

A Mini-Review of Structural Glasses—A Personal View—

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(Received January 9, 2009; Accepted February 12, 2009)

After explaining nature of glassy systems including discussions of associated mysterious phenomena we discuss some representative theoretical ideas. We start with early ideas like the Kauzmann paradox and the Adam-Gibbs theory. More recent theories are exemplified by the mode coupling theory (MCT), the dynamical density functional theory (DDFT), and geometrical frustration.

Key words: Structural Glass, Mode Coupling, Dynamical Density Functional Theory, Geometrical Frustration

1. Introduction

This article introduces non-experts to some of the fascinations of the structural glass, which is one of the few problems in condensed matter physics which still defy complete understanding. This is contrasted with critical phenomena. Here the long-standing mysteries associated with critical anomalies were completely solved almost during one decade centered around 1971. This is the year when the first successful treatment of critical phenomena by renormalization group method was published^{*1}. In comparison, despite quite long history of glass research the field is still very young with many mysteries and expectations. See a text book by Binder and Kob (2005). (We used the word “structural glass” to distinguish it from spin glass (Binder and Kob, 2005).)

When a liquid is cooled below its melting temperature very slowly, it is supposed to undergo crystallization. However, quite often the system freezes into states other than a crystal. Such states are categorized generally as glass. However, the feature that distinguishes glasses from other states of matter is that a glassy state generally depends on how it is formed, and lowering the temperature is just one of numerous means of forming a glass. Even the cooling rate affects glass-forming temperature. This means that a glassy state cannot be uniquely specified by giving thermodynamic variables of that state like pressure and temperature. In other words, a glass is not in a thermodynamic equilibrium state. This is the source of all the difficulties in constructing a theory of glass.

Here we list some features that distinguish glass formers from other systems.

- Rapid growth of relaxation time revealed, for example, by increase of viscosity over short interval of temperature. For the class of fragile glasses the growth rate almost suddenly increases below the so-called mode coupling critical temperature denoted as T_c . Another category of glasses which are called strong glasses are those with definite activation energies associated with

viscous relaxation such as window glass. Here we will be exclusively interested in fragile glasses.

- Vanishing of entropy or specific volume as measured from their values in crystalline states (also called configurational entropy), when extrapolated to lower temperature. Since these quantities cannot assume negative values, this behavior is generally known as the Kauzmann paradox and the corresponding temperature as the Kauzmann temperature T_K .
- Sharp cross over of dynamical behavior occurs at T_c which is above the glass transition temperature T_g .
- There are more of related phenomena, details of which will be skipped such as dynamical heterogeneity and (possibly related) break-down of Stokes-Einstein relation between shear viscosity and self-diffusion constant which generally holds for dense liquids.
- There are other set of unexpected peculiar phenomena which defy understanding. A typical example is excess light scattering from supercooled liquids which is well beyond the level expected from the Landau-Placzek ratio of equilibrium fluid. A direct way to explain this excess scattering is to assume some sorts of heterogeneous objects floating in fluids such as dust. The group of E. Fischer went through very careful analyses of such possibilities, but concluded that the excess scattering does not disappear and hence is not an experimental artifact. This problem is now known as the problem of Fischer’s clusters. A detailed up to date review is given in Bakai and Fischer (2004). Here we mentioned the Fischer cluster problem as an example of strange phenomena associated with supercooled liquids and glasses, and we refrain from discussing more of these because of lack of source materials needed for that.

2. Theoretical Proposals

2.1 Early attempts

In view of complex nature of glass-forming systems, early attempts to understand glasses are either on phenomenological levels such as the Adam-Gibbs theory or de-

^{*1}See the following for critical phenomena: Herbut (2007).

tailed studies of simple toy models such as those studied for spin glasses with quenched disorder. See De Dominicis and Giardina (2006). Nevertheless these studies brought about important concepts which are still relevant today. The examples are the ideal glass transition where configurational entropy of the system appears to vanish which we discussed earlier and the Adam-Gibbs theory developed for enormous slowing down of dynamics as glass transition is approached whose relaxation time τ is typically represented by the following Vogel-Fulcher formula:

$$\tau = A \exp B/(T - T_0) \quad (1)$$

where A and B are some constants and T_0 is a characteristic temperature which happened to be very close to the Kauzmann Temperature T_K .

