

# CORRELATION PHENOMENA IN THE GLASS-FORMING LIQUIDS

A.S. Bakai

National Science Center "Institute of Physics & Technology", Kharkov, Ukraine

A theory of the long-range correlations of density fluctuations is presented for the glass-forming liquids. The supercooled heterophase liquid (HPL) is considered as composed of solid-like and fluid-like species with many types of the short-range order (SRO). The random field Ginzburg-Landau (GL) equations are deduced for the HPL. The variety of the SRO originates the local random fields. It is shown that optimization of the free energy gives rise to the medium and long-range correlations of the random fields and order parameter. Conditions for observation of such correlations are deduced. Time dependent GL equations are used to establish the ultra-slow dynamics and annealing kinetics of the long-range correlations.

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## 1. INTRODUCTION

Long-range correlation (LRC) of density fluctuations, which are known as Fischer cluster, are revealed in one component glass-forming liquids and polymers [1,2]. They have puzzling features:

1) They do exist in a rather large temperature range,  $\sim 100\text{K}$ , above  $T_g$ .

2) The correlation length is up to 300 nm while the molecular interaction radius  $r_0$  is  $\sim 1$  nm.

3) No critical behavior of the heat capacity, compressibility, thermal expansion coefficient is observed in the temperature region above  $T_g$ .

4) The correlation of density fluctuations has a fractal structure of dimension  $D < 3$ . The dimension depends on temperature,  $T$ , and substance. It differs from the universal critical exponent of the pair correlation function.

5) Ultra-slow modes characterizing the Fischer cluster dynamics are some order of magnitude faster than the Fischer cluster equilibration (annealing) time.

6) The  $\alpha$ -relaxation processes are insensitive to the Fischer cluster formation. The ultra-slow dynamics is considerably slower than the  $\alpha$ -relaxation processes.

A few papers are devoted to theory of Fischer cluster. In [3] the LRC are treated as the long-range critical fluctuations. They are described within the framework of the model with two order parameters. But the features 3)-5) still have no proper explanation in [3].

In this paper it is shown that the observed LRC appears as result of aggregation of liquid domains having the same SRO. We start from the idea that glass-forming liquid has heterophase mesoscopic structure consisting of solid-like and fluid-like species. The average lifetime of each specimen is nearly the  $\alpha$ -relaxation time,  $\tau_\alpha$ . The species can change their type and SRO but the average concentration of species possessing the same SRO is constant at fixed pressure,  $P$ , and temperature,  $T$ . The fraction of molecules belonging to the solid-like species,  $n_s(x,t)$ , is chosen as the order parameter. In one or another form this idea was used by others the free energy of the HPL is

described in the mean field approximation. Equations proposed in [5,6] show that the HPL could have a critical point. Moreover these equations are isomorphic to Van der Waals theory of the gas-liquid critical point (see e.g. [7]). Adding to the Van der Waals free energy the gradient term one can get the GL description of the system. The same procedure allows using GL equation for HPL [7]. Assuming that the supercooled liquid above  $T_g$  is close to the critical point one can get an explanation of LRC: it is correlation of critical fluctuations. But it is not satisfactory because the properties 3) – 5) are not explained within that theory. To come up with a solution of the problem staying in the framework of the HPL model, one has to consider the SRO statistic and correlations. This way we immediately come to the random field Ginzburg-Landau model (RFGLM). Subsequent minimization of the free energy leads straightforwardly to the description of the correlation phenomena. It turns out that a liquid with LRC that obey (1) – (6) minimizes the free energy.

GL approach is valid out of the fluctuational critical region [7]. It turns out that the fluctuational region strongly depends on the random field properties. We have obtained an applicability condition of the developed model.

