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Glass transition and viscosity in metallic glasses and liquids

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Abstract

Experimental results on the structure and dynamics of metallic liquids and glasses are most frequently discussed in terms of phenomenological theories, such as the free-volume theory and the mode-coupling theory. However, the atomistic bases for these theories have been lacking. We propose a more fundamental, microscopic approach that may fill this gap. It is based upon the concept of fluctuating topology of atomic bonds described in terms of the atomic-level stresses. While this approach is still under development, it already has enabled quantitative description of some of the properties of metallic glasses, including glass transition, viscosity and glass formation.

Keywords: Glass transition; Viscosity; Glass formation; Atomistic theory

1. Introduction

Formulating a microscopic theory of glasses and liquids is difficult, since, unlike gasses liquids and glasses are condensed matter with strong positional and dynamic correlations. For this reason even describing their atomic structure is already a formidable challenge. In the absence of accepted fundamental theories experimentalists tend to rely upon phenomenological theories, such as the free-volume theory and the mode-coupling theory. However, the atomistic bases of these theories are unclear at best. Actually recent computer simulations seriously challenged the reality of the free-volume mechanism [1]. We propose an alternative view point, based upon the topology of the network formed by nearest neighbor atom connectivity. We first establish the connection between the topology and the local energy landscape by expressing topology in terms of the atomic-level stresses and strains [2]. We then show that the fluctuation in the atomic-level stresses, thus the local topology, is directly related to temperature, and suggest that the frustration between the continuum geometry and the discreteness of the local topology results in freezing of fluctuation and glass transition. We also suggest that the difference in the energetics between the liquid state and the solid state produces a pseudogap in the topological excitation spectrum that suppresses atomic transport and increases viscosity.

2. Phenomenological theories

Free-volume is the most widely used concept in explaining diffusion, structural relaxation and other mechanical properties, even though the idea of free-volume is nearly a century old [3,4], and the formulation by Cohen and Turnbull is already a half-century old [5–7]. Free-volume is defined as excess space between atoms which is necessary for atomic movements. This concept is intuitively appealing, particularly since it is not so difficult to measure the volume of a glass or liquid precisely and volume correlates well with the properties of a glass. For instance if a liquid is rapidly cooled the glass thus obtained has a larger volume, and is less stable. Upon annealing the volume slightly decreases as the glass relaxes. Thus volume provides a most convenient expression of the fictive temperature of the system. While this is often confused by many as the proof of validity of the model, the reality of the free-volume theory has been decisively challenged by computer simulations. They demonstrated that atomic diffusion occurs by collective small atomic motions rather than a big jump as assumed by the free-volume theory [1].

In the free-volume theory atoms can jump when a space opens up at a neighboring site which is almost as large as an atomic volume [5–7]. When this view was developed molecular dynamics simulation has not been invented, and Cohen and Turnbull had to be guided by the knowledge of the atomic transport process in crystalline solids. Thus it was natural to assume that atoms move from “site to site” through a jump by an atomic distance. But in glasses there is no “atomic sites” specified by

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the lattice, and atoms do not have to make a jump by the "atomic distance" in order to move. In fact this was pointed out by Argon [8] who proposed a "distributed free-volume model", in which atoms move by small collective steps. Recent computer simulations proved that Argon model was closer to the reality [1]. Thus even though the free-volume theory was created as an atomistic theory, its real value is as a very useful phenomenology.

Another phenomenology which has been quite successful in recent years is the mode-coupling theory [9]. It is a hydrodynamic theory extended to include non-linear effects, and has been exceptionally successful in describing the dynamic properties of supercooled liquid. It assumes that there is a critical temperature, called the mode-coupling temperature, T_C, below which density fluctuations become coupled to a slow dynamics through a feedback mechanism, resulting in increase in viscosity. The dynamic correlation functions derived from the theory agree well with experimental data, such as the dynamic structure factor by neutron or light scattering. It also provides an intuitive understanding of the feedback process that leads to glass transition. However, the microscopic basis for this theory is rather opaque.

3. Local topology and atomic-level stresses

We have been developing a theory of topological fluctuation, which may form the atomistic basis for these successful phenomenological theories. The mode-coupling theory is based upon the concept that the density functional, $n(\boldsymbol{r})$, is the basis for the description of the structure and dynamics of the system. The basic philosophy of this approach is that we are interested in viscosity, which is a low frequency, long-wave property, thus what matters is only the fluctuations close to $q = 0$ (q is the wavevector or momentum) which can be described by hydrodynamic equations. While this is true at high temperatures, at low temperatures the atomic structure, which needs description by short-wave fluctuations, intervenes in the dynamics. Thus our strategy is to start with the description of the topology of atomic structure, and try to relate the topology to energy landscape and thus to thermodynamics. For this purpose we describe the system with a tensorial quantity, a local stress tensor, $\sigma(\boldsymbol{r})$, which describes the local topology of the atomic connectivity, rather than with a scalar quantity $n(\boldsymbol{r})$.

The network of atomic connectivity, or the topology of the atomic structure, is reasonably well defined even in metallic liquids, since the interatomic potential has a negative curvature a little beyond the potential minimum, which tends to separate the second neighbor from the first neighbor and makes the definition of the nearest neighbor metallic bond meaningful [7]. At high temperatures these bonds are not static, but are cut and formed at a rate similar to the vibration frequency of an atom. That is why the atomic vibration is strongly damped. Now, in order to describe the dynamics of such topological fluctuations we have to relate it to the energy landscape.

The most obvious way to characterize the local atomic connectivity is to consider the local coordination number of an atom, N_C, or the number of the nearest neighbors. Interestingly the variation in N_C has a very direct physical meaning. The best way to picture this is to consider a void surrounded by a certain number of atoms, N_C. It is obvious that when N_C is large the void is also large. One would simply argue that N_C should scale with the surface area of the void, by,

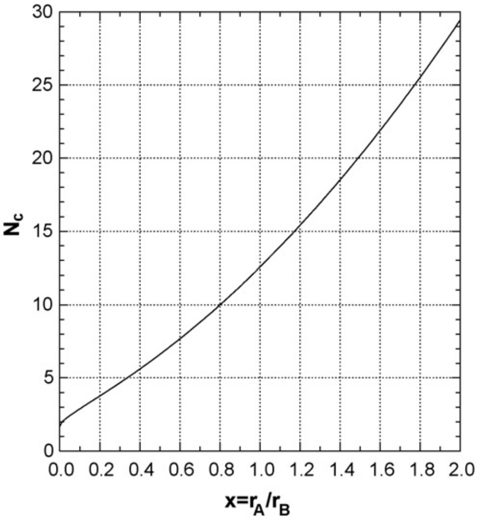

Fig. 1. Average coordination number, N_C, of an atom A with the radius r_A, embedded in the liquid or glass of atom B with the radius of r_B. The ratio of the radii is $x = r_A/r_B$ [10].

$$N_C \propto r_v^2, \tag{1}$$

where r_v is the radius of the void, since near neighbors would fill the surface of the void with a similar packing fraction. Indeed it is possible to make this scaling more quantitative. If a spherical atom with the radius r_A is embedded in the glass of atoms with the radius r_B, the average in the local coordination number N_C is approximately given by [10],

$$N_C(x) = 4\pi\left(1 - \frac{\sqrt{3}}{2}\right)(1+x)\left(1 + x + \sqrt{x(x+2)}\right), \tag{2}$$

where $x = r_A/r_B$ (Fig. 1). This equation was heuristically derived and confirmed by computer simulation [10], but a more rigorous proof is yet to be formulated. Then, if we insert an atom of which radius is different from r_A, it would result in the local pressure. In other words for a fixed atomic size the fluctuation in the local coordination means the fluctuation in the local atomic-level pressure. If we define the local atomic-level pressure of an ith atom, $p(i)$, as the local increase in the energy due to volume strain, then it is given by

$$p(i) = \frac{1}{\Omega_i}\sum_j \boldsymbol{f}_{ij} \cdot \boldsymbol{r}_{ij}, \tag{3}$$

where Ω_i is the local atomic volume of the ith atom, $\boldsymbol{f}_{ij}$ the two-body force and $\boldsymbol{r}_{ij}$ is the separation, between the atoms i and j [2]. The local pressure thus defined is indeed correlated with the local coordination number, N_C [11].

Now the local topology of the atomic bonds can be described not only by the number of the bonds, N_C, but by the anisotropy of the connection. For instance a hoop of atoms in the x–y plane may be different from that in the x–z plane. The central atom may be bound tightly in the x–y plane, but loosely in the x–z plane. This gives rise to the local shear stress. In general the atomic-level stress tensor can be defined by [2],

$$\sigma^{\alpha\beta}(i) = \frac{1}{\Omega_i}\sum\nolimits_j f_{ij}^{\alpha} r_{ij}^{\beta}, \tag{4}$$

where α and β are Cartesian coordinates. Similarly the local elastic moduli, $C^{\alpha\beta\gamma\delta}$, can be defined [11], and thus the local strain,

$$\varepsilon^{\alpha\beta}(i) = \frac{\sigma^{\gamma\delta}(i)}{C^{\alpha\beta\gamma\delta}(i)}. \tag{5}$$

Since the stress tensor is symmetric there are just six independent components, which include the pressure (3) and five shear stresses. The total shear stress, $\tau(i)$, is given as the sum of the square of the five shear stress components. In average only two elastic moduli remain; the bulk modulus, B, and the shear modulus, G [11]. The G/B ratio is related to the Poisson's ratio through,

$$\frac{G}{B} = \frac{2(1-2\nu)}{3(1+\nu)}. \tag{6}$$

4. Glass transition and viscosity

In high temperature liquids local topology rapidly fluctuates with time. The amplitude of fluctuation should depend on the local energy landscapes for such fluctuations. It was found that the atomic-level stresses provide a very simple description of the temperature dependence [11,12],

$$\frac{\langle p^2\rangle}{2BV} = \frac{BV}{2}\langle\varepsilon_v^2\rangle = \frac{1}{5}\frac{\langle\tau^2\rangle}{2GV} = \frac{GV}{2}\langle\varepsilon_s^2\rangle = \frac{kT}{4}, \tag{7}$$

where $\langle\ldots\rangle$ is thermal and temporal or ensemble average, V the atomic volume, ε_v the local volume strain and ε_s is the local shear strain. This means that the total potential energy per atom, $3kT/2$, is equally divided among the six stress components that represent local topological fluctuations. Now Eq. (7) extrapolates to zero at $T = 0$, which means all the atomic-level stresses are zero, and all the bonds have to be the ideal length. However, it is impossible to achieve this in the dense random packed (DRP) structure because of topological frustration. This means that the system will not be able to achieve thermal equilibrium and becomes non-ergodic, in other words freezes into a glassy structure.

Another view of this transition is to consider the frustration between the local discrete topology and the global continuum topology. For a monoatomic system Eq. (2) gives the ideal coordination number, $N_C = 4\pi$. At high temperatures local coordination is rapidly changing with time and it is possible to achieve such a non-integral coordination in time average. However, at low temperatures as the dynamic of fluctuation slows down, discreteness of the local atomic bonds becomes apparent. Thus some atoms become locally locked in certain coordination, and resist movement. This should happen when the fluctuation in the local coordination number, ΔN_C, becomes of the order of unity. From Eq. (2) we get,

$$\left.\frac{\partial N_C(x)}{\partial x}\right|_{x=1} = \frac{2\pi}{3}\left(\sqrt{3}+\frac{3}{2}\right), \quad \mathrm{d}x = \frac{1}{\pi}\left(\sqrt{3}-\frac{3}{2}\right)\mathrm{d}N_C. \tag{8}$$

Now the local atomic-level volume strain is

$$\varepsilon_v = \frac{3}{2}\mathrm{d}x = \frac{3}{2\pi}\left(\sqrt{3}-\frac{3}{2}\right)\mathrm{d}N_C. \tag{9}$$

Thus we expect that glass transition to occur at a corresponding pressure level.

Yet another view is to consider the difference in the energetics between the liquid state and the glassy state. The basis of Eq. (7) is that the atomic-level stresses are totally localized, and the stresses at neighboring sites are uncorrelated. This assumption is no longer valid when the system freezes into a glass, since the local stress produces a long-range stress field to contain it. This long-range stress field can be calculated in continuum approximation with the Eshelby theory [13]. For the local pressure the total elastic energy is given by

$$E_v = \frac{\langle p^2\rangle}{2BV}K_\alpha = \frac{BV}{2K_\alpha}\langle(\varepsilon_v^{\mathrm{T}})^2\rangle, \tag{10}$$

$$K_\alpha = \frac{3(1-\nu)}{2(1-2\nu)}, \tag{11}$$

where $\varepsilon_v^{\mathrm{T}}$ is the volume strain before the environment relaxes [11]. Thus instead of Eq. (7) we expect,

$$\frac{BV}{2K_\alpha}\langle(\varepsilon_v^{\mathrm{T}})^2\rangle = \frac{kT}{4}, \tag{12}$$

with the difference being the factor of K_α. As shown in Fig. 2, the equilibrium line for a glass lies under that of the liquid. Thus

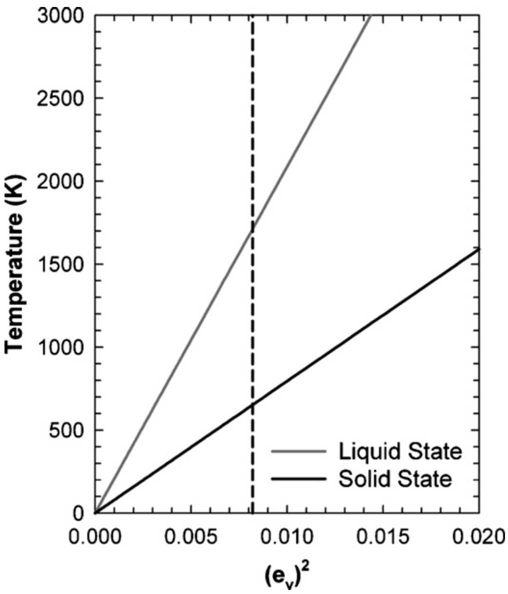

Fig. 2. Temperature dependence of the square of the local volume fluctuation, in the liquid state, Eq. (7), and in the solid state, Eq. (12), for $BV = 9$ eV and $\nu = 0.3$ representing Fe [11]. The dashed line indicates the square of the volume strain at the glass transition.

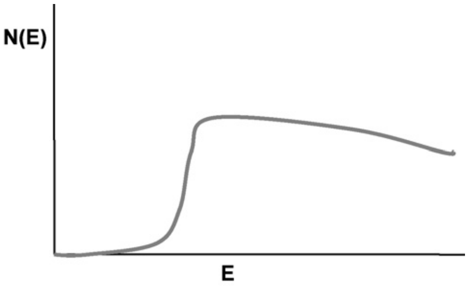

Fig. 3. Psedogap in the density of states, *N*(*E*), of topological excitations that suppresses atomic transport.

for a glass to become a liquid of the same topology extra energy has to be supplied to unrelax the long-range stress field. This creates a pseudogap in the excitation spectrum for topological fluctuation as schematically shown in Fig. 3. This pseudogap suppresses atomic transport, and is the principal cause of the increase in viscosity, leading to glass transition. Since the pseudogap is proportional to K_α, it increases with the Poisson's ratio, and diverges for $\nu = 0.5$. This has a direct relation to the dependence of the liquid fragility on the Poisson's ratio discovered recently [14], as will be discussed elsewhere [15].

Now glass transition is defined to occur when the viscosity reaches 10^{13} poise. Thus at that temperature the system should obey Eq. (12) rather than Eq. (7). Indeed recently we found that the dependence of the glass transition temperature on the Poisson's ratio is given by

$$\frac{kT_g}{4} = E_v^{\text{crit}} = \frac{BV}{2K_\alpha}\langle(\varepsilon_v^{\text{T,crit}})^2\rangle, \tag{13}$$

with impressive accuracy [15]. Interestingly the value of $\varepsilon_v^{\text{T,crit}}$ is equal to 0.091, so that the corresponding value of ΔN_C from Eq. (9) is 0.82, close to the "critical free-volume", v^*, considered by Cohen and Turnbull [5]. This implies that the fluctuation in the topology of atomic environment does not require real free-volume as large as v^*, but only the local dilatation of about 9% that allows the change in the coordination by about unity.

5. Formation and deformation of metallic glasses

Eq. (2) relates the local coordination number, N_C, to local strain. For a static structure this means that if the local strain exceeds a certain amount corresponding to a change by unity in the coordination the structure should become unstable. Actually for thermally activated systems the change of only 1/2 in coordination is enough to make the system unstable by thermal activation to the next coordination system. This argument was the basis for the compositional limit for alloy instability, thus glass formation, for the binary system [16]. The critical volume strain is given by,

$$\varepsilon_v^{\text{crit}} = \frac{3}{2}\Delta x\bigg|_{x=1} = \frac{6\sqrt{3}-9}{8\pi} = 0.0554. \tag{14}$$

Thus when the volume expands more than 6% the structure should become unstable. Indeed this condition appears to be satisfied by many elements upon melting [17]. This condition leads to an approximate expression,

$$c_B^{\min} = 0.1\frac{V}{|\Delta V|}, \tag{15}$$

where $c_B^{\min}$ is the minimum concentration of the B element to form a glass when alloyed into the A matrix, and $\Delta V = V_A - V_B$ [16].

Free-volume theory is widely used also to explain the mechanical deformation of metallic glasses [18]. However, in metallic glasses the Stokes-Einstein relationship holds only with an unrealistic value of a^2 [1], suggesting the implausibility of explaining the mechanical properties (viscosity) and atomic transport (diffusion) by a single mechanism. A more realistic approach is to consider deformation from the point of view of atomic bond rearrangement [19]. If the structure is defined by the topology of atomic connectivity, deformation should involve changes in the bond arrangement. Since it is most likely that the total number of bonds is conserved during the rearrangement, deformation proceeds mostly by bond exchange [20]. When a static stress is applied such bond exchange will result in the bond orientational anisotropy (BOA), which was actually observed by X-ray diffraction experiment [20].

6. Conclusions

In the absence of a fundamental theory of liquids and glasses phenomenological theories, such as the free-volume theory and the mode-coupling theory, have been widely used in explaining the properties of glasses and liquids. However, their atomistic basis is rather unclear. We propose a theory of local topological fluctuations that could provide such microscopic underpinning to the phenomenological theories. In this theory topology of atomic connectivity is represented by the atomic-level stresses, and evolution of their distribution with temperature determines various thermal properties. Glass transition, structural relaxation, glass formation and mechanical deformation have been well described by this theory. While the details need to be worked out by further studies, this promises to be the first fundamental theory, at least for metallic glasses, and possibly for other kinds of glasses with appropriate extension.

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