If we rewrite Eq. (1) in the form,

$$\tau = A \exp \Delta E(T)/T \quad (2)$$

with $\Delta E(T) \equiv T/B(T - T_0)$, $\Delta E(T)$ appears as an effective temperature dependent activation energy. Use of this effective activation energy is illustrated in Tarjus *et al.* (2005), figure 2 to analyze appearance of super-Arrhenius behavior of viscosity of glass-forming liquids.

We now explain the Adam-Gibbs theory (Binder and Kob (2005)). The basic idea of this theory is the following. In low temperature dense liquids the relaxation of the system takes place through sequential transitions occurring independently in sub-domains of the system named cooperatively rearranging regions (CRR). This process is dominated by those occurring in the smallest domains containing, say, z^* molecules since relaxation times occurring in larger domains are much slower. This transition rate is proportional to the factor $e^{-\beta z^* \Delta \mu}$ where β is the inverse of the product of the Boltzmann constant k_B times the absolute temperature T , and $\Delta \mu$ is the chemical potential change at the transition of CRR which is assumed to be a constant. Now, the system containing N molecules is supposed to be divided into those belonging to the different smallest CRR, each containing z^* molecules. If the configurational entropy of the entire system is denoted as S_c and that of a CRR by s_c , the number of the smallest domains contained in the system is given by

$$n(z^*, T) = S_c/s_c = N/z^*. \quad (3)$$

Hence the shear viscosity $\eta(T)$ and the relaxation time $\tau(T)$ (which is proportional to $\eta(T)$) are both given by

$$\eta(T), \tau(T) \propto e^{C/s_c} \quad (4)$$

with $C \equiv N\beta s_c \Delta \mu$ a smooth quantity in this theory. If we remind that the configurational entropy vanishes at T_K which is taken to be the same as T_0 , then near this temperature we have $S_c \approx D(T - T_0)$. This reproduces the Vogel-Fulcher form Eq. (1) with $B = C/D$.

If a CRR has a diameter, say, $\xi(T)$ and assume a relation like $\Delta E(T) \propto \xi(T)^\mu$ near the Kauzmann temperature, this implies that a CRR has the linear size behaving as $\xi(T) \propto (T - T_0)^{1/\mu}$.

Note that the source of singularity at $T = T_0$ comes from ever growing size of CRR.

2.2 First principle theories

2.2.1 Mode coupling theory (MCT) In the preceding subsection we have been concerned with thermodynamic and macroscopic properties of the system such as heat capacity and viscosity, or the overall relaxation time. Under such circumstances, when the first principle theory of structural glasses was proposed under the name of mode coupling theory (MCT) of glass transition in the mid eighties. See Götze (1991), and Götze and Sjögren (1992). This theory appears to be greeted with a great surprise but more with skepticism. There is a good reason for skepticism. The MCT was originally developed for critical dynamics where one deals with fluctuations with diverging length and time scales (see Herbut (2007) and Hohenberg and Halperin (1977)). Therefore it makes a great sense to forfeit molecular details in favor of collective large length scale fluctuations, whereas primarily the dynamics on microscopic length scales was thought to play major role in glass transition^{*2}, Götze (1991), Götze and Sjögren (1992), and Götze (2009). Also see Miyazaki (2007) for an up-to-date review of MCT including diverging length scales.

Here we outline the MCT formalism developed for one-component fluid. The formalism used here has basically the same framework as that developed for critical fluids. See Kawasaki (1970, 1971, 1976). However, the physical contents are totally different. In critical dynamics critical singularity that appears in dynamical behavior simply reflect that of equilibrium critical phenomena. In contrast, equilibrium properties of supercooled liquids are assumed to be smooth functions of thermodynamic parameters, and any singularity has to be generated by analyzing the MCT equation itself. See Götze (1991), Götze and Sjögren (1992), and Götze (2009).

A simplest indication that this might actually happen was embodied by the earlier work of Geszti (1983). Here we consider supercooled liquid to be characterized by the shear viscosity $\eta(T)$ and the self-diffusion constant $D(T)$. Note that the self-diffusion constant reflects motion of a single labeled atom in contrast to more common mutual diffusion in binary fluid mixtures. Then the fact that viscosity is enhanced by difficulty of atomic motions reveals itself by increase of the relaxation time, which in turn is proportional to the inverse self-diffusion constant. Therefore we may write

$$\eta(T) = \eta_0 + b(T)D^{-1}(T) \quad (5)$$

where η_0 is a constant background and $b(T)$ is a smooth coefficient. On the other hand shear viscosity and self-diffusion constant are connected by the Stokes-Einstein relationship which was originally derived for a large sphere floating in fluids but is known to be qualitatively correct for a labeled atom in the fluid consisting of the same kind of atoms:

$$D(T) = \frac{k_B T}{6\pi a \eta(T)} \quad (6)$$

where a is the atomic diameter.