## 2. RANDOM FIELD GL MODEL OF HETEROPHASE LIQUIDS

Let us take that the liquid is consisting of statistically independent species having different SRO and  $k_0$  is the average (on the all species) number molecules per specie. Each type of SRO is characterized by the average minimal energy per molecule,  $\varepsilon_i$ , and by number of configurations,  $w_i$ , or configurational entropy  $\zeta_i = k_B \ln w_i / k_0$  ( $k_B$  is Boltzmann's constant, "i" denotes ith specie). The main concept of the heterophase fluctuations (or HPL) is that the liquid is composed by solid-like and fluid-like species. Denoting by  $\mu_i = \varepsilon_i - \zeta_i T$  the chemical potential per

molecule of  $i$ th specie we assume, in accord with the HPL models, that there are two sets of chemical potentials,  $\{\mu\}_s = \mu_{s1}, \dots, \mu_{sk_s}$ , and  $\{\mu\}_f = \mu_{f1}, \dots, \mu_{fk_f}$ . Here “ $s$ ” and “ $f$ ” are indexes denoting quantities and sets belonging to the fractions of solid-like and fluid-like species respectively;  $k_{s,f} = N_{s,f}/k_0$  are fractions of the solid-like and fluid-like species;  $N_s$  and  $N_f$  are the total numbers of molecules within these fractions,  $N_s + N_f = N$ . The difference of chemical potentials of solid-like and fluid-like species is assumed to be considerable,

$$\langle \mu_s \rangle - \langle \mu_f \rangle > (\delta_s + \delta_f)/2 \quad (1)$$

Here  $\langle \dots \rangle$  denotes an spatial average;  $\delta_s, \delta_f$  are variances of  $\mu_s, \mu_f$  respectively.

Positivity of the interfacial free energy,

$$\Delta \mu_{\text{int}} = \mu_{\text{int}} - \frac{1}{2} (\langle \mu_s \rangle - \langle \mu_f \rangle) > 0 \quad (2)$$

is necessary for the phase separation,  $\mu_{\text{int}}$  is the free energy per molecule on the solid-fluid interface. Positive  $\Delta \mu_{\text{int}}$  provides “repulsion” of the solid-like and fluid-like species. We assume that the conditions (1), (2) are fulfilled.

In a continuous approach the space distributions and time evolution of the solid-like and fluid-like species can be described by the fields  $\mu_i(x,t) \equiv \langle \mu_i \rangle + \tilde{\mu}_i(x,t)$ ,  $i = s, f$ . The free energy of liquid is a functional of the three fields,  $n_s(x,t)$ ,  $\mu_s(x,t), \mu_f(x,t)$ . As it was mentioned above, this functional has the GL form in which the coefficients depend on the fields  $\mu_i(x,t)$ . Since  $\tilde{\mu}_i(x,t)$  are some random fields (with variances  $\delta_s, \delta_f$ ), their correlation functions must be found by minimization of the free energy functional.

The solid-fluid phase coexistence curve (which is a direct analog of the critical isochore in the Van der Waals theory) is determined by an equation,

$$\bar{n}_s(P,T) = 1/2 \quad (3)$$

where  $\bar{n}_s$  is the space average of  $n_s(x,t)$ . At a fixed pressure (3) determines the coexistence temperature,  $T_e(P)$  [9].

The free energy functional in the vicinity of coexistence curve can be presented as follows:

$$G(P,T) = G_0(P,T_e) + G_1(P,T)$$

$$G_1 = v^{-1} \int \left[ \frac{1}{2} A (\nabla \alpha)^2 + \frac{1}{2} B \alpha^2 + \frac{1}{4} c \alpha^4 - h \alpha \right] d^3 x \quad (4)$$

here  $v$  is the specific volume,

$$\alpha(x) = n_s(x) - \frac{1}{2};$$

$$A = r_0^2 A_0, \quad r_0 \sim k_0^{1/3} \sim 1 \text{ nm}, \quad A_0 \sim T;$$

$$B = 4 k_0 T_e - 2 \Delta \mu_{\text{int}}; \quad C = 4 k_0^{-1} T \quad (5)$$

$$h = \bar{h} + \tilde{h},$$

$$\bar{h} = \bar{\mu}_s - \bar{\mu}_f; \quad \tilde{h}(x) = \tilde{\mu}_s(x) - \tilde{\mu}_f(x)$$

and  $G_0(P, T_e)$  is the mean field free energy at  $T = T_e$ ;  $\bar{h}, \bar{\mu}_s, \bar{\mu}_f$  are averaged quantities.

