

## Glass Transition within Cluster Variation Method

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Thermodynamic framework of Crystal-Glass transition is described based on the free energy of the Cluster Variation Method (CVM). Constrained free energy of  $L1_0$  ordered phase is calculated as a function of a Long Range Order parameter which is regarded as an order parameter of the Crystal-Glass transition. It is demonstrated that the  $T_0$  temperature terminates at a *tricritical* point at which the entropy of the liquid phase becomes identical with the one of a defective crystal. This is the indication of the ideal glass transition. It is shown that the glass transition temperature corresponds to the spinodal ordering temperature of the order-disorder transition.

Key words: Glass transition, Spinodal ordering, Cluster Variation Method

### 1. INTRODUCTION

Recent development of first-principles calculations of phase stability and phase equilibria is quite remarkable. For certain systems, the transition temperatures have been predicted with surprisingly high accuracy and various effects on the phase stability can be separated out to reveal an essential mechanism of stabilization or de-stabilization.[1] In the first-principles calculation, the free energy is described based on the accurate atomistic information such as pair and many-body interaction energies, cluster correlations, symmetry of the discrete lattice etc. Such an accuracy claimed in the high precision calculation, however, is sometime a stumbling block against the applicability in the wide class of materials and matters.

Phenomenological description of the free energy, on the other hand, generally discards the details of atomistic information, therefore one can not expect to derive physical quantities in high accuracy. However, a big advantage over the first-principles scheme is the versatility to cover wide range of phenomena including systems with a low symmetric structure. In fact, numerous kinds of phase transition phenomena including Liquid-Crystal transition and Crystal-Glass (CG) transition, which are the main concern of the present study, have been described and analyzed based on phenomenological free energies. The essential process of the phenomenological description is that a key quantity(s) to control the phenomenon of interest is identified and is efficiently parameterized as an order parameter. In most cases, a phenomenological free energy is given in the series expansion of an order parameter(s) and coefficient terms reflect essential physics behind the phenomena such as the symmetry of the system. For the description of the first-order transition, a common practice is to describe the free energy in the series expansion of order parameter(s) up to 6<sup>th</sup> order, while for the second order transition, the expansion terminates at the 4<sup>th</sup> order. Mathematically, such a series expansion is quite transparent and proves useful for the analysis of Liquid-Crystal and Crystal-Glass (CG) transitions.

In the present study, however, a different approach is attempted. We employ atomistic free energy based on the Cluster Variation Method (CVM) [2] and adopt a Long Range Order parameter as an order parameter to describe the CG transition in a phenomenological manner. Among various attractive features of the CVM in studying order-disorder (OD) transitions, the capability of analyzing the intrinsic stability of the system is addressed. In particular, *spinodal ordering* [3] which takes place upon the spontaneous loss of stability with respect to an infinitesimal configurational fluctuation has been extensively investigated both in real space and k-space formulations.[4] The locus of the spinodal ordering temperature is obtained from the vanishing condition of the 2<sup>nd</sup> order derivative of the free energy functional, and the diffuse intensity spectrum calculated by the Fourier transformed free energy is directly comparable with a scattering experiment.

The onset of the spinodal ordering is closely related to the order of the transition. When the spinodal ordering temperature coincides with a transition temperature, the transition is of the second order, while the first order character is emphasized by the deviation of these two temperatures. For the first order transition, the existence of the metastable state(s) is essential and is indicated by the local minimum of the free energy. By lowering temperature, however, the free energy surface at the local minimum state flattens and finally metastable state vanishes at a certain temperature. This characteristic temperature is nothing but the spinodal ordering temperature which has been amply discussed [5,6] for disorder- $L1_0$  transition, a typical example of the first-order transition.

In view of the fact that a CG transition is associated with the liquid-solid transition which is another typical first order transition, the author is motivated to examine the applicability of the CVM free energy for the  $L1_0$ -disorder transition to describe CG transition. [7] It is fully understood that the CVM has been employed for the OD transition on a highly symmetric Bravais lattice, while CG transition yields a topologically disordered structure which can not be dealt by a conventional CVM.