^{*2}Recently different views are expressed saying that dynamics of diverging length scales may show up in supercooled liquids in some subtle ways. See Berthier *et al.* (2007a, b).

By combining these two Eqs. (5) and (6) we recover

$$\eta(T) = \frac{\eta_0}{[1 - 6\pi ab(T)/k_B T]}. \quad (7)$$

The viscosity obtained is seen to diverge at the temperature T_c determined by

$$6\pi ab(T_c)/k_B T_c = 1. \quad (8)$$

This is a self-consistent theory and its physical picture is clear: in dense fluids movement of any atom is hampered by the presence of neighboring atoms. Movement of any one of neighboring atoms itself is hampered by its neighbors including the original atom. This feedback mechanism is revealed through Eqs. (7) and (8).

The above explanation of the self-consistent caging is too simple for quantitative prediction. For the latter purpose more sophisticated theoretical framework is needed. Here the mode coupling theoretical framework originally developed for critical dynamics enters. Our objective is the time correlation function of Fourier components of the density fluctuations $\rho(\mathbf{r}) - \rho_0$ or its Fourier transform $\rho_{\mathbf{k}}$ defined by

$$\begin{aligned} \Phi_k(t) &\equiv \frac{\langle \rho_{\mathbf{k}}(t)\rho_{-\mathbf{k}}(0) \rangle}{\langle \rho_{\mathbf{k}}(0)\rho_{-\mathbf{k}}(0) \rangle} \\ \rho_{\mathbf{k}}(t) &\equiv \int d\mathbf{r} [\rho(\mathbf{r}, t) - \rho_0] e^{-i\mathbf{k}\cdot\mathbf{r}} \end{aligned} \quad (9)$$

where $\langle \dots \rangle$ stands for equilibrium average where a supercooled state is regarded as equilibrium as long as its life-time is large enough, the case we will be concerned with here. Also $\rho(\mathbf{r}, t)$ is the local density at the position $\mathbf{r}$ and the time t and $\rho_0 \equiv \langle \rho(\mathbf{r}, 0) \rangle$ is the constant equilibrium density.

Here we start from continuum stochastic equations for $\rho(\mathbf{r}, t)$ and the momentum density $\mathbf{j}(\mathbf{r}, t)$ rather than a microscopic molecular model. This approach due to Das and Mazenko (1986) is obviously influenced by what was done in critical dynamics described for instance in Kawasaki (1970, 1971, 1976). In the latter problem this starting point is justified if one works in the mesoscopic space-time scales intermediate between microscopic and macroscopic scales. In non-critical liquids this is not obvious since there is no such obvious mesoscopic regime. This is done here since the simplest resulting mode coupling equation for $\Phi_k(t)$ is identical to those that start from microscopic models and projector formalism (Götze, 1991; Götze and Sjögren, 1992), and is flexible enough to contemplate improving the approximation used.

The starting equations of motion are^{*3}

$$\begin{aligned} m \frac{\partial}{\partial t} \rho(\mathbf{r}, t) &= -\nabla \cdot \mathbf{j}(\mathbf{r}, t) \\ \frac{\partial}{\partial t} \mathbf{j}(\mathbf{r}, t) &= \mathbf{f}(\mathbf{r}, t) - \frac{v_0}{m\rho_0} \mathbf{j}(\mathbf{r}, t) + \zeta^0(\mathbf{r}, t). \end{aligned} \quad (10)$$

Here m is the mass of one molecule, v_0 is the kinetic viscosity of molecular origin (that is, the bare viscosity, see

^{*3}The set of Eq. (10) in general are not consistent with the detailed balance condition for which quadratic terms in the momentum density are required (private communication of B. Kim). Here we do not go into details.

