Heterophase liquid states: thermodynamics, structure, dynamics

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The problem

- The fragility parameter (C.A. Angell, 1992),

\[ m = T_g^{-1}\left[ \frac{d(\log \tau_\alpha)}{d\beta} \right] = \frac{E_{ac}}{T_g \ln 10} \]

is a key characteristic of glass-forming liquid

- The theoretical problem: the temperature dependent quantities \( \tau_\alpha(T), E_{ac}(T) \) and parameter \( T_g \) have to be determined using a model of the liquid-to-glass transformation
Subproblems

1) Choice of a proper order parameter

2) Formulation of the free energy in terms of the order parameter

3) Deduction and solution of the equation of state, determination of the characteristic temperatures: $T_g, T_A, ...$

4) Formulation of the relaxation dynamics equation in terms of the order parameter

5) Determination of the fragility parameter
Basics

• A glass-forming liquid is heterophase (J. Stewart, R. Morrow, 1927)

• Its structure is consisting of the fluid-like and solid-like fractions (A.R. Ubbelohde, 1965)

• The fluid-like and solid-like fractions are consisting of transient mesoscopic species (fluctuons) identified by SRO (M.H. Cohen, G.S. Grest, 1979; A.S. Bakai, 1994)
The order parameter

Let us assume that

1. There are the fluid-like fluctuons and m types of the solid-like fluctuons
2. The number molecules per any fluctuon is a constant, \( k_0 \), independently on its SRO. The fluctuon size, \( r_0 \sim k_0^{1/3} \)

Thus, \( N \) molecules of liquid are forming \( m+1 \) fractions of molecules belonging to the fluctuons possessing different SRO

\[
N = N_f + N_1 + N_2 + .... + N_m
\]

• Ratios

\[
c_i(P,T) = \frac{N_i(P,T)}{N}
\]

are components of the order parameter

\[
\{c\} = (c_f, c_1, c_2, \ldots c_m)
\]
there are... BILLIONS OF GLASSES, of different packing energies, jammed

Bounded Statistics

Improbable configuration

Potential energy

Ideal glass

Crystal

Packing, or configuration, coordinate

“ENERGY LANDSCAPE”
Conditions of glass formation

• To get a glass, the long-range topological order has to be excluded,

\[ \tau_{LRO} \gg \tau_{obs} \]

• From the other hand

\[ \tau_{obs} \gg \tau_{SRO}(T) \sim \tau_{\alpha}(T) \]
The bounded partition function

- Due to the conditions of the glass formation

\[ \tau_{LRO} >> \tau_{obs} >> \tau_{SRO}(T) \]

the states with developed topological and orientational order have to be excluded from the statistics of a glass-forming liquid.

Obtained under this condition partition function, is the **bounded (restricted)** one. It can be used in accordance with the Gibbs statistics rules to describe the equilibrium states of the glass-forming liquid.
Corollary

The configurational entropy of the equilibrium glass is not equal to zero at $T \to 0$.

It includes: orientational + mixing + interfacial entropies of the statistically independent species.
Mesoscopic Hamiltonian

- Efficient mesoscopic Hamiltonian (L.D. Landau, 1958)

\[
\hat{Z}(P,T,N) = \hat{\mathcal{G}} \exp \left( \frac{\hbar}{2} \sum_{q} G_{N}(\{c_{q}\}) \right) \mathcal{G}^{0} \\
\mathcal{G}^{0} = -\beta \sum_{q} G_{N}(\{c_{q}\}) \mathcal{G}^{0}
\]

- Here

\[
G(\{c\}) = \hat{\mathcal{G}} g(x,P,T) d^{3}x
\]

with the efficient mesoscopic Hamiltonian

\[
g(x;P,T) = g_{0}(P,T) + \hat{\mathcal{A}} c_{i}(x) g_{i}^{0}(P,T) + \frac{1}{2} \hat{\mathcal{A}} c_{i}(x) c_{k}(x) g_{ik}(P,T) + T \hat{\mathcal{A}} c_{i}(x) \ln c_{i}(x)
\]

It is isomorphic to the Ising Hamiltonian with \((m+1)\)-component spin and specified exchange interactions and external fields.
Equations of the heterophase liquid equilibrium state

