Condensed Matter Physics, 2000, Vol. 3, No. 3(23), pp. 675–681

CONDENSED MATTER PHYSICS

Heterophase fluctuations in glass-forming liquids and random field Ising model

A.S.Bakai

National Science Center “Kharkiv Institute of Physics and Technology”, 61108 Kharkiv, Ukraine

Received May 29, 2000

The liquid-to-glass transition is a process of supercooled liquid solidification. Rather large density fluctuations are revealed experimentally in many of the glass-forming liquids above the glass transition temperature while no phase transitions are identified [1,2]. In [3–5], the inhomogeneities are treated as heterophase fluctuations (HPF). The process of glass formation gets there a natural description as a continuous phase transformation. The theory of strong HPF was developed in a mean field approximation which ignores the mesoscopic structure of the inhomogeneities which is an issue of extensive experimental investigations and discussions [1,2,5]. In the present communication the HPF are considered in the model of interpercolating heterophase states and in Ginzburg-Landau (GL) approach. It is shown that the GL approach results in the random field Ising model (RFIM) for HPF. It permits to get a description of the medium range and long-range correlations of the HPF. RFIM is very useful in studying the spin systems with a frozen-in disorder. Therefore the theory developed makes it possible to compare the phase states with frozen-in (spin systems) and self-consistent (heterophase liquids) disorders. In particular, it turns out that the heterophase liquids are similar (but not identical) to Griffiths phase of disordered spin systems. It is seen that the developed model bridges the theories of disordered spin systems and glass-forming liquids.

Key words: *glass-forming liquids, heterophase fluctuations, continuous phase transformation, random field Ising model*

PACS: *64.70.Pf, 61.20.Lc*

1. Introduction

Phase transformations and phase transitions belong to the most challenging problems in the condensed matter physics (see e.g. [6]). The liquid-to-glass transitions have been investigated for a long time. A lot of fascinating ideas were formulated on this way though none had a decisive success. In this paper the physics of HPF in glass-forming liquids is considered. It is believed that the HPF are responsible for the known properties of the glass-forming liquids and that they play a decisive role in the glass forming process.

In a macroscopically homogeneous phase, heterophase fluctuations do exist. Usually they are weak due to a comparatively high free energy of formation. Nevertheless, as it is shown by Frenkel [7], they are not negligible in the vicinity of the phase coexisting curve on the (P,T)-plane. Investigations of thermodynamics and phase transitions in the droplet approach [7–9] show that the critical point (end point on the phase coexisting curve) is determined by the condition that the interfacial free energy equals to zero. In this case, in the supercritical region no phase separation is possible and no heterophase fluctuations can occur. It means that the phase is microscopically homogeneous in the supercritical region in accordance with the droplet models.

Recently [3–5,9] the thermodynamics of heterophase states was reconsidered within the framework of the interpercolating heterophase state model. This model was developed to be applicable to the studies of the states where heterophase fluctuations are not weak and their volume fraction exceeds a percolation threshold. It turns out that the interfacial free energy is positive at the critical point and that there exists a domain of the supercritical region where phase separation is possible. Therefore, a mesoscopically heterophase state does exist in this region though the phase is macroscopically homogeneous and no phase transitions take place with crossing of the coexisting curve. Therefore if P and T are changing to pass around the critical point, from one side of the coexisting curve to another, a continuous phase transformation takes place. The mesoscopic heterophase substructure is changing with that transformation but no phase transitions occur. The fraction of a "pure" phase is a natural order parameter of the heterophase state. In the vicinity of the critical point, the free energy of the heterophase state can be presented in the standard Landau series on the degrees of the order parameter. The GL approach can also be applied. A break through the frame of the mean field approximation leads to RFIM model as it will be seen.

2. HPF of glass-forming liquids in the mean field approximation

Above T_{g} the heterophase liquid (HPL) is assumed to consist of a fluid fraction and non-crystalline solid clusters. The HPF can be described using the model of interpercolating heterophase states. This model in the mean field approximation gives the following expression for the free energy per molecule:

$$\begin{aligned}\mu(P,T) &= n_{\mathrm{s}}\mu_{\mathrm{s}}(P,T)+(1-n_{\mathrm{s}})\mu_{\mathrm{f}}(P,T)+n_{\mathrm{s}}(1-n_{\mathrm{s}})\Delta\mu_{\mathrm{int}}(P,T)\\ &\quad+\frac{k_{\mathrm{B}}T}{k_0}[n_{\mathrm{s}}\ln n_{\mathrm{s}}+(1-n_{\mathrm{s}})\ln(1-n_{\mathrm{s}})], \qquad (1)\\ \Delta\mu_{\mathrm{int}}(P,T) &= \mu_{\mathrm{int}}(P,T)-[\mu_{\mathrm{s}}(P,T)+\mu_{\mathrm{f}}(P,T)/2]. \qquad (2)\end{aligned}$$

Here n_s is the fraction of molecules belonging to solid clusters; $\mu_\mathrm{s}, \mu_\mathrm{f}$, and μ_int are chemical potentials of molecules in the "pure" solid, fluid, and within the interfacial layer respectively; k_0 is the associativity (or the mixing ability parameter) of molecules; k_B is Boltzmann's constant.