To consider changes of the order parameter driven by the random field  $\tilde{h}$  we set  $\alpha(x) = \bar{\alpha} + \tilde{\alpha}(x)$ . Then the saddle point equation of (4) gives

$$(B + 3C \delta_\alpha^2) \bar{\alpha} + C \bar{\alpha}^3 = \bar{h}, \quad (6)$$

$$- A \Delta \tilde{\alpha}(x) + (B + 3C \bar{\alpha}^2 + 3C \delta_\alpha^2) \tilde{\alpha}(x) = \tilde{h}(x) \quad (7)$$

In the close vicinity of the coexistence curve, where  $\bar{h}$  and  $\bar{\alpha}$ , are negligible, equation (7) has the following solution

$$\tilde{\alpha}(x) = \frac{1}{4\pi A} \int K(|x - x'|) \tilde{h}(x') d^3 x' \quad (8)$$

$$K(r) = r^{-1} \exp(-r/R_c),$$

$$R_c^{-2} = \tilde{B}/A, \quad \tilde{B} = B + 3C \delta_\alpha^2. \quad (9)$$

Some important conclusions follow already from (5), (7) - (9). Parameter  $\tilde{B}$  shows how close the system is to the critical point. A simple consideration shows that  $|\tilde{B}| > b (T_e \delta_h^2)^{1/3}$ , where  $b$  is a constant  $\sim 1$  and  $R_c^2 < r_0^2 T_e / b (T_e \delta_h^2)^{1/3}$ ; here

$$\delta_h^2 = \langle \tilde{h}^2(x) \rangle = \delta_s^2 + \delta_f^2 - 2 \langle \tilde{\mu}_s(x) \tilde{\mu}_f(x) \rangle. \quad (10)$$

Thus the critical fluctuations of the order parameter are driven by the random fields  $\tilde{h}(x,t), \tilde{\mu}_s(x,t), \tilde{\mu}_f(x,t)$ .

This conclusion is correct when thermal fluctuations are weak compared to those driven by the random fields. Repeating the argument used to obtain the Levanyuk-Ginzburg criterion [7] we get the condition

$$\delta_h^2 \gg \Delta_h^2 = T_e^2 (a/r_0)^{18} \quad (11)$$

which determines the domain where the random field driven fluctuations are much stronger than the thermal fluctuations of the order parameter and where the application of RFGLM is valid. Here  $a$  is an effective radius of the molecular forces.

The variance of the field  $\tilde{h}$ , (10), depends on the correlator of the fields  $\tilde{r}_s(x)$ ,  $\tilde{r}_f(x)$  which has to be found by minimization of the free energy. As it follows from (4) and (8) the random field driven contribution into the free energy is

$$\begin{aligned} \tilde{G}_v + \tilde{G}_1 &\sim \frac{1}{2v} \int A(\nabla \tilde{\alpha})^2 d^3 x - \\ &- \frac{N}{8\pi A} \int K(|y|) \langle \tilde{h}(0) \tilde{h}(y) \rangle d^3 y. \end{aligned} \quad (12)$$

Since the Green's function,  $K(r)$ , has considerable values,  $\sim 1$ , for  $r \leq R_c$ , the short-range correlations of the fields  $\tilde{h}$  and  $\tilde{\alpha}$  are important. The gradient term,  $\tilde{G}_v$  is positive while the next one,  $\tilde{G}_1$ , is negative. It is seen from (8), (12) that  $\tilde{G}_v$  has minimal value,  $\tilde{G}_v \sim NA_0 r_0^2 k^2 \langle \tilde{\alpha}^2 \rangle$ , if  $\tilde{h}(0)\tilde{h}(x) \approx \tilde{h}^2(0)$  with  $|x| < R_c$ , i.e. if the field  $\tilde{h}$  is strongly correlated on the distance  $\sim R_c$ . It means that the field  $\tilde{h}$  has a granulated structure: it can be approximately viewed as consisting of correlated domains (CD) of radius  $R_c$ . Within each of CD  $\tilde{h}$  is nearly constant. Thus the CDs are specified by the values of  $\tilde{h}$ .