Hohenberg and Halperin (1977)), and $\mathbf{f}(\mathbf{r})$ is the force density acting at a fluid element located at $\mathbf{r}$ due to the intermolecular force (here and after we often suppress arguments t in defining physical quantities), which can be shown to be expressed as

$$\mathbf{f}(\mathbf{r}) \equiv -\rho(\mathbf{r}) \nabla \frac{\delta H(\{\rho\})}{\delta \rho(\mathbf{r})} \quad (11)$$

where $H(\{\rho\})$ is the total free energy functional when the density profile $\{\rho\}$ is given, and is called the free energy density functional. The last two terms on RHS of the second member of (10) are the reminder that we are in fact dealing with molecular systems and represent effects left out in this continuum treatment. In particular these two terms are related through

$$\langle \zeta^0(\mathbf{r}, t) \zeta^0(\mathbf{r}', t') \rangle = 2k_B T v_0 \mathbf{1} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'). \quad (12)$$

Here $\mathbf{1}$ is the unit tensor of space and the free energy density functional is yet to be chosen. It is common to choose the Ramakrishnan-Yussouff form (Ramakrishnan and Yussouff, 1979) as follows though use of this is not quantitatively justified in general:

$$\begin{aligned} H(\{\rho\}) &= k_B T \int d\mathbf{r} \rho(\mathbf{r}) \left[\ln \left(\frac{\rho(\mathbf{r})}{\rho_0} \right) - 1 \right] - \frac{1}{2} k_B T \\ &\quad \cdot \int d\mathbf{r} \int d\mathbf{r}' c(\mathbf{r} - \mathbf{r}') (\rho(\mathbf{r}) - \rho_0) (\rho(\mathbf{r}') - \rho_0). \end{aligned} \quad (13)$$

Here $c(\mathbf{r})$ is the direct correlation function whose Fourier transform $c_{\mathbf{k}}$ is related to the static structure factor $S_{\mathbf{k}}$ through $c_{\mathbf{k}} = \rho_0^{-1} (1 - S_{\mathbf{k}}^{-1})$ and is a sort of effective intermolecular interaction potential (Hansen and McDonald, 2006).

We shall not be interested in effects of microscopic degrees of freedom represented by the last two terms of Eq. (10), which hence will be omitted where their effects come in solely through contacts with heat bath having the temperature T . Then, if the force density $\mathbf{f}(\mathbf{r})$ were linear in $\delta\rho(\mathbf{r}) \equiv \rho(\mathbf{r}) - \rho_0$ and $\mathbf{j}(\mathbf{r})$ the equation of motions Eq. (10) are linear in these variables and these equations describe trivial local oscillations in fluid. Hence, to gain any significant results it is essential that we keep nonlinearity of Eq. (11), which is displayed as follows where linear and nonlinear parts are indicated by superfixes l and nl , respectively:

$$\begin{aligned} \mathbf{f}(\mathbf{r}) &= \mathbf{f}^l(\mathbf{r}) + \mathbf{f}^{nl}(\mathbf{r}) \\ \mathbf{f}^l(\mathbf{r}) &\equiv -k_B T \nabla \left[\delta\rho(\mathbf{r}) - \rho_0 \int d\mathbf{r}' c(\mathbf{r} - \mathbf{r}') \delta\rho(\mathbf{r}') \right] \\ \mathbf{f}^{nl}(\mathbf{r}) &\equiv k_B T \int d\mathbf{r}' c(\mathbf{r} - \mathbf{r}') \delta\rho(\mathbf{r}) \delta\rho(\mathbf{r}'). \end{aligned} \quad (14)$$

Our basic starting equation is now written after Fourier transformation and elimination of the momentum density as

$$\frac{\partial^2}{\partial t^2} \rho_{\mathbf{k}}(t) = -\Omega_k^2 \rho_{\mathbf{k}}(t) + \frac{R_{\mathbf{k}}(t)}{m} \quad (15)$$

with $\Omega_k \equiv k\sqrt{k_B T / m S_k}$ and

$$R_{\mathbf{k}} \equiv k_B T \frac{1}{(2\pi)^3} \int d\mathbf{q} \mathbf{k} \cdot \mathbf{q} c_{\mathbf{q}} \rho_{\mathbf{k}-\mathbf{q}} \rho_{\mathbf{q}}. \quad (16)$$

Here Ω_k is the frequency of local short wavelength oscillations in fluids and R_k is the remaining nonlinear contribution. Note that R_k contains large numbers of density fluctuations with various wave vectors which give it a random variable character in time. Thus, Eq. (15) takes the form of a generalized Langevin equation of the Brownian particle with the inertia term. We now return to the time correlation function introduced by (9). By the well-known technique originally due to Mori (see e.g. Kawasaki, 2000), this generalized Langevin-type equation gives rise to the following equation for $\Phi_k(t)$

$$\frac{d^2}{dt^2} \Phi_k(t) = -\Omega_k^2 \Phi_k(t) - \int_0^t ds M_k(t-s) \frac{d}{ds} \Phi_k(s) \quad (17)$$

where the memory kernel $M_k(t)$ is

$$M_k(t) \equiv \frac{1}{m^2 \langle |\dot{\rho}_k|^2 \rangle} \langle R_k(t) R_{-k}(0) \rangle. \quad (18)$$