The phase coexisting curve is determined by the equation

$$\mu_\mathrm{s}(P,T) = \mu_\mathrm{f}(P,T). \tag{3}$$

Solution of this equation gives the temperature of the phase equilibrium, $T_\mathrm{e}(P)$.

It is shown [4] that a critical point on the coexisting curve is determined by the following equation

$$\Delta\mu_\mathrm{int}(P,T) = 2T_\mathrm{e}/k_0\,. \tag{4}$$

In the region where

$$0 < \mu_\mathrm{int} \leqslant 2T_\mathrm{e}/k_0 \tag{5}$$

no phase transitions take place on the coexisting curve. In the vicinity of this curve, with $0,15 < n_\mathrm{s} < 0,85$, infinite interpercolating solid and fluid clusters do coexist. If the liquid is cooled down passing the region (5), the continuous (without phase transitions) transformation of the fluid in non-crystalline solid state takes place.

The local order in amorphous states changes from site to site. The above used chemical potentials of the solid and fluid fractions are averaged on the local (short range) disorder. HPF have a coarse grained mesoscopic structure which can be studied using the GL approach. This approach is valid on the scales which are larger than the intermolecular distance, a. Let us consider the classic field of the order parameter $n_\mathrm{s}(x)$ and include the contribution of the field gradients into the free energy. Then instead of (1) one has the following equation for the free energy:

$$G(P,T) = v^{-1}\int[A(\nabla\alpha)^2 + B\alpha^2 + C\alpha^4 + h\alpha]\mathrm{d}x. \tag{6}$$

Here

$$\begin{aligned}
\alpha(P,T) &= n_\mathrm{s}(P,T) - 1/2, && (7)\\
B &= 2k_0^{-1}T_\mathrm{c} - \Delta\mu_\mathrm{int} \cong 2k_0^{-1}T_\mathrm{c} - \Delta\mu_\mathrm{int}(T_\mathrm{e}), && (8)\\
C &= 2k_0T_\mathrm{e}/3, && (9)\\
h &= \mu_\mathrm{s} - \mu_\mathrm{f} \cong (s_\mathrm{f} - s_\mathrm{s})(T - T_\mathrm{c}). && (10)
\end{aligned}$$

In (10) s_f and s_s are entropies per molecule of the fluid and solid phases respectively, v is the specific volume. Coefficient A in (6) is proportional to interfacial energy.

Note that the "external field", h, depends on the temperature. Properties of the system (6) can be analyzed using the approaches of the theory of critical phenomena. Results of the analysis will be published elsewhere [10]. Here we give just the expression determining the correlation length, R_c, which is a natural scale of the mesoscopic inhomogeneities of HPL:

$$R_\mathrm{c} \approx |B/A|^{-\nu},\ h \ll h_\mathrm{c}(B); \qquad R_\mathrm{c} \approx |h|^{-\mu},\ h \ll h_\mathrm{c}(B), \tag{11}$$

where $h_c(B) = B(B/C)^{1/2}$, and ν, μ are critical exponents.

The parameter $\tau = B/T_e$ determines how close to a critical point the system is in the vicinity of the coexisting curve. Because the thermodynamic quantities of the glass-forming liquids as a rule possess no singularities of above T_g, one can conclude that the parameter τ is not very small. In the estimations we can put $\tau \approx 10^{-1}$. For this reason the correlation length R_c is usually comparatively small, $R_c \sim 10a$ (a is the intermolecular distance). Therefore the HPL possesses the coarse grained heterophase structure and R_c is the characteristic scale of the grains.