Turning to  $\tilde{G}_1$  one can see that if the field  $\tilde{h}$  is not correlated on a scale larger than  $R_c$  then

$$\tilde{G}_1(\xi) \sim -N \delta_h^2 R_c^2 \sim -N (T_e \delta_h^2)^{1/3} \quad (13)$$

Expression (13) shows that  $\tilde{G}_1(\xi)$  decreases when  $\delta_h^2$  increases. It follows from (10) that the maximal value of  $\delta_h^2$  (which minimizes  $\tilde{G}_1$ ),  $\max \delta_h^2 = (\delta_s + \delta_f)^2$ , can be accomplished due to correlation of the fields  $\tilde{r}_s(x)$ ,  $\tilde{r}_f(x)$ :

$$\tilde{r}_s(x) \approx -(\delta_s / \delta_f) \tilde{r}_f(x). \quad (14)$$

This relation means that the SROs of the solid-like and fluid-like species are correlated.

The free energy  $\tilde{G}_1$  decreases if the correlation lengths,  $\xi(\tilde{h})$ , of the pair correlation functions of CDs, are much larger than  $R_c$ . The physical meaning of these correlations is transparent: CDs of the same value  $\tilde{h}$  are aggregating. They form correlated aggregates because the correlation, as will be shown, lowers the free energy.

Let us take the pair correlation function  $H(\tilde{h}, r)$  of the specified by  $\tilde{h}$  CDs in the following form,

$$H(\tilde{h}, r) \sim \begin{cases} \tilde{h}^2, & r < R_c \\ \tilde{h}^2 \left( \frac{r}{R_c} \right)^{D-3} \exp(-r/\xi(\tilde{h})), & r > R_c, D < 3 \end{cases} \quad (15)$$

Then

$$\langle \tilde{h}(0) \tilde{h}(r) \rangle = \int P(\tilde{h}) H(\tilde{h}, r) d\tilde{h} \quad (16)$$

where the distribution of the  $\tilde{h}$  values is given by

$$P(\tilde{h}) = V^{-1} \int \tilde{h}(x) \delta[\tilde{h}(x) - \tilde{h}] d^3 x \quad (17)$$

Expression (15) is the pair correlation function of CDs composing a fractal aggregate of dimension  $D$  and correlation length  $\xi_{av}$  [10]. The choice of this form of the correlation function is hinted also by the experimental evidence [2,6].

Combining (12), (15)-(17) we have the following relation for the free energy  $\tilde{G}_1$ :

$$\tilde{G}_1 \sim -N (T_e \delta_h^2)^{1/3} \left[ 1 + 4 e^{-1} \left( \frac{\xi_{av}}{R_c + \xi_{av}} \right)^{D-1} \right] \quad (18)$$

Here  $\xi_{av}$  is an average correlation length.

Comparing (13) and (18) we see that the aggregation of CDs really lowers the free energy. The described long-range correlations are resulting in the correlations of the density fluctuations which are proportional to the fluctuations of the order parameter. Since random field driven fluctuations have nothing to do with the thermal fluctuations they give an excess of intensity of small angle light scattering that was reported in [1,2,6].

The correlation length  $\xi(\tilde{h})$  can be estimated as follows. The average concentration of CDs within a fractal is [10]

$$c(\tilde{h}) \approx \frac{3}{4\pi} \left( \frac{\xi(\tilde{h})}{R_c} \right)^{D-3}. \quad (19)$$

On the other hand this quantity can be determined using the distribution function (17) and noting that the thermal fluctuations of  $\tilde{h}$  within a CD are  $\sim \Delta_h^2$ , as it follows from (11). Therefore

$$c(\tilde{h}) \approx 2P(\tilde{h}) \Delta_h \quad (20)$$

and

$$\xi(\tilde{h}_c) = R_c [c(\tilde{h}_c)]^{1/(D-3)} \sim R_c [2P(\tilde{h}) \Delta_h]^{1/(D-3)}. \quad (21)$$

Since  $P(\tilde{h}) \sim \delta_h^{-1}$  we have  $c(\tilde{h}) \approx \Delta_h / \delta_h \ll 1$  and, as a result,  $\xi(\tilde{h}) \gg R_c$ . The experimentally measured correlation lengths of Fischer clusters are  $\sim 10^2 nm$  [1,2]. With  $R_c \sim 1 nm$  we have an estimate:  $c(\tilde{h}) \sim 10^{-2} \ll 1$ . Thus condition (11) is evidently satisfied.