- Standard variational procedure leads to the mean-field equations of the heterophase liquid equilibrium state

\[
\mu_f(P,T) = \mu_1(P,T) = \ldots = \mu_m(P,T) = -\lambda
\]

\[
\mu_i(P,T) = g_i^0 + \sum_k c_k(x)g_{ik} + T \ln c_i(x)
\]

\[\lambda\] is the Lagrange multiplier

Free energy per fluctuation and coefficients of the pair fluctuation interactions are phenomenologic coefficients of the model.
Equations of the heterophase liquid equilibrium state, Cntd

- The equation of state describing the fluid-like and solid-like fractions

\[
\left(1 - 2 \bar{c}_s\right) \tilde{g}_{sf} + T \ln \frac{\bar{c}_s}{1 - \bar{c}_s} = h_{sf}
\]

\[
\bar{c}_s = \sum_{i=1}^{m} \bar{c}_i \quad \bar{c}_s + \bar{c}_f = 1
\]

\[
g_{sf}' = g_{sf} - g_{ss} / 2; \quad h_{sf} = g_f^0 - g_s^0 - g_{ss} / 2;
\]

\[
g_s^0 = \sum_k c_k^* g_k^0 + T \sum_k c_k^* \ln c_k^*
\]

- \(g_{ss}\) is the frustration parameter

\[
g_{ss} = \sum_i g_{ik} c_i^* c_k^*; \quad c_i^* = c_i / \bar{c}_s
\]
Solutions of the equation of state

1) $c_s << 1$

$$c_s^{(0)}(T) = \exp\{[D_s f, s(T_e^0 - T) - g_{sf}] / T_e^0\}$$

$$g_f^0(P, T_e^0) = g_s^0(P, T_e^0) \quad \Delta s_{f,s} = s_f - s_s$$

2) $1 - c_s << 1$

$$c_s(T) = 1 - \exp\{[D_s f, s(T - T_e^1) - g_{sf}] / T_e^1\};$$

$$g_f^0(P, T_e^1) = g_s^0(P, T_e^1) + g_{ss}$$

3) $|c_s - \frac{1}{2}| << 1$

$$c_s = \frac{1}{2} + \frac{\Delta s_{sf}(T - T_e)}{2 g_{sf}} + O((T - T_e)^3)$$

$$g_f^0(P, T_e) = g_s^0(P, T_e) - g_{ss} / 2;$$

Solutions 1) and 2) obtained by Ya. Frenkel, 1937
Solutions of the equation of state

\[ \tilde{g}_{sf}(P, T_e) > 2T_e \]

\[ \tilde{g}_{sf}(P, T_e) < 2T_e \]

- At \( \tilde{g}_{sf} = 2T_e \) the critical point exists

\[ T_e^0 - T_e^1 \approx \frac{g_{ss}}{\Delta s_{f,s}} \] is the width of the glass transition temperature range
Liquid structure states

- **Structure of the heterophase states at** $T_e^0, T_e, T_e^1$

\[ T = T_e^1, \ c_s \to 1; \ c_f \sim \exp\left(-\frac{g_{sf}}{T_e^1}\right) \]

Frenkel's solution at the phase coexistence temperature

- **Ya. Frenkel, 1937**

\[ T = T_e, \ c_s = c_f = 1/2 \]

\[ T_e^0 - T_e^1 = \frac{g_{ss}}{s_f - s_s} \]

- **Frenkel's solution at the phase coexistence temperature**

\[ T = T_e^0, \ c_f \to 1; \ c_s \sim \exp\left(-\frac{g_{sf}}{T_e^0}\right) \]
Liquid structure states, cntd

• Structure of the heterophase states at $T_e^0, T_e, T_e^1$ with multiple types of the solid-like fluctuons

\[ T = T_e^1, \ c_f \sim \exp\left(\frac{-g_{sf}}{T_e^1}\right) \]
Frenkel's solution at the phase coexistence temperature

\[ T = T_e, \ c_s = c_f = 1/2 \]

\[ T = T_e^0, \ c_s \sim \exp\left(\frac{-g_{sf}}{T_e^0}\right) \]
Frenkel's solution at the phase coexistence temperature
Example: structure of metallic glasses

- Structure of the heterophase states at $T_e^0, T_e, T_e^1$

\[ T < T_g, \ c_s = 1 \]

a) FIM Zr41Ti14Cu12.5Ni10Be22.5

b) FIM Al-Sm
F. Vurpillot et al. (2007)
Structure of a metallic glass, cntd

- Subclusters possessing different compositional and topological order

a) FIM Zr41Ti14Cu12.5Ni10Be22.5, the scale bar is 5 nm


b) Size distribution of subclusters in BMG Zr41Ti14Cu12.5Ni10Be22.5
Liquid-liquid transformations induced by ordering in the solid-like subsystem I