The equation obtained here for $\Phi_k(t)$ is not yet useful since $R_k(t)$ and $R_{-k}(0)$ are both bilinear in the density fluctuations. It is common to factorize this four-body correlation function into the sum of the products of the pair correlation functions Φ 's themselves. This gives rise to

$$M_k(t) \approx \frac{\rho_0 k_B T}{2mk^2} \frac{1}{(2\pi)^3} \int d\mathbf{q} [\mathbf{k} \cdot \mathbf{q} c_q + \mathbf{k} \cdot (\mathbf{k} - \mathbf{q}) c_{|\mathbf{k}-\mathbf{q}|}]^2 \cdot S_q S_{|\mathbf{k}-\mathbf{q}|} \Phi_q(t) \Phi_{\mathbf{k}-\mathbf{q}}(t). \quad (19)$$

Combining this with Eq. (17) we obtain a nonlinear integral equation to determine $\Phi_k(t)$ selfconsistently where the initial conditions are

$$\Phi_k(0) = 1, \quad \left. \frac{d}{dt} \Phi_k(t) \right|_{t=0} = 0. \quad (20)$$

Here the time independent quantities entering the above set of equations such as ρ_0 , T , m , S_k , c_k are regarded as external control parameters. We are primarily interested in the long time behaviors of $\Phi_k(t)$. Quite often this function tends to zero at the infinite time (i.e. an ergodic state), but in some times there remains a finite component (i.e. nonergodic state). This depends on where we are in the parameter space, and one can observe transition from an ergodic state to a nonergodic state and *vice versa* which marks a phase boundary. This aspect of the problem was studied in great detail both analytically and mostly numerically (Das, 2004).

The above mentioned theoretical framework is the celebrated mode coupling theory (MCT) of glass transition by Götze (1991), Götze and Sjögren (1992) and Götze (2009) and is the only existing theory that starts from the first principles. The theoretical results were successfully compared with experiments and computer simulations. See Götze (1999) and Binder and Kob (2005). In particular the theory was even quantitatively successful for colloidal solutions where arrangements of colloidal particles in solvent display completely disordered moving state (fluid), or regular (crystal) and disordered frozen (glassy) state (Zaccarelli *et al.*, 2003).

Now, we must touch on some negative aspects of MCT. Successful comparison with experiments and simulations are primarily those occurring on relatively short length and time scales like those explored by neutron scattering, synchrotron radiation scattering, etc. However traditional glass research focused on macroscopic behavior like viscosity and heat capacity which cannot be successfully treated by MCT. For instance, MCT predicts divergence of viscosity at the MCT critical point where a transition from ergodic to nonergodic state is predicted. If we follow the temperature, this transition occurs somewhere above the normal glass transition temperature, where the observed viscosity does not show a divergence, but often cross-over from one behavior to another behavior. This difference is believed to result from the important effects of thermal noise which destroys frozen structures appearing in MCT non-ergodic states. Attempts have been made to remedy this short coming, but the current situation can be summarized just by saying it is utterly confusing. We suggest that a way out of this is to treat the noise problem differently as we shall explain in the next section.

It is of some interest to compare use of MCT in critical dynamics and glasses. The original MCT in critical dynamics described in Kawasaki (1970, 1971, 1976) derived dynamical equation for correlation functions where all the static properties with their critical singularities were regarded as given input. Thus the outcome of the theory reflects both critical anomalies in the input data as well as those generated by solving the equation. On the other hand in glasses these input were given as smooth quantities and any singularities must come out of solving the self-consistent equation. On the other hand, if we take up dynamical renormalization group (DRG) approach to critical dynamics reviewed in Hohenberg and Halperin (1977), all the inputs of the theory are assumed to be constants or at most smooth quantities. Here any critical anomalies must come out of solving the equations of the theory, that is, the dynamical renormalization group equations containing only non-singular parameters. In this sense the latter has some similarities to MCT for glasses. A close formal relationship between MCT and DRG approaches for critical dynamics was discussed in Kawasaki and Gunton (1976).

Now, the crucial message of MCT is that when certain variable set describing dynamics of the system is slowly varying in time i.e. slow variables, functions of this set of variables including their products equally change slowly. This suggests a possibility of treating the slow variables and their products on the same footing, whereby constructing more general theories of slow dynamics. Such treatments have been proposed in the literature. See Machta and Oppenheim (1982) and Szamel (2007) and the intervening publications by many authors (e.g. Andersen, 2003a, b). If one pushes this point of view further, one eventually arrives at the probability functional of slow variables, here the probability density functional, which will be treated in 2.2.2.