Dynamics of the Fischer cluster (ultra-slow modes) can be described using the conventional time dependent GL equations. Because the concentrations  $c(\tilde{h})$  are conserved quantities, the spectrum of the ultra-slow modes has the following form:

$$\tau_q^{-1} \sim \tau_\alpha^{-1} R_c^2 q^2 \tilde{B} (1 + \gamma_1 R_c^2 q^2) \quad (22)$$

where  $\gamma_1$  is a constant,  $\tau_\alpha$  is the  $\alpha$ -relaxation time.

Noting that  $q^2 \sim \xi^{-2}$  and  $\tilde{B} \ll 1$  we see why the ultra-slow process is much slower than the  $\alpha$ -relaxation. Experimental evidences of the ultra-slow dynamics are reported in [1,2]. They are in accord with (22).

The derivative of  $\tilde{G}_1$  (18) w.r.t.  $\xi_{av}$  is the thermodynamic driving force of the aggregates formation. It is proportional to  $\delta_h^{2/3}$  and to  $(R_c / \xi_{av})^2$ . A simple version of the fractal aggregation kinetics [25] can be used to estimate the characteristic annealing time,  $\tau_\xi$ , of the Fischer cluster,

$$\tau_\xi \sim \tau_\alpha (\xi / R_c)^{D+2}. \quad (23)$$

In the exponent of (23) the coefficient of 2 is coming from the thermodynamic driving force while the appearance of  $D$  is due to the dimension of the growing aggregate. It is easy to ascertain that  $\tau_\xi \gg \tau_q$ , ( $q \sim \xi^{-1}$ ) because  $\tau_\xi \tau_q^{-1} \sim (\xi / R_c)^D \sim 10^3$ . This estimate has many experimental confirmations [1,2].

We see that the theory developed here describes the observed properties structure and dynamics of a Fischer cluster. According to it a Fischer cluster has a polychromatic fractal heterophase structure. Polychromatic cluster structures are described e.g. in [11] in connection with the percolation problem. If clusters have a property described by a parameter, this last one can be used as a «color», specifying clusters. Several interpercolating clusters form a polychromatic structure. In the heterophase liquid  $\tilde{h}$  plays a role of a color for the CD aggregates. It parameterizes the chromatic spectrum of CDs. A specific feature of these polychromatic structures is the ability of CDs to change their color restoring the structure's ergodicity. The life time of a CD is  $\sim \tau_\alpha$  while the aggregate growth and rearrangement processes take much longer times.

### 3. DISCUSSION AND CONCLUSIONS

The developed theory, based on the RFGL equations and on the concept of heterophase fluctuations, takes into account the multiplicity of the SRO which is a basic property of the glass-forming liquids. In particular this property manifests itself in the developed inherent structure and in the free energy landscape. The  $\alpha$ -relaxation process is a cooperative. It involves cooperatively rearranging regions (CRR) of a few  $nm$  size. According to our estimates  $R_c$  is of the same scale. Of course the sizes of CRR and CD can be different because CRR is connected to dynamics while CD appears as a characteristic scale of the medium-range order. Nevertheless both are conditioned by the

medium range correlations. To some extent the noted genetic connection between CRR and CD reminds about a similar correspondence of CRR and CD in the Adam-Gibbs and Gibbs-Di Marzio theories but this problem has to be considered in more detail.

The relation of the the present theory to the other models of a supercooled liquid and to the theory of the critical point was already elucidated in the Introduction. To emphasize this connection it should be noted that the developed RFGLM can be reduced to the models of supercooled liquid proposed in [5,6]. For example, to get from (4), (5) to the equations of the Van der Waals approximation we have to put  $\delta_s^2 = \delta_f^2 = A = 0$ .