- Equation of state of the solid-like subsystem

\[ (1 - 2c_1^*)c_s \Phi_{12} + T \ln \frac{c_1^*}{1 + c_1^*} = h_{12} \]

- The condition of the phase transition in the solid-like subsystem is

\[ |\Phi_{12}|/2 \overset{\circ}{=} T_c > T_g \]

- The phase separation (1\textsuperscript{st} order phase transition) takes place at

\[ 0 < c_s \Phi_{12} / 2 < T_c \]

- The “antiferromagnetic” fluctuonic ordering takes place at

\[ 0 > c_s \Phi_{12} / 2 > T_c \]
Liquid-liquid transformations induced by ordering in the solid-like subsystem II

- At these phase transitions the entropy of the solid-like fraction decreases. With that the temperatures $T_{e1}$ and $T_g$ decrease due to the relation

$$T_{e1} \rightarrow T_e - \frac{g_{ss}}{2(s_f - s_s)}$$
Correlated domains (CD) and cooperatively rearranging domains (CRD)

• Close fluctuons are mutually ordered due to interactions \((g_{ik})\). The direct pair correlation function determines the fluctuonic SRO. Its correlation length determines the size of CD, \(R_{CD}\). At short-range fluctuon-fluctuon interactions \(R_{CD} \sim 2r_0\).

• Cooperative relaxation dynamics is connected with cooperative rearrangements of fluctuons connected with destruction of the fluctuonic correlations. Therefore size of CRD, \(R_{CRD}\), is comparable with \(R_{CD}\).

• As assessed value one can take for molecular liquids

\[ R_{CRD} \sim R_{CD} \sim 2r_0 \sim 2\text{-}3nm \]
Static structure factor of heterophase liquid is nearly equal to linear superposition of the structure factors of the fluid-like and solid-like fractions

\[ \tilde{\sigma}(q,T) \approx \left[ 1 - \bar{c}_s(T) \right] \tilde{\sigma}_f(q) + \bar{c}_s(T) \tilde{\sigma}_s(q) \]

\[ \tilde{\sigma}_s(q) \approx \frac{1}{\bar{c}_s} \sum_{i=1}^{m} c_i \tilde{\sigma}_i(q) \]

- Salol, WAXS: \( \tilde{\sigma}_s(q), \ \tilde{\sigma}_s(q) \) is shown
Cooperative dynamics

- Assuming that CRD is rearranging when it is "molten", i.e. when all fluctuons within the CRD are fluid-like, E.W. Fischer and A.S. Bakai, 1999 have deduced expression for the mean value of the activation energy of alpha relaxation

\[ E_{ac} = \frac{A}{(1-T_K/T)^2} + z_{\text{CRD}} (H_f - H_s)k_0^{-1}c_s + O(c_s^2) \]

- \( z_{CD} \) is the number of molecules per CRD; \( H_f, H_s \) is the enthalpy of liquid-like and solid-like fraction per molecule
The glass transition temperature

- The glass transition temperature $T_g$ depends on the observation time ($\sim 10^{-1} - 100$ sec) or liquid cooling

$$T_g = \frac{E_{ac}|_{c_s=1}}{\ln(\nu_0 \tau_{obs})}$$

$\nu_0$ is the attempts frequency, usually $\sim 10^{11} - 10^{12}$ sec$^{-1}$
An example: thermodynamics, structure and dynamics of salol

- Salol: thermodynamics, structure, alpha-relaxation

\[
C_{s,\text{cal}} = \frac{(H_f - H_{\text{exp}})}{(H_f - H_s)}
\]

\[
C_{s,\text{WAXS}} = \frac{(\omega_f - \omega_{\text{exp}})}{(\omega_f - \omega_s)}
\]

\[
E_{ac} = \frac{A}{(1 - T_K/T)^2} + z_{CD}(H_f - H_s)k_0^{-1}c_s + O(c_s^2)
\]
Fragility parameter

• Combining results obtained, we have finally

\[
m = T_g^{-1} \left[ \frac{d \left( \log \tau_\alpha \right)}{d \beta} \right] = \frac{E_{ac}}{T_g \ln 10} \bigg|_{T_g} \sim \frac{z_{CRD} T_e \left( s_f - s_s \right)}{T_g \ln 10}
\]

• For example, fragility parameter of salol estimated using this formula is nearly equal to 67
Thank you, Austen, and all, all, all...