3. Mesoscopic heterogeneity

Investigations of the thermodynamics of the solid clusters in liquid [11] show that the potential relief minima of molecules being random obey a Gaussian distribution. Because the potential relief formation is a cooperative phenomenon, it is natural to assume that the depths of the minima are highly correlated at least on the scale $\sim R_c$ which is a consequence of the coarse graining. With this assumption, the distribution found in [11] is as follows:

$$\psi_s(\varepsilon, N) = \frac{1}{(\pi N_s \delta_s^2)^{1/2}} \exp[N_s\zeta_s - N_s(\varepsilon - \overline{\varepsilon_s})^2/\delta_s^2], \qquad (12)$$

$$\delta_s^2 = (R_c/a)^3 \delta_{0s}^2\,, \qquad (13)$$

where ζ_s is the configurational entropy, δ_{0s}^2 is the variance with $R_c = a$, and $\overline{\varepsilon_s}$ is the average depth of the potential well. The index s marks the quantities related to a solid cluster.

Simple calculations give the following expression of the averaged with (12) μ_s:

$$G_s(N_s, P, T) = N_s[\overline{\varepsilon_s} - \delta_s^2/T - \sigma_s T + \mu_{s,\mathrm{vib}}(P,T)]. \qquad (14)$$

Here $\mu_{s,\mathrm{vib}}(P,T)$ is the contribution of the vibrational motions. The solid cluster in the liquid is assumed to be ergodic.

An expression similar to (12) can also be obtained for the chemical potential of a liquid cluster:

$$G_f(N_s, P, T) = N_f[\overline{\varepsilon_f} - \delta_f^2/T - \zeta_f T + \mu_{f,\mathrm{vib}}(P,T)]. \qquad (15)$$

The index f marks the quantities related to solid cluster.

4. The RFIM of the HPF

When substituted in (1) the chemical potentials (12) and (15) determine the free energy in the mean field approximation. Our goal is to take into account spatial fluctuations of the chemical potentials:

$$\delta\mu_{s,f}(x) = \mu_{s,f}(x) - \overline{\mu_{s,f}}\,. \qquad (16)$$

To this end, we have to include them in the external field term of (6):

$$h = \mu_{\mathrm{s}} - \mu_{\mathrm{f}} \cong (s_{\mathrm{f}} - s_{\mathrm{s}})(T - T_{\mathrm{c}}). \tag{17}$$

Because of (12) and (15), the random field δh obeys to the Gaussian distribution:

$$P(\delta\tau) = p_0 \exp\left[-\frac{\int |\delta\tau(x)|^2 \mathrm{d}^3x}{4\xi_h^3\delta^2}\right], \tag{18}$$

$$\delta^2 = \delta_{0\mathrm{s}}^2 + \delta_{0\mathrm{f}}^2 . \tag{19}$$

The quantity ξ_h is the correlation length of the random field h. Evidently $\xi_h \geqslant R_{\mathrm{c}}$.

The equations (6), (17)–(18) describe a RFIM with the Gaussian random field. Systems of this type are under investigation in the theory of disordered spin systems (DSS) [12,13]. An important difference between the HPF and a DSS has to be pointed out. In the DSS the disorder is frozen in, it is static and is determined by a history of the system preparation. The random field of the HPF model is self-consistent. Because of the ergodicity of the liquid it is not static. The distribution (18) describes the HPF in a fixed time. A more general description should include equations for correlation functions of $h(x,t)$. They have to be considered elsewhere [10]. One can expect that the correlation time of $h(x,t)$, τ_h, is proportional to $\xi_h^2\tau_\alpha$; τ_α is the α- relaxation time. With $t \ll \tau_h$ one can use the static approximation (18).

It is known from the physics of RFIM (see e.g. [14]) that the critical temperature is effected by the random field:

$$T_{\mathrm{c}}(\delta) = T_{\mathrm{c}}(0) - c_1\delta^{2/\varphi} - c_2\delta^2, \tag{20}$$

δ is the variance of the random field, c_1, c_2 are constants. For spin systems $\varphi \approx 1.42$. In accordance with (20) the critical temperature is depressed by the field disorder. Considering the HPF we have to replace the criterion (4) by (20) putting $T_{\mathrm{c}}(0) = k_0\mu_{\mathrm{int}}/2 > 0$. Thus

$$T_{\mathrm{c}}(\delta) = k_0\mu_{\mathrm{int}}/2 - c_1\delta^{2/\varphi} - c_2\delta^2 < T_{\mathrm{e}} \tag{21}$$

no phase transitions take place on the coexisting curve.

It is seen that not only weak interfacial energy but also strong random field fluctuations exclude phase transitions in the HPL and lead to the continuous phase transformation in the vicinity of T_{e}. Because too many liquids and polymers are good glassformers, we have no reason to expect that in all of them the interfacial free energy, μ_{int}, is negligible while the multiplicity of the local ordering of molecules with a wide variance of energies looks like their common feature. Therefore we can conclude that the multiplicity and correlation of the low energy molecular configuration in solid clusters are important factors of glass formation.