It is worth noting is that condition (11) is satisfied if the field  $\tilde{h}$  changes criticality, location of the critical point, and the order of the phase transition at the critical point. The critical point location (dependent on the parameter  $B(T_e)$ ) is determined from

$$B(T_e) \equiv 4T_e(P) - 2\Delta \mu_{int} = B_{crit} = -2(C\delta_h^2)^{1/3}. \quad (24)$$

The phase transition that takes place at this point is not of the second but of the first order, the order parameter jump is  $\sim (\delta_h / T_e)^{1/3}$ . Relation (24) shows that the random field lowers the critical value of  $T_e(P)$ . This is a reason why the majority of the glass-forming liquids do not have a polymorphous liquid-liquid phase transition.

To compare the theory of LRC presented here with the conventional theory of LRC in the vicinity of critical point let us consider the two-fluid model developed in [3]. Bendler and Shlessinger have treated the supercooled liquid as a binary heterophase mixture of defect and nondefect structures (fluid 1 and fluid 2 respectively) above a critical point  $T_c < T_g$ . They have noted that their model is related to the ideas of Frenkel [12] and Ubbelohde [13]. In [12,13] the thermodynamics of heterophase fluctuations is described within the framework of droplet approach. (It has to be noted that the thermodynamics of the heterophase systems gas-liquid and fluid-solid in the droplet approach was developed in [14] and [5] respectively). The defects of fluid 1 are mobile at high temperature but with temperature decreasing these defects starts aggregating. The aggregated defects are immobile while the relaxation kinetics is controlled by the mobile, non-aggregated, defects. The point  $T_c$  of phase separation (defect condensation) in [3] is identified with the Kauzmann temperature. The mobile defects disappear at  $T_c$ . The correlation length of the density fluctuations in mean-field approximation is given by

$$\xi_c = r_0 [T / (T - T_c)]^{1/2} \quad (25)$$

where  $r_0$  has the same meaning as in (5). According to Eq. (25), at  $r_0 \sim 1nm$ , in a close vicinity of  $T_c$ , i.e. at  $T - T_c \sim 10^{-4} T_c$  the correlation length is about  $10^2 nm$ ,

whereas at  $T - T_c \sim 10^{-1} T_c$  it is equal to several  $nm$ .

To check that the order of magnitude of  $r_0$  chosen here is nearly the same as in [3] one can use the expression for  $\tau_\alpha$  obtained in [3]:

$$\tau_\alpha = \tau_0 \exp \left[ - \left( \frac{\xi_c}{a} \right)^3 \frac{\ln(1-\varphi)}{\beta} \right] \equiv \tau_0 \exp \left[ B \left( \frac{T}{T - T_c} \right)^{3/2} \right]. \quad (26)$$

Here  $\varphi < 1$  is the concentration of defects in the two-fluid system and  $\beta$  is the Kohlrausch stretch exponent ( $0 < \beta \leq 1$ ).

By comparing (25) and (26) one has

$$B = - \left( \frac{r_0}{a} \right)^3 \frac{\ln(1-\varphi)}{\beta}. \quad (27)$$

As a realistic estimate (given in [3]) we can take  $\varphi \sim 0.1$  and  $\beta = 0.5$ . Then (27) gives  $r_0 \approx a(5B)^{1/3}$ .

By fitting to experimental data, it was found in [3] that for ortho-terphenyl (OTP)  $T_c=195$  K and  $B = 20$ . Thus, according to (27) for OTP  $r_0 \approx 4.6a \approx 3nm$  i.e., is comparable with the value taken above for estimations.

The experimentally determined value of the correlation length for OTP at  $T = 298$  K is to  $86 nm$  at  $T = 293$  K. [1,2]. The relation (25) at  $T = 295K$ , with  $r_0 = 3nm$ , gives  $\xi_c \approx 1,7r_0 \approx 5nm$  which is more than one order of magnitude less than the values obtained from the light scattering and X-ray scattering data [1,2].

The temperature  $T = 293$  K is estimated to be close to  $T_e$  for OTP [15], therefore it lies within the temperature range where the relation (21) is valid. Taking for OTP  $R_c \approx 3nm$  and a reasonable value for  $\langle c(\tilde{h}) \rangle = 0.07$  (see (20)) we obtain  $\xi_{av} \approx 10^2 nm$ .

The performed comparison shows that the temperature dependence of the correlation length predicted by conventional theories of critical density fluctuations does not fit the experimentally observed LRC even if the features 3)-5) of the Fischer cluster (described by the theory presented here) are ignored.

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