solids or liquids. The interactions between molecules in a cluster is governed by relatively weak forces, such as Van der Waals force. On the time scale, the average lifetime of a cluster is much shorter than in solids or liquids of the order of picoseconds (ps, 10^{-12} s). In addition, in the vicinity of the critical point (T_{crit}, p_{crit}), where the thermal conductivity and specific heat attain their maximum values, it is expected that new types of reactions involving clusters can be used and that by changing the conditions of the SCF medium, the selectivity of reactions can be adjusted. For example, it has been shown that the reaction rate in supercritical fluids is enhanced near the critical point.

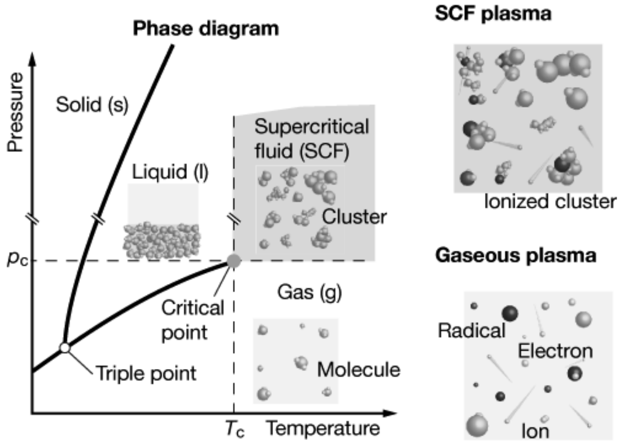

Fig.1 Supercritical fluid (SCF) & SCF Plasma
The phase diagram of pure substance and illustration of species present in SCF and gaseous plasmas.

Therefore, plasmas generated in supercritical fluids (Fig. 1) contain excited species such as radical and ion clusters, in addition to electrons, ions and radicals present normally in conventional gaseous plasmas. In combination with the advantageous properties of supercritical fluids (i.e. high density, high diffusivity, high thermal conductivity, low surface tension, molecular clustering and density fluctuation near the critical point), this allows to realize new reaction fields which can be used for the synthesis of nanomaterials.

So far, plasmas generated in supercritical fluids have permitted the synthesis of carbon nanomaterials such as carbon nanotubes, under more moderate conditions of temperature and pressure compared to supercritical fluid processing without plasma, while high-density dielectric barrier discharge and pulsed laser plasmas have allowed the synthesis of various molecular diamonds, so-called diamondoids (Fig. 2), including novel ones.

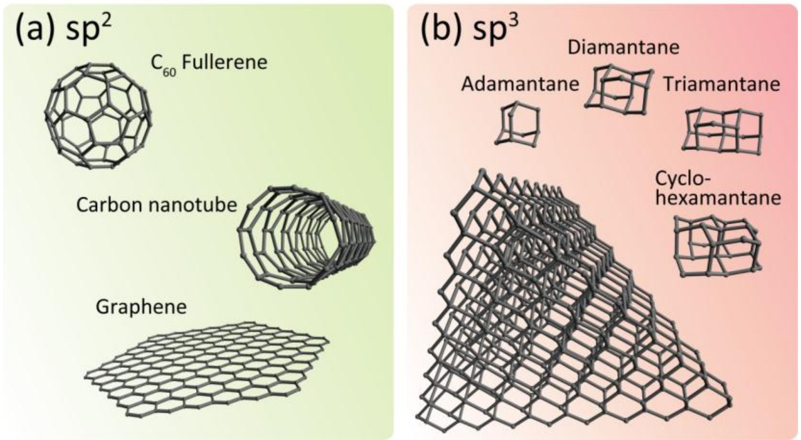

Fig.2 Carbon nanomaterials. (a)sp^2 materials (C_{60}, carbon nanotube and grapheme), (b)sp3 materials (diamondoid and diamond).

Diamondoids are sometimes referred to as the fourth carbon nano-material following (1) fullerenes, (2) carbon nanotubes, and (3) graphenes. They are expected to play an increasingly important role in many fields such as pharmaceutics, electronics and display technology.

In this talk, we highlight the research on plasmas in supercritical fluids, their generation, either by electric discharges or lasers, and their main characteristics. In addition their differences in comparison to gaseous plasmas is discussed. Finally, we discuss further opportunities of plasmas generated in supercritical fluids and their relation with other ionized states of matter .

References

1) T. Ito & K. Terashima, Appl. Phys. Lett., **80**, 2854-2856 (2002).
2)T. Ito, H. Fujiwara & K. Terashima, J. Appl. Phys., **94**, 5411-5415 (2003).
3) T. Ito, K. Katahira, Y. Shimizu, T. Sasaki, N. Koshizaki & K. Terashima, J. Mater.Chem., **14**, 1513-1515 (2004).
4) M. Sawada, T. Tomai, T. Ito, H. Fujiwara, & K. Terashima, J. Appl. Phys., **100**, 123305 (5) (2006).
5) T. Tomai, T. Ito & K. Terashima, Thin Solid Films,**506–507**,409-414 (2006).
6) T. Tomai, K. Katahira, H. Kubo, Y. Shimizu, T. Sasaki, N. Koshizaki & K. Terashima, J . Supercritical Fluids, **41**, 404-411(2007).
7) H. Kikuchi, H. Kubo, T. Tomai & K. Terashima, Thin Solid Films, **51, 6**6677-6682 (2008).
8) T. Tomai, H. Yui, & K. Terashima, Appl. Phys. Lett. **94**, 151501(3) (2009).
9)プラズマ核融合学会誌 2010 年 6 月号「超臨界流体環境下でのプラズマ」の小特集
宮副裕之、シュタウス・スベン、寺嶋和夫. *J. Plasma Fusion Res.* **86**, 305–311 (2010).
10) S.Nakahara, S.Stauss, H.Miyazoe, T.Shizuno, M.Suzuki, H.Katakoka, T.Sasaki, & K.Terashima, *Appl. Phys. Express* **3**, 096201–1–3 (2010).
11) S.Stauss, H.Miyazoe, T.Shizuno, K.Saito, T.Sasaki & K.Terashima, *Jpn. J. Appl.Phys*. **49**, 070213–1–3 (2010).
12) H.Kikuchi, S. Stauss, S.Nakahara, K. Matsubara, T. Tomai, T. Sasaki, K. Terashima, *J. Supercrit. Fluids* (refereed) **55**, 325–332 (2010).
13) T.Shizuno, H.Miyazoe, K.Saito, S.Stauss, M.Suzuki, T.Sasaki & K.Terashima *Jpn. J. Appl. Phys.* **50**, 030207-1-3 (2011).
14) S.Nakahara, S.Stauss, T.Kato, T. Sasaki, & K.Terashima. *J. Appl. Phys.*, **109**, 123304-1-8 (2011).
15) F.Oshima., S.Stauss, C.Ishii, D.Z.Pai & K.Terashima, *J. Phys. D* **45**, 402003-1-5 (2012).
16) D.Lacoste, H.Muneoka, D.Z. Pai, S.Stauss & K.Terashima, *Plasma Sources Sci. Technol.* , **21**, 052003-1-4 (2012)