Then, one can not expect any structural information pertinent to the CG transition out of the present calculations. However, recent development of Continuous Displacement Cluster Variation Method (CDCVM) [8,9] allows the local breaking of a crystal symmetry and, therefore, is expected to be directly applicable to the CG transition. The present study is attempted to establish a thermodynamic framework for the CG transition within the conventional CVM prior to the application of sophisticated CDCVM, and a particular focus is placed on the clarification of glass transition in the mold of OD transition.

## 2. CVM FREE ENERGY

Within the tetrahedron approximation [10] of the CVM which is the main concern of the present study, the free energy of the  $L1_0$  ordered phase is given as,

$$F^{L10} = \frac{1}{2} \cdot N \cdot \sum_{i,j} e_{ij} \cdot (y_{ij}^{\alpha\alpha} + 4y_{ij}^{\alpha\beta} + y_{ij}^{\beta\beta}) - k_B T \cdot \ln \frac{\left\{ \prod_{i,j} (N y_{ij}^{\alpha\alpha})! \right\} \left\{ \prod_{i,j} (N y_{ij}^{\alpha\beta})! \right\}^4 \left\{ \prod_{i,j} (N y_{ij}^{\beta\beta})! \right\} N!}{\left\{ \prod_i (N x_i^\alpha)! \right\}^{5/2} \left\{ \prod_i (N x_i^\beta)! \right\}^{5/2} \left\{ \prod_{i,j,k,l} (N w_{ijkl}^{\alpha\alpha\beta\beta})! \right\}^2} \quad (1)$$

where the first and second terms are internal energy and entropy, respectively,  $k_B$  is the Boltzmann constant,  $T$  the temperature,  $e_{ij}$  the atomic interaction energy between species  $i$  and  $j$ ,  $x_i$ ,  $y_{ij}$  and  $w_{ijkl}$  are cluster probabilities of finding atomic arrangement specified by the subscript(s) on the point, pair and tetrahedron clusters, respectively, and  $N$  is the number of the lattice point. The superscript(s) distinguishes the sub-lattice.

The cluster probabilities are mutually related through normalization conditions and geometrical conditions given by

$$\sum_i x_i = \sum_{i,j} y_{ij} = \sum_{i,j,k,l} w_{ijkl} = 1 \quad (2)$$

and

$$x_i = \sum_j y_{ij} = \sum_{j,k,l} w_{ijkl} \quad (3)$$

respectively. Note that in order to avoid complicity, the distinction of the sub-lattice by superscript is omitted in the eqs.(2) and (3). Then, for the sake of mathematical transparency, it is more convenient to introduce correlation functions [11,12],  $\{\xi_i\}$ , which form a set of independent variables and are defined as the ensemble average of spin variable  $\sigma_p$  which takes either +1 or -1 depending upon A or B atom, respectively, on the lattice point  $p$ . The subscript  $l$  represents a number of lattice points in the cluster. It has been demonstrated [11,12] that a cluster probability and a set of correlation functions are related through a linear transformation. Then, the free energy given in eq.(1) can be symbolically rewritten as

$$F^{L10} = F(T, \{e_{ij}\}; x_i^\alpha, x_i^\beta, y_{ij}^{\alpha\alpha}, y_{ij}^{\alpha\beta}, y_{ij}^{\beta\beta}, w_{ijkl}^{\alpha\alpha\beta\beta})$$

$$= \hat{F}^{L10}(T, \{\xi_{ij}\}, \xi_1^\alpha, \xi_1^\beta, \xi_2^{\alpha\alpha}, \xi_2^{\alpha\beta}, \xi_2^{\beta\beta}, \xi_3^{\alpha\alpha\beta}, \xi_3^{\alpha\beta\beta}, \xi_4^{\alpha\alpha\beta\beta}) \quad (4)$$

