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## LETTER TO THE EDITOR

# Random solutions from a regular density functional Hamiltonian: a static and dynamical theory for the structural glass transition

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**Abstract.** A simple model density functional Hamiltonian is shown to lead to a consistent static and dynamical theory of the structural glass transition where glassy metastable free-energy states play a key role. The crucial concept introduced is a probabalistic order parameter description that results when multiple solutions of the density functional theory are considered where each solution is given a canonical weight. The theory suggests that there are two distinct transition temperatures (or densities). At the higher transition temperature an extensive number of well defined global metastable states appear for the first time. At the lower transition temperature the number of relevant glassy metastable states becomes non-extensive.

In this letter we present a consistent static and dynamical description of a model liquid approaching a structural glass (STG) transition (for a recent review of structural glasses, see [1]). Physically our model calculation implies that below a temperature (region) denoted  $T_A$  the long-time dynamics is controlled by multiple metastable glassy free-energy states. To develop these concepts we think it is crucial to view the glass transition as *both* a static and a dynamical phenomenon. Even when a liquid is kinetically trapped in a locally stable metastable state, that state can be described using a static theory. In order to control our calculations we will use a somewhat unrealistic model density functional Hamiltonian (DFH) for the liquid state. Because of this, the ideas presented here should be regarded as a possible theoretical scenario for the STG transition. Throughout this letter we also ignore the fact that in general the STG transition will occur only if crystallisation is avoided by rapid quenching [1]. If the time it takes to form a crystal is long compared with the relatively slow cooling, one can obtain disordered glassy states while maintaining the liquid close to (metastable) equilibrium. This is the case for good glass-forming materials. For metallic glasses on the other hand where the natural relaxation times are quite short ( $\sim 10^{-10}$  s) one requires rapid cooling to prevent the system from forming nucleating centres leading to crystallisation. Thus metallic glasses are systems far from equilibrium and hence are different from the systems considered here. The theoretical scenario presented here is concerned with generic glass-forming materials and hence we focus only on the random solutions of an equilibrium DFH.

The model DFH is<sup>†</sup>

$$\beta\mathcal{H} = -\mu \int d\mathbf{x}_1 \delta n(\mathbf{x}_1) + \frac{1}{2} \int d\mathbf{x}_1 d\mathbf{x}_2 \delta n(\mathbf{x}_1) \chi_0^{-1}(\mathbf{x}_1 - \mathbf{x}_2) \delta n(\mathbf{x}_2) \\ + \frac{1}{3} g_3 \int d\mathbf{x}_1 (\delta n(\mathbf{x}_1))^3 + \frac{1}{4} g_4 \int d\mathbf{x}_1 (\delta n(\mathbf{x}_1))^4 - \int d\mathbf{x}_1 H(\mathbf{x}_1) \delta n(\mathbf{x}_1) \quad (1a)$$

where  $\beta$  is the inverse temperature,  $\mu$  is the chemical potential,  $\delta n(\mathbf{x}_1) = n(\mathbf{x}_1) - n_0$  is a density fluctuation from the mean density  $n_0$ ,  $H(\mathbf{x}_1)$  is a small ( $\rightarrow 0$ ) symmetry-breaking external field (whose role is discussed in the context of the static approach), and  $g_3$  and  $g_4$  are small non-linear coupling constants whose magnitude will be chosen such that a systematic expansion in density fluctuations is possible.  $\chi_0(k)$  ( $k =$  wavenumber) is related to a bare static structure factor,  $\chi_0(k) = n_0 S_0(k)$ , and contains information on the short-ranged order present in liquids. In dense simple fluids  $S(k)$  is sharply peaked at an ordering scale  $k_0 (\sim 2\pi/\sigma, \sigma \sim$  molecular diameter). In (1a) this implies that there is a local tendency for spherically symmetric ordering as is found in liquids and in some glasses. DFH such as (1a) can be derived from standard statistical mechanical ensembles by constraining the microscopic number density to have a specified value and then integrating over all microscopic phases, and retaining terms up to  $O((\delta n)^4)$ . In general the cubic and quartic terms are non-local in space. Because this feature does not modify our calculations we ignore this complication<sup>‡</sup>. Below, we argue that a controlled dynamic and static description of a glassy phase transition is possible if we assume