RFIM developed for the HPF in the glass-forming liquids gives good grounds for theoretical investigations of heterogeneity and dynamics in the vicinity of T_{g}.

Because the structure of a liquid above T_g is inherited by glass below T_g, we have also good grounds for dealing with mesoscopic heterogeneity of glass.

In disordered spin systems the Griffiths phase exists in the temperature region

$$T_c(0) > T > T_c(\delta). \tag{22}$$

HPF exist in the form of droplets with $\mu_{int} > 0$ but the interpercolating heterophase state appears just in the vicinity of the coexisting curve. It is worth noting that the glass-forming liquids possess the dynamic properties (characteristic relaxation laws) similar to those of Griffiths phase. It is considered to be an important similarity.

5. Conclusions

RFIM developed for the HPF permits to reveal the impact of disorder on the structure of the glass-forming liquids as well as on the phase transitions and phase transformations within them. Besides, it directly bridges up the theories of the disordered spin systems and glass-forming liquids.

6. Acknowledgements

It is my big pleasure to acknowledge E.W.Fischer for extensive helpful discussions.

References

1. Sillescu H. // J. Non-Cryst. Solids, 1999, vol. 243, p. 81.
2. Fischer E.W. // Physica A, 1993, vol. 201, p. 183.
3. Bakai A.S. // Low Temp. Phys., 1996, vol. 22, p. 733.
4. Bakai A.S. – In: The Polyclaster Concept of Amorphous Solids in Glassy Metals. III. (ed. by H. Beck and H.-J. Guntherodt) Heidelberg, Springer, 1994, p. 209.
5. Fischer E.W., Bakai A.S. Slow dynamics in complex systems. – In: AIP Conf. Proc., 469, (ed. M. Tokuyama, I. Oppenheim), 1999, p. 325
6. Yukhnovskii I.R. Phase Transitions of the Second Order. Collective Variables Method. Singapore, World Sci. Publ. Co. Ltd., 1987.
7. Frenkel J. // J. Chem. Phys., 1938, vol. 7, p. 200, p. 538.
8. Fisher M.E. // Physics, 1967, vol. 3, p. 255.
9. Bakai A.S. // Low Temp. Phys., 1998, vol. 24, p. 20.
10. Bakai A.S. // (in preparation).
11. Bakai A.S. // Low Temp. Phys., 1994, vol. 20, p. 373, p. 379.
12. Dotsenko V.S. // Uspekhi Fis. Nauk, 1995, vol. 165, p. 481.
13. Spin Glasses and Random Fields. (ed. A.P. Young) Singapore, World Sci. Publ. Co. Ltd., 1998.
14. Belanger D.P. – In: Spin Glasses and Random Fields. (ed. A.P. Young) Singapore, World Sci. Publ. Co. Ltd., 1998.

Гетерофазні флуктуації у склоутворюючих рідинах і модель Ізінга у випадковому полі

О.С.Бакай

Національний Науковий Центр
"Харківський фізико-технічний інститут",
61108 Харків

Отримано 29 травня 2000 р.

Утворення скла є процесом твердіння переохолодженої рідини. Експериментально виявлено досить великі флуктуації густини в багатьох склоутворюючих рідинах вище температури вітрифікації, але, разом з тим, жодних ознак фазового переходу не спостерігається [1,2]. В [3–5] ці неоднорідності розглядаються як гетерофазні флуктуації (ГФФ), процес утворення скла описується як неперервне фазове перетворення. Теорію сильних ГФФ тут розвинуто в наближенні середнього поля, в якому ігнорується мезоскопічна структура неоднорідностей, які є предметом інтенсивних експериментальних досліджень та обговорювань [1,2,5]. В цьому повідомленні ГФФ розглянуто в межах моделі інтерперкольованих кластерів та в підході Гінзбурга-Ландау (ГЛ). Показано, що наближення ГЛ приводить до моделі Ізінга у випадковому полі (МІВП). Це дозволяє розглядати кореляції ГФФ на проміжних та довгих масштабах. МІВП широко використовується при розгляді спінових систем з вмороженим безладом. Через це розроблена теорія дає можливість порівнювати фазові стани систем з вмороженим (спінові системи) та самоузгодженим (гетерофазні рідини) безладами. Зокрема виявляється, що гетерофазні рідини є подібні (але не ідентичні) до фази Гріфіца невпорядкованої спінової системи. Як бачимо, розроблена модель встановлює зв'язок між теоріями спінових систем та склоутворюючих рідин.

Ключові слова: *склоутворююча рідина, гетерофазні флуктуації, фазові перетворення, модель Ізінга з випадковими полями*

PACS: *64.70.Pf, 61.20.Lc*