Physics 563 Term Paper

Liquid-Liquid Phase Transition

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1   Introduction

In recent experiments, it was found that a single-component liquid may have two or more kinds of liquid states, different in density. The transition between them is called "liquid-liquid phase transition"(LLPT). Many liquids were found to have this interesting phenomenon. Theorists argue a physical picture that all liquids have locally favored structures, which compete with normal-liquid structures, i.e. liquids may choose to behave as what they prefer under specific condition. In this paper, I'd like to give four experimental examples of LLPT, and then talk about a theoretical view, which suggests a "cooperative medium-range bond ordering" in liquid and introduces a "bond order parameter" to describe the existence of the critical point of LLPT. [1]

2   Observed phenomena about LLPT

2.1 Al_2O_3-Y_2O_3

Al_2O_3-Y_2O_3 system is an important industrial and technological material. The garnet $Y_3Al_5O_{12}$ belongs to this. S. Aasland and P. F. McMillan observed in the supercooled melt of Al_2O_3-Y_2O_3 that two liquid phases with the same components coexist just above the glass transition at ambient pressure. [2]

The liquid with 24-32 mol% Y_2O_3 could be supercooled to hundreds degrees below the liquidus (1300-1400°C) without changing the liquid phase. When continuing cooling the supercooled liquid at the rate of 300-400 degree/sec, however, two kinds of glasses could be quenched - one (glassy inclusions) formed as bubbles in the other (glassy matrix) (see Fig.[1]). Glassy inclusions have lower mass density and lower refractive index compared with the glassy matrix, but both of them have the same composition.

The properties of glasses indicate the coexistence of two liquids with the same composition but different density before quenching, which is an evidence of LLPT of Al_2O_3-Y_2O_3 system.
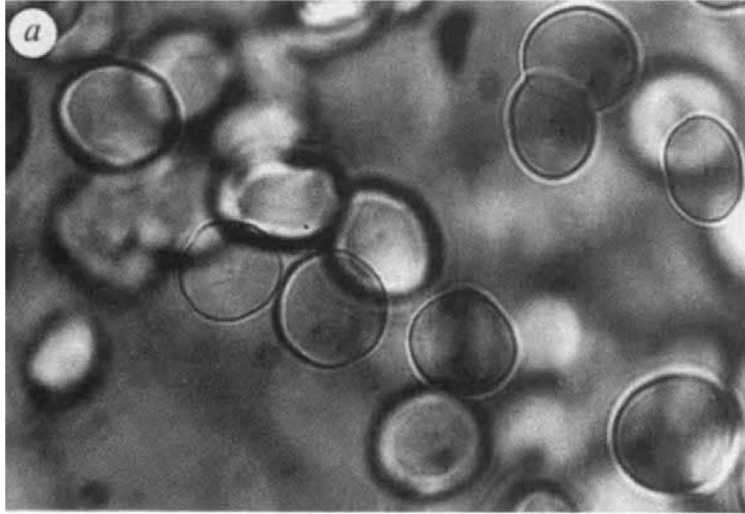
Figure 1: (from ref. [2])A micrograph of the Al_2O_3-Y_2O_3 sample in the glass-forming region. The bubbles are the glassy inclusions, and the background is the glassy matrix. The size of the field of view is about $100 \times 150\mu m$.

2.2 Carbon

M. Togaya measured the melting temperature of graphite and the electrical resistivity of liquid carbon at various pressure. [3] According to his result, the melting line of graphite has a maximum of 4790K at 5.6 GPa(see Fig.[2], left). The slope of the melting line changes sign at the maximum point, which point out a probability of a first-order phase transition in liquid carbon. Besides, the electrical resistivity of liquid carbon behaves irregularly near the critical point, which indicates a change in electrical state followed by a structural phase transition(see Fig.[2], right).