$$\chi(k \sim k_0, \tau) \simeq A\tau / [\tau^2 + (k - k_0)^2] \quad (1b)$$

with  $\tau$ ,  $g_3$  and  $g_4$  all self-consistently small. We also assume in (1) that  $\tau$  is the only variable with a strong temperature dependence and that  $\tau$  is a decreasing function of  $T$ . Notice that in this oversimplified model,  $\chi(k \sim k_0, \tau)$  is not of the Ornstein-Zernicke (OZ) form because of the large ( $\sim 1/\tau$ ) coefficient multiplying the  $(k - k_0)^2$  term. The form chosen in (1b) allows us to treat the coupling constants  $g_3$  and  $g_4$  as self-consistently small. The calculations presented here can be repeated using OZ forms for  $\chi$  and one would arrive at similar conclusions if one truncated at a self-consistent one-loop order. We show below that the theory necessarily predicts a glass transition before  $\tau = 0$  can be reached. In this letter we do not consider the possibility that under appropriate conditions the solution to the theory may also result in periodic density waves indicating a transition to a periodically ordered state.

Substitution of (1b) into (1a) gives a  $(k - k_0)^2$  term with a large coefficient,  $\sim 1/\tau$ , for the assumed small  $\tau$ . Therefore our basic model is mean-field like with only one length scale dominating and it is this feature that allows for a controlled perturbation expansion<sup>§</sup>. We next show by using both static and dynamical techniques that the equations (1) lead to a glass transition.

We start with the dynamical approach. Our basic philosophy is that the glass transition is both a static and dynamic phenomenon and there must be a connection

<sup>†</sup> For related earlier ideas in STG physics, see [2].

<sup>‡</sup> In general the non-linear terms in (1a) arise from an ideal gas entropy term and higher-order direct correlation function terms. The direct correlation function terms are in general non-local in space. However, if we use  $\chi$  given by (1b) the non-locality is of no consequence since only one wavenumber,  $k_0$ , is relevant.

<sup>§</sup> In traditional mean-field theories the square gradient term in the effective Hamiltonian has an infinite coefficient.

between the two approaches. Establishing such a connection is only possible if the particular dynamics used is irrelevant for the  $t \rightarrow \infty$  behaviour. We choose conservative relaxational dynamics, which reflects the fact that at scale  $k_0$ , density fluctuations are diffusive [3]. The dynamical equations are

$$\frac{1}{\Gamma_0} \partial_t \delta n(\mathbf{x}_1 t) = \nabla^2 \frac{\delta(\beta \mathcal{H})}{\delta(\delta n(\mathbf{x}_1 t))} + \xi(\mathbf{x}_1 t) \quad (2)$$

with  $\xi(\mathbf{x}_1 t)$  the usual Gaussian noise term and  $\Gamma_0$  a bare kinetic coefficient which sets the microscopic timescale. More general dynamics including ‘mode coupling’ terms will be considered elsewhere.

We consider the density time correlation function,  $C(k, t)(2\pi)^d \delta(k + k_1) = \langle \delta n(k, t) \delta n(k_1) \rangle$ . The glassy state is defined by frozen density fluctuations or by a non-zero Edwards-Anderson order parameter (for a recent review of spin glasses, see [4]),  $q(k) = q_{EA}(k) = \lim_{t \rightarrow \infty} C(k, t)$ , and we assume that the glassy state is statistically homogeneous and isotropic. The fact that the glassy state has the same statistical properties as the liquid states is necessary to establish connections between static and dynamical approaches.

Treating the non-linear terms in (1) as small, the self-consistent one-loop approximation for  $\hat{C}(k, \omega)$ , the one-sided Fourier transform of  $C(k, t)$ , is

$$\hat{C}(k, \omega) = C(k, t=0)(-i\omega + \Gamma_R(k, \omega)/C(k, t=0))^{-1} \quad (3a)$$

with  $C(k, t=0)$  being the renormalised static structure factor, equation (1b), and  $\Gamma_R(k, \omega)$  a renormalised kinetic coefficient

$$\Gamma_R^{-1}(k, \omega) = \frac{1}{\Gamma_0 k^2} + 2g_3^2 \int_{k_1} \int_0^\infty dt \exp(i\omega t) C(k - k_1, t) C(k, t). \quad (3b)$$

In (3), terms of  $O(g_4^2, g_3^2 g_4, g_3^4)$  have been neglected. They are small if, in dimensionless form,  $1 \gg g_4 \gg g_3^2$ . Examining higher-loop terms one finds that they are no more singular than (3b), even when  $q(k)$  is non-zero.