It is probably worthwhile to remind again that the current MCT of supercooled liquids originated from that for critical dynamics, and hence inherits its weaknesses. In other words, the current MCT can deal with effects of cru-

cial nonlinearity to the extent that can be dealt with by the renormalized perturbation theory. The difficulty of standard MCT for glass-forming ideal gas discussed in the last section seems to exemplify a serious problem faced by MCT. In critical dynamics, this restricts the theory to higher spatial dimensionality, presumably $d \geq 3$. In lower dimensionality, say, at two dimensions, topological defects can play dominant role where plane wave modes are clearly inadequate. See Herbut (2007). There are other cases where renormalized perturbation theory is quite inadequate, such as fully developed turbulence (Frisch, 1995) and late stage phase-ordering dynamics. The latter is reviewed in Bray (1994) and in Kawasaki (2000).

2.2.2 Dynamical density functional theory (DDFT)

The original density functional theory (DFT) of liquids was motivated to gain informations about heterogeneous equilibrium liquids like those near a wall (we do not consider here its original quantum counterpart). As a typical example let us consider the Ramakrishnan-Yussouff density functional (Ramakrishnan and Yussouff, 1979)

$$H(\{\rho\}) = k_B T \int d\mathbf{r} \rho(\mathbf{r}) \left[\ln \frac{\rho(\mathbf{r})}{\rho_0} - 1 \right] - \frac{1}{2} k_B T \cdot \int d\mathbf{r} \int d\mathbf{r}' c(\mathbf{r} - \mathbf{r}') (\rho(\mathbf{r}) - \rho_0) (\rho(\mathbf{r}') - \rho_0) \quad (21)$$

where the direct correlation function $c(\mathbf{r})$ is that for a uniform liquid in equilibrium. Now, suppose that we place the liquid under the influence of an external potential $u(\mathbf{r})$, say, to bring it into a heterogeneous state. The external field $u(\mathbf{r})$ may, for instance, mimic effects of a boundary wall. The density profile $\rho(\mathbf{r})$ that is actually realized is obtained by minimizing the total free energy functional $H(\{\rho\}) - \int d\mathbf{r} u(\mathbf{r}) \rho(\mathbf{r})$ with respect to $\rho(\mathbf{r})$:

$$\frac{\delta}{\delta \rho(\mathbf{r})} H(\{\rho\}) = u(\mathbf{r}). \quad (22)$$

Actually, quantitatively speaking, the density functional (DF) given by Eq. (21) turned out to give generally poor results since this is basically a quadratic approximation of the free energy functional in powers of the density fluctuation around the uniform density, and many proposals of more complicated free energy functionals have been proposed with quite good quantitative results. However, it seems to the author that all these are more or less of engineering type in the sense that choices are made for $H(\{\rho\})$ so as to produce good results. We focus on dynamics with $H(\{\rho\})$ given by Eq. (21) and we shall not deal with these modified DF.

Now, the spirit of the dynamical density functional theory (DDFT) is, in one word, to adiabatically eliminate the momentum density from the equation like Eq. (10) assuming that the momentum density changes much faster than the density, which has been justified by some intuitive arguments by Cohen and also by computer simulation. See the review of Das (2004). This makes sense since our interest is primarily on the slow dynamics exhibited by the density. The outcome of this with some simplifications is succinctly expressed by the following functional equation of motion

for time evolution of the probability that a density profile $\{\rho\}$ is realized:

$$\frac{\partial}{\partial t} P(\{\rho\}, t) = -L \int d\mathbf{r} \frac{\delta}{\delta \rho(\mathbf{r})} \nabla \cdot \rho(\mathbf{r}) \nabla \left[T \frac{\delta}{\delta \rho(\mathbf{r})} + \frac{\delta H(\{\rho\})}{\delta \rho(\mathbf{r})} \right] P(\{\rho\}, t) \quad (23)$$

where L is a kinetic coefficient. The first term on RHS following the big square bracket above with T is the thermal noise which was missing in the MCT of the preceding subsection.