Also, J. N. Glosli and F. H. Ree use atomistic simulation methods and Brenner's bond order potential to get the critical point of LLPT in liquid carbon [4]. Their result is the first unempirical evidence of LLPT between thermodynamically stable fluids.
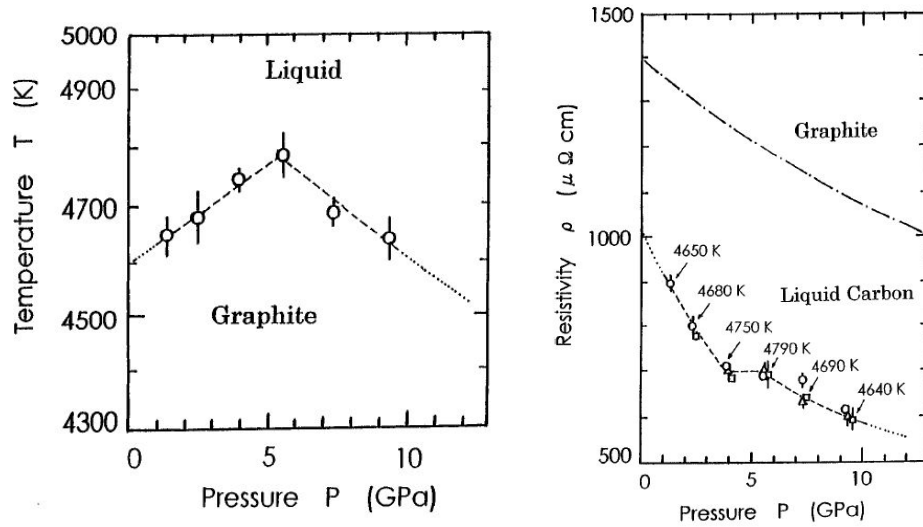
Figure 2: (from ref. [3])Left: melting temperature of graphite vs pressure. Right: Electrical resistivity of liquid carbon with pressure along the melting line.
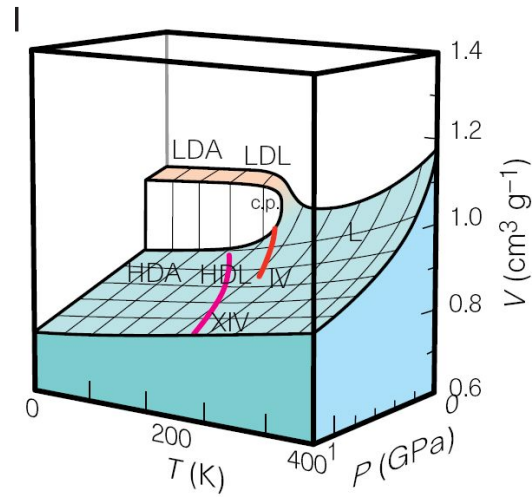

Figure 3: (from ref. [5])Phase diagram of water, including a critical point, and the high density liquid(HDL), low density liquid(LDL), high density amorphous(HDA), and low density amorphous(LDA) , ice IV, ice XIV, and normal liquid(L) phases.

2.3 Water

The physical behavior of liquid water is mysterious and complicated. The understanding of all the anomalies of this liquid is still incomplete. Some of these anomalies happen in the supercooled region. O. Mishima and H. E. Stanley found the melting line of ice IV encounter a discontinuity at pressure $P_c \approx 0.1$ GPa and temperature $T_c \approx 220$K, where a LLPT is proposed.(see Fig.[3]) [5]