Equations (3) are structurally identical to the equation proposed previously for the glass transition (for a review, see [5]). There are, however, some conceptual differences which we shall emphasise later. These equations have been studied in detail elsewhere [5]. There is a continuous slowing down and freezing at a (density) temperature we denote by  $T_A$ . An interpretation of  $T_A$  will be given below. A simple equation of state is obtained by assuming  $q(k)$  is non-zero and using the fact that  $S(k)$  is sharply peaked at  $k_0$ , so that we can consistently focus (this step is consistent with the previous approximations) on  $C(k_0, t \rightarrow \infty) \equiv n_0 S(k_0) \bar{q}$ . From (3) we obtain

$$\bar{q} = \bar{g}_3^2 \bar{q}^2 [\tau + \bar{g}_3^2 \bar{q}^2]^{-1} \quad (4)$$

where  $\bar{g}_3$  is a dimensionless cubic coupling constant. Assuming  $\bar{q} \neq 0$  gives  $\bar{q} = \frac{1}{2} [1 \pm (1 - 4\tau/\bar{g}_3^2)^{1/2}]$ .  $T_A$  is defined when this equation first has a non-trivial physical (real) solution,  $\bar{q}(T = T_A) = \frac{1}{2}$  and  $\tau(T = T_A) = \frac{1}{4} \bar{g}_3^2$ . These results imply that there is a spontaneous glassy freezing before the liquid-state spinodal is reached ( $\tau = 0$ ), and that at  $T_A$  we can consistently take  $\tau$ ,  $\bar{g}_3$  and  $\bar{g}_4$  to be small. Also note that the term  $\Gamma_0 k_0^2$  in (3c) does not appear in (4) in accord with our philosophy that the particular dynamics used is irrelevant and that  $T_A$  can also be found within a purely static approach.

Finally, we note that Siggia’s objection [6] does not apply to our calculation. Our theory is controlled because  $\tau$ ,  $\bar{g}_3$  and  $\bar{g}_4$  can all be taken to be small *and* because the

wavenumber integrals inherent in the perturbation theory eliminate any  $\tau^{-1}$  terms in the expansion. In Siggia's model there would be  $\tau^{-1}$  terms in the perturbation expansion leading to an uncontrolled theory for small  $\tau$ . Physically, our model has an infinite number of degrees of freedom while Siggia's model [6] has only one degree of freedom, and consequently cannot undergo any phase transition. We expect, within our model, that retaining any finite number of higher-order loop terms in (3b) will not remove the apparent phase transition at  $T_A$ . Higher-order terms will shift the location of  $T_A$  by a small amount if  $\tau$ ,  $\bar{g}_3$  and  $\bar{g}_4$  are small. For some non-perturbative arguments see below and elsewhere [7].

We next derive  $T_A$  and (4) within a static theory. The mathematical manipulations used in the static treatment are identical to those used in the TAP approach to the spin-glass problem using systematic perturbation theory. We then use the static description to interpret the significance of the temperature we have denoted by  $T_A$ . We introduce two related key notions. First we imagine an order-parameter description in terms of frozen density fluctuations. Since the glassy state is amorphous or aperiodic the density order parameter is most naturally specified by a probability measure  $[\delta n]$ . Secondly, we allow for a large number of pure states (at least on a given timescale)<sup>†</sup>. These states can be characterised as follows. Denote a particular macroscopic state by the label  $s$ , with the density field in that state given by  $n_s = n_0 + \delta n_s$ . We denote the free energy of this state by  $F_s$ . The fields  $\delta n_s$  are given by the extremum property of  $F_s$ . Next, compute  $F_s$  from (1) by standard loop expansion techniques (see e.g. [9]). We then allow for a possibly large number of statistically similar but different states by using a partition function given by [10]

$$Z = \sum_s \exp(-\beta F_s) = \int D[\delta n] \exp^{(-\beta F)\Delta(\delta n)} \prod_{x_1} \delta\left(\frac{\delta BF}{\delta(\delta n(x_1))}\right). \quad (5a)$$

Here  $\Delta(\delta n) = |\det \delta^2 F / \delta n^2|$  normalises the delta function in (5a). Using an integral representation of