In the present study, the discussion is confined to a fixed concentration of 1:1 stoichiometry. Then, from the symmetry of the  $L1_0$  ordered phase, one of the point correlation functions can be replaced by the negative of the other point correlation function. The same is held for the three body correlation functions. Also, it can be shown that the pair correlation function of the *like*-sublattices,  $\alpha\alpha$ , is equivalent to the one for the other *like*-sublattices,  $\beta\beta$ . The number of correlation functions is, therefore, reduced to five to give the free energy as

$$F^{L10} = F(T, \xi_1^\alpha, \xi_2^{\alpha\alpha}, \xi_2^{\alpha\beta}, \xi_3^{\alpha\alpha\beta}, \xi_4^{\alpha\alpha\beta\beta}) \quad (5)$$

Here, the point correlation function  $\xi_1^\alpha$  is the Long Range Order parameter (LRO) while the others are Short Range Order parameters.

When the free energy is minimized with respect to all the correlation functions, one obtains the equilibrium state, which is the general practice for phase diagram calculations. In the present study, however, we minimize the free energy under a specified LRO, which is termed a constrained minimization. This procedure provides us with the free energy as a function of LRO and temperature,  $F(T, \eta)$ , in which LRO  $\xi_1^\alpha$  is replaced by an order parameter  $\eta$  for the description of a CG transition. It should be noted that the introduction of the new order parameter to describe the CG transition is not at all trivial. The original LRO  $\xi_1^\alpha$  is defined on the discrete lattice, whereas the order parameter  $\eta$  within the CG transition discards such a meaning and is defined on the phenomenological basis.

## 3. CRYSTAL GLASS TRANSITION

For  $\eta$ , 0 and 1 are assigned to indicate a perfect crystal and liquid, respectively. It has been demonstrated [7] that at the transition temperature  $T_i$ , the free energy  $F(T, \eta)$  has the two identical minima to which a common tangent line can be drawn, and that there exists an energy hump between the minima, which are the indication of the first order transition. In the context of CG transition,  $T_i$  is regarded as the melting temperature. Below the melting temperature, one of the two minima becomes grand minimum near  $\eta = 0$  and the other becomes local minimum indicating the metastable super-cooled liquid phase. However, below a certain temperature  $T_L$  the free energy hump diminishes and the crystal state is identified as a unique stable state by the absolute minimum. This is a critical temperature at which super-cooled liquid is no more sustainable and the infinitesimal fluctuation of order parameter induces the spontaneous loss of the stability, which may lead to a glass or crystal transition depending upon a system.

From the discussion above,  $\eta$  can be regarded as an amount of generalized defect  $s$  introduced in the system

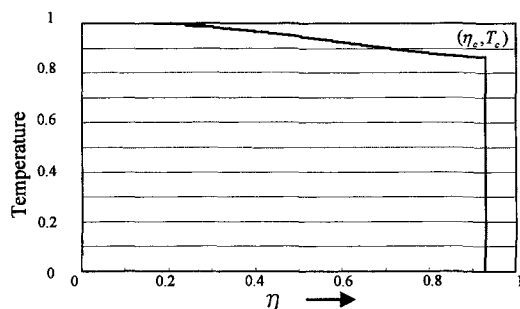


Figure 1.  $T_0$  diagram indicating a tricritical point which is the ideal glass-transition temperature. The vertical axis corresponds to a normalized temperature.[7]

which break the symmetry of the crystal to induce the liquid transition. According to Okamoto et al. [13], these defects can be impurities, dislocations, atomic displacement within the Lindemann's sense. The specification of the particular defect, however, is not essential in the framework of the present attempt of the thermodynamic description.