2.4 Phosphorus

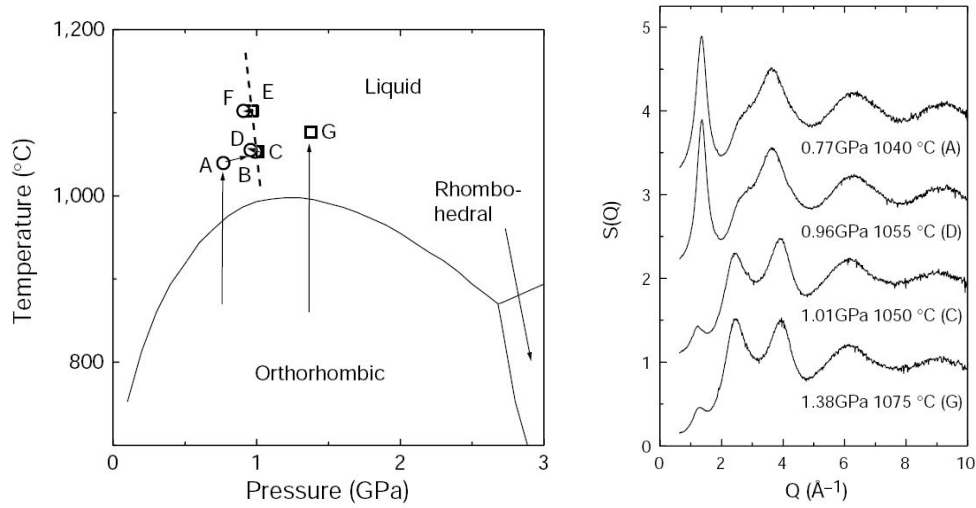Figure 4: (from ref. [6])Left: A phase diagram of black P. Right: Structure factor, $S(Q)$, for liquid P at several presure, suggesting a existense of phase transition at 0.96-1.01GPa and 1050-1055°C.

Solid phosphorus is known to have some allotropes, such as white P that comprises tetrahedral P_4 molecules and red P that is amorphous. Similarly, liquid phosphorus could have different structures. Besides the molecular liquid which consist of tetrahedral P_4 molecules, Y. Katayama etc. found a polymeric form of liquid phosphorus. [6]

4

In phase diagram, the melting curve of black P (layered structure) reaches its maximum around 1000°C and 1 GPa(see Fig.[4], left). The measurement of structure factor also shows an obvious difference below and above 1 GPa (see Fig.[4], right). Furthermore, from the X-ray diffraction patterns it can be seen clearly that the low-pressure form of liquid phosphorus transforms to the high-pressure form of liquid phosphorus directly, and that both phases coexist during the transition process.

3   A theoretical view of LLPT

3.1   Cooperative medium-range ordering

In general, density ρ is taken as the only order parameter of gas-liquid phase transition. However, the evidence of LLPT tells us there are at least two order parameters. Considering the local structure of liquid, or cooperative medium-range ordering, which is due to packing effects and specific symmetry-selective interactions, we can introduce another parameter, called a bond order parameter. [1] The density parameter and the bond order parameter are both needed for the full physical picture of view. The former tends to lower the interaction energy of long-range ordering and leads to crystallization, which usually increases the density, while the later tries to lower the interaction energy of medium-range ordering and causes the formation of local favored structures, which usually decreases the density.

Such two kinds of ordering compete with each other. We can build a two-state model that successfully gives the possibility of LLPT.

3.2   A two-state model

The definition of the bond order parameter, $S(\mathbf{r})$, can be the local fraction of locally favored structures in a small volume near a point $\mathbf{r}$. Let E_i, v_i, and g_i be the energy, specific volume, and degeneracy of the i state. $i = \rho$
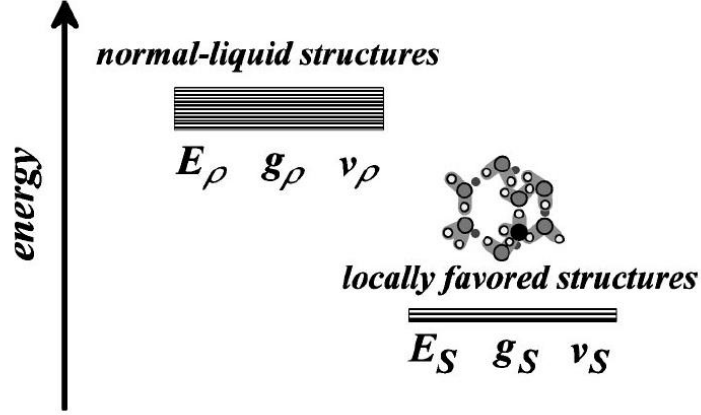
Figure 5: (from ref. [1])Schematic figure representing the energy levels of normal-liquid and locally favored structures.

is for the state of normal liquid structures, and $i = S$ is for locally favored structures. Generally speaking, $E_S < E_\rho$, $v_S > v_\rho$, and $g_S \gg g_\rho$.(see [Fig. 5])