The second term there containing $(\delta H(\{\rho\}))/\delta \rho(\mathbf{r})$ gives a deterministic change of the density which was treated in the MCT. The factor $\rho(\mathbf{r})$ sandwiched between the two ∇ shows the fact that the thermal noise here is of the multiplicative type, which distinguishes this model from more conventional time-dependent Ginzburg-Landau equations where noise is of additive type. Indeed this is the most crucial feature of Eq. (23), which permits one to derive from it the self-consistent equation for $\Phi_k(t)$ given in 2.2.1 if we use the factorization approximation of the kind used in 2.2.1. Here is a caveat in applying the factorization for purely dissipative type model systems like ours in contrast to that in 2.2.1. In general, if we use the usual factorization approximation for purely dissipative nonlinear stochastic equations, we often times end up with unphysical queer results like the correlation function exhibiting spurious divergences or even change of sign. A way out is to first transform memory kernel into the so-called irreducible form (e.g. Kawasaki, 1995, 1997). In simple words the question boils down to whether one is concerned with the renormalization of relaxation rate or the relaxation time. For glassy behavior we are obviously concerned with the life-time renormalization.

In this connection it is useful to mention that in Eq. (17) where the mode coupling is of reversible type the memory kernel is folded onto *time derivative* of $\Phi_k(t)$, which is in contrast to the case of dissipative mode coupling. In order to see this we generalize Eq. (17) by adding a dissipative mode coupling term as the second term on RHS of the following equation^{*4}

$$\frac{d^2}{dt^2} \Phi_k(t) = -\Omega_k^2 \Phi_k(t) - \int_0^t ds N_k(t-s) \Phi_k(s) - \int_0^t ds M_k(t-s) \frac{d}{ds} \Phi_k(s). \quad (24)$$

Here the dissipative memory kernel $N_k(t)$ is folded onto $\Phi_k(t)$ itself. We now consider the long time behavior of Eq. (24) where the term with second time derivative is dropped and the memory kernels assumed to have zero duration, that is, they behave as a delta function in time. Then we see that the reversible MC tends to enhance inverse of the relaxation rate (i.e. life time) whereas dissipative MC tends to enhance the relaxation rate itself.

^{*4}Equation (24) might better be regarded as an equation concocted to explain two types of mode coupling rather than that derived from other equation by generalization.

The main objective of DDFT is not the rederivation of the MCT equation just described but to move on one step forward, in particular, to include effects of thermal noise neglected in the standard MCT. This is important especially in the long time where the system is trapped in a local minimum of free energy landscape. Transitions among such local minima are possible only by including thermal noise, which should be possible if we return to Eq. (23). Before moving on to this problem we must mention that we can use this equation to compute $\Phi_k(t)$ if we use factorization approximation of the kind used before. However, note the fact that Eq. (23) has as its stationary state solution the equilibrium solution with the Boltzmann weight:

$$P(\{\rho\}, t = \infty) = \mathcal{N} \exp[-\beta H(\{\rho\})] \quad (25)$$

where $\mathcal{N}$ is the normalization factor. Barring possible singular behavior of the operator in front $-L \int d\mathbf{r} (\delta/\delta\rho(\{\mathbf{r}\})) \nabla \cdot \rho(\{\mathbf{r}\}) \nabla$ the equilibrium solution (25) is unique if the conserved quantity $\int d\mathbf{r} \rho(\mathbf{r})$ is fixed.

Direct numerical analysis of (23) is difficult because of the extra factor $\rho(\mathbf{r})$ giving rise to multiplicative noise. We have mapped this equation onto a kinetic lattice gas and analyzed it with Monte-Carlo method (Fuchizaki and Kawasaki, 2002). The results were rather striking. When the overall density exceed a certain limit, a number of heterogeneous random structures appear and overlaps among different such states can be obtained. Overlaps are more widely distributed with increasing probability width as the overall density increases. Also we monitored overlaps of one heterogeneous state at one fixed time and at later times. This way we followed time evolution. Overlap of the initial heterogeneous state with that at later times clearly exhibit barrier crossing from one metastable heterogeneous state to another.

2.3 Geometrical frustration

More than half a century ago Charles Frank noted that in dense liquid consisting of atoms interacting with the Lennard-Jones potential, the energy contained in a small region is smaller if the atoms are locally arranged in tetrahedral structures rather than in closest packing structures (fcc and hcp). However, if one attempts to fill the entire space with tetrahedra, one finds that perfect packing is impossible leaving a gap of $7(1/2)^\circ$ around the common edge of five touching tetrahedra. If one tries to eliminate this gap by distorting each tetrahedron a little bit, this will cost some elastic energy. This building up of elastic energy per unit volume grows with some positive power of the system size. This is an example of geometrical frustration. A way to relieve this frustration is to release this excess elastic energy by introduction of a disclination line network. An extensive theoretical work exists along this line of thoughts, which is due to Nelson and many others. For an up-to-date review, see Tarjus *et al.* (2005).