For a specified value of order parameter  $\eta$ ,  $F(T, \eta)$  provides the temperature dependency of the free energy of a defective crystal and is now rewritten as  $g_\eta(T)$ . Then, the intersection of  $g_\eta(T)$  with  $g_{\eta=1}(T)$ , which is the temperature dependence of the liquid free energy, yields the melting point of a defective crystal. By repeating this procedure for various values of  $\eta$ , one obtains the diagram shown in Fig.1 [7] which indicates the melting temperatures of defective crystals. One sees that the melting temperature decreases with the increase of defects. It should be noted that the equality of the free energies suggested in the figure does not guarantee the equilibrium transition. In this sense, this is not a phase diagram and is termed  $T_0$  diagram.

What is important in Fig.1 is that  $T_0$  terminates at a tricritical point which is found at  $\eta_c = 0.976$  and  $T_c = 0.861$ . It was shown [7] that, at this critical value of  $\eta_c$ ,  $g_{\eta_c}(T)$  merges into  $g_{\eta=1}(T)$  at  $T_c$ , without intersection, indicating that the entropy of a defective crystal which is nothing but a slope of  $g_\eta(T)$  becomes identical with the one of a liquid. In fact, this kind of  $T_0$  diagram is typically found [13] for the glass transition, and the tricritical point at which the equality of the entropies is attained is interpreted as the ideal glass transition temperature. Above  $T_c$ , the ideal glass transits to a super-cooled liquid and above  $\eta_c$ , a defective crystal transits to an ideal glass.

Coming back to the original  $F(T, \xi_1^\alpha)$  in eq.(5), on the other hand, it is found that at this combination of  $(\xi_1^\alpha)_c = 0.976$  and  $T_c = 0.861$ , the second order derivative of  $F(T, \xi_1^\alpha)$  with respect to  $\xi_1^\alpha$  vanishes, which is the indication of the onset of the spinodal ordering in the OD transition. [4] Hence, it is concluded that in the framework of CVM thermodynamics, glass transition

temperature is identical with the spinodal ordering temperature. It should be, however, noticed that the proper understanding of CG transition needs kinetics considerations. In fact, the glass transition has been interpreted as a consequence of increased viscosity which hinders the liquid-crystal transition in an ordinary laboratory time scale. Such kinetics is simulated by employing Path Probability Method [14] which is the natural extension of the CVM to time domain. This is another advantage to employ CVM and one can expect to perform a consistent study of CG transition covering both thermodynamics and kinetics.[7]

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#### References

- [1] T. Mohri and Y. Chen, *J. Alloys and Compounds*, **383**, 23 (2004). and references therein.
- [2] R. Kikuchi, *Phys. Rev.*, **81**, 998 (1951).
- [3] D. de Fontaine, *Acta Metall.* **23**, 553 (1975).
- [4] T. Mohri, J.M. Sanchez and D. de Fontaine, *Acta Metal.*, **33**, 1711 (1985).
- [5] T. Mohri, *Modeling Simul. Matter. Sci. Eng.*, **8**, 239 (2000).
- [6] T. Mohri, "Properties of Complex Inorganic Solid" 2, ed. A. Meike, (Kluwer Academic/Plenum Publishers, 2000), 123.
- [7] T. Mohri, submitted to "The Science of Complex Alloy Phases", Proceeding of TMS 2005 Meeting.
- [8] R. Kikuchi, *J. Phase. Equilibria*, **19**, 412 (1998).
- [9] H. Uzawa and T. Mohri, *Mat. Trans.*, **43**, 2185 (2002)
- [10] R. Kikuchi, *J. Chem. Phys.*, **60**, 1071 (1974).
- [11] J.M. Sanchez and D. de Fontaine, *Phys. Rev.*, **B17**, 2926 (1978).
- [12] T. Mohri, J.M. Sanchez and D. de Fontaine, *Acta Metal.*, **33**, 1463 (1985).
- [13] P. R. Okamoto, N.Q. Lam and L.E. Rehn, "Solid State Physics", vol. **52**. ed. by H. Ehrenreich (Elsevier Academic Press, San Diego, 1999) and references therein.
- [14] R. Kikuchi, *Prog. Theor. Phys. Suppl.*, **35**, 1 (1966).

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