The entropy σ of the system is

$$\sigma(S) = -k_B[S \ln \frac{S}{g_S} + (1 - S) \ln \frac{1 - S}{g_\rho}] \tag{1}$$

The energy with cooperative effects up to the second order terms is

$$U = SE_S + (1 - S)E_\rho + JS(1 - S) \tag{2}$$

Note $J > 0$, because the structure units prefer to be neighbors with those of the same type rather than those of the different type. The Gibbs' free energy is hence calculated as

$$
\begin{aligned}
f(S) &= U - T\sigma + [Sv_S + (1 - S)v_\rho]P \\
&= SE_S + (1 - S)E_\rho + [Sv_S + (1 - S)v_\rho]P \\
&\quad + k_BT[S \ln \frac{S}{g_S} + (1 - S) \ln \frac{1 - S}{g_\rho}] + JS(1 - S) \tag{3}
\end{aligned}
$$

6

The critical point satisfies the conditions $f_S'(S_c) = 0$, $f_S''(S_c) = 0$, $f_S^{(3)}(S_c) = 0$, and $f_S^{(4)}(S_c) > 0$. A first-order phase transition can happen at temperature $T_t < T_c$. T_t and pressure P obey

$$T_t = \frac{\Delta E - P \Delta v}{\Delta \sigma} \tag{4}$$

where $\Delta E = E_\rho - E_S > 0$, $\Delta v = v_S - v_\rho$, and $\Delta \sigma = k_B \ln(g_\rho/g_S) > 0$. The sign of the slope of $T_t(P)$ is determined by Δv.

3.3   Possible types of LLPT

Let's focus on the different types of phase diagram of the two-state system, which can be classified by the value of ΔE and J. Each type corrresponds to a real physical system.
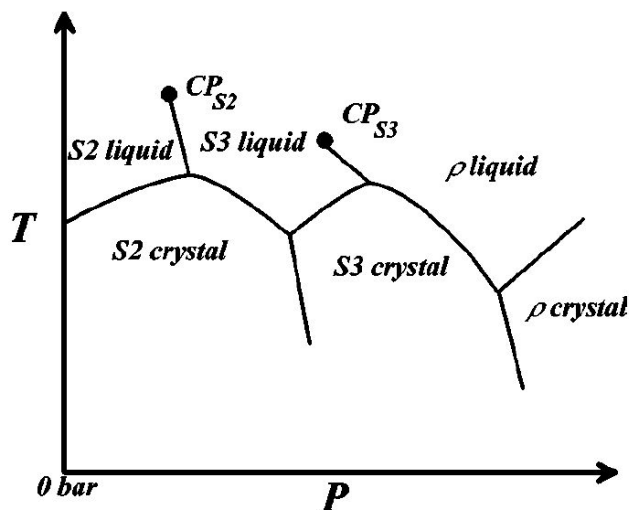
3.3.1   Liquid with large ΔE and J

Figure 6: (from ref. [1])Schematic P-T phase diagram of a liquid with large ΔE and J such as liquid carbon.

7

Phosphorus and carbon are such materials having large ΔE and J. As far as carbon is concerned(see Fig.[6]), there exist several locally favored structures, corresponding to $sp(S_1)$, $sp_2(S_2)$, and $sp_3(S_3)$ bonding. CP_{S_2} and CP_{S_3} are critical points with respect to S_2 and S_3 ordering separately. The type of liquid changes continuously above the critical points. Below the critical point, there is a LLPT line with negative slope($\Delta v > 0$), connecting the critical point and the triple point. There should be S_1 liquid in a negative pressure region. In fact, the relation of the density of each phase is that S_2 liquid $< S_2$ crystal $< S_3$ liquid $< S_3$ crystal $< \rho$ liquid $< \rho$ crystal. For carbon, the S_2 crystal is graphite and the S_3 crystal is diamond. The melting line obeys the Clausius-Clapeyron relation. This diagram also predicts another critical point, CP_{S3}, which needs to be proved by experiments.
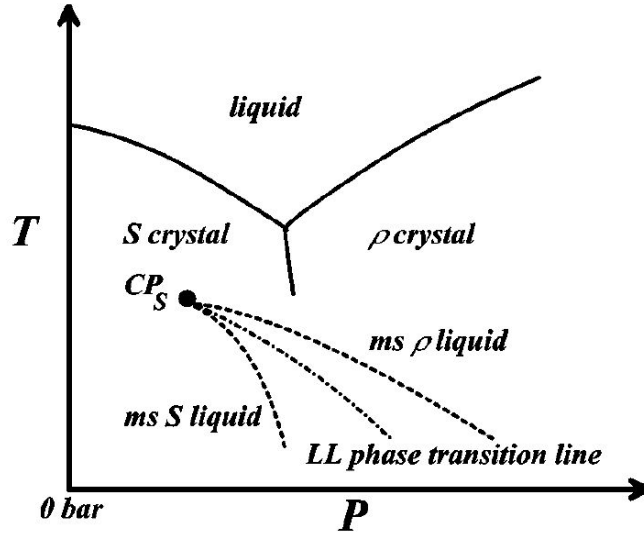
3.3.2 Liquid with intermediate ΔE and J

Figure 7: (from ref. [1])Schematic P-T phase diagram of a liquid with intermediate ΔE and J such as liquid water. ms means "metastable".

An example of a material with intermediate ΔE and J is water(see

Fig.[7]). The critical point and the LLPT line are below the melting line (in metastable state). S crystal is ice Ih, while ρ crystal corresponds to ices III, V, etc. The density of liquid state is higher than S crystal but lower than ρ crystal. Because of the hydrogen bonding, water molecules have a strong symmetry-selection tendency, and easily form locally favored structures. The van der Waals interaction, however, simply maximizes the density. Therefore there is a competition between ρ and S. Experiments and simulations suggest a critical point in the metastable region, corresponding to the description of this model.
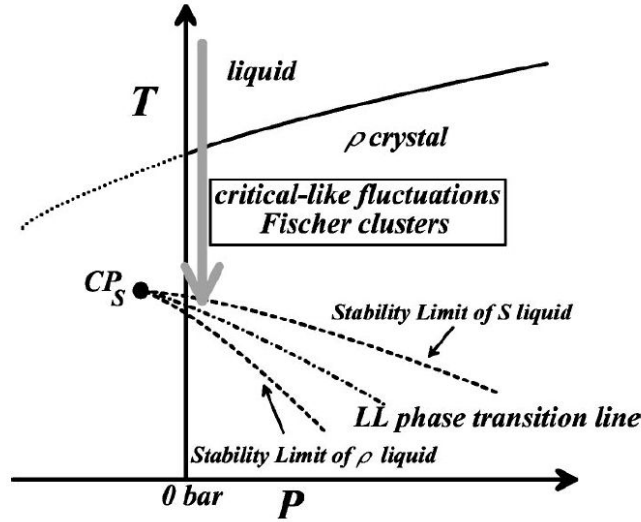
3.3.3   Liquid with small ΔE and J

Figure 8: (from ref. [1])Schematic P-T phase diagram of a liquid with small ΔE and J for a case of $\Delta v > 0$.

Even if it's hard to be detected, a general liquid with small ΔE and J may also have a LLPT(see Fig.[8]). The critical point may be in the negative pressure region for this case. This model gives a probable description of Fischer clusters, which are density fluctuations of long-range correlations with

9

typical scale 100-300nm, observed in supercooled liquids. [7] Fischer clusters can be viewed as critical-like fluctuations of S, which is the consequence of the existence of the cooperative medium-range ordering. Thus, it's implied in this theory that liquids having Fischer clusters may also have a LLPT at lower temperature.

In brief, much experimental evidence has revealed the existence of liquid-liquid phase transition. The theoretical model gives an intuitive and simple view of this mysterious phenomena. We still need further studies to understand the whole picture, such as to detect the long-lived locally favored structure directly, or to see the specific vibration modes of them.

References

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[3] M. Togaya, Phys. Rev. Lett. 79, 2474 (1997).

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