A purely continuum approach was also developed to simulate frustrated systems. A simple version starts from the following free energy functional for a d -dimensional system with $\psi(\mathbf{r})$ an appropriate local order parameter:

$$\mathcal{H}[\psi] = \int d\mathbf{r} \left\{ -\frac{1}{2} r_0 \psi(\mathbf{r})^2 + \frac{v}{2} (\nabla \psi(\mathbf{r}))^2 \right\}$$

$$+ \int d\mathbf{r} \int d\mathbf{r}' \frac{Q}{2} \frac{1}{|\mathbf{r} - \mathbf{r}'|^{d-2}} \psi(\mathbf{r}) \psi(\mathbf{r}'). \quad (26)$$

Here r_0 and v are some positive constants, and Q gives a strength of long-range interaction giving rise to an excess elastic energy. The energy density is given by

$$\int d\mathbf{r}' \frac{Q}{2} \psi_0^2 \frac{1}{|\mathbf{r} - \mathbf{r}'|^{d-2}} \sim V^{\frac{2}{d}} \quad (27)$$

where ψ_0 is the average of $\psi(\mathbf{r})$ and V is the system volume. This gives a contribution to $\mathcal{H}$ behaving as $V^{1+2/d}$, which is clearly superextensive. For further details, see Tarjus *et al.* (2005) again.

Since this approach focuses on well-localized objects, this will complement the MCT-DDFT approach where plane wave type excitations are dominant. However, dynamical aspects of the geometrical frustration approach are yet to be developed.

3. Summary and Discussion

We have given a brief overview of the current status of our understanding of structural glasses. In view of author's limited experience in this field, this review is necessarily one-sided. Probably too much space is devoted to first principle approaches. Nevertheless there is some justification since we have seen enormous progress in the field of first principle approaches in the last two decades or so during the long history of structural glass research.

What are then the remaining problems? There is plenty and here we can mention only a small fraction of important problems that have come to author's mind.

- Systematize higher order renormalized perturbation calculation starting from MCT as the zeroth order. There are two types of proposals put forward so far: (1) field-theoretical formulation where particular attention is paid to preserve the fluctuation-dissipation relationship at each order of calculation. See Andrenov *et al.* (2006), and also Kim and Kawasaki (2007, 2008), and (2) algebraic approach to renormalized perturbation theory and its diagrammatic representation. See Andersen (2002, 2003a, 2003b), and Szamel (2007). In this connection, use of models with the Kac-type potential may be worthwhile in view of a smallness parameter of perturbation theory. See, e.g. Franz (2008).
- To extend the current MCT and TDFT to the problems far from equilibrium like aging and systems under imposed shear flow.
- Questions about glass-forming ideal gas models. See Charbonneau *et al.* (2008). Naive applications of MCT failed because interactions enter here only through static correlations as input that are only for ideal gas without a trace of interactions responsible for freezing. There are lots of non-trivial points one can think of in this simple-minded applications of MCT. For instance $\langle \delta\rho_{\mathbf{k}}(t=0)\delta\rho_{\mathbf{k}} \rangle$ can be different from that for equilibrium.
- Phase diagram of ergodic-nonergodic transition is currently based on solving MCT equation and extrapolating the solution to the infinite time. Why not there be an entirely static calculations for this, e.g. by replica

technique? See for instance Mézard and Parisi (2000). An attempt in this direction was recently made by Crisanti (2008).

- Current MCT uses only plane wave modes, which is because the systems treated so far are transitionally invariant. This need not be always the case. As an example, if the system is confined to a finite space, and diverging length scales are involved, modes other than plane waves can necessarily enter^{*5}.
- In view of the limitation of Subsec. 2.2 in treating strong nonlinearities the approach that deals with topological defects associated with geometrical frustration shows us a direction to proceed in future.

Acknowledgments. It is a pleasure to thank Bongsoo Kim for continued collaboration and unfailing assistance over many years. Thanks are also due to him and Kuni Miyazaki for useful comments on this work. The author gratefully acknowledges a financial support of Research Grant No. 20540381 of the Japan Society for Promotion of Science.

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^{*5}Recently Krakoviack (2008) considered confined fluids. However, he looked at fluids confined randomly, and the randomness is averaged out afterwards. Thus the translational invariance is recovered, for which plain wave modes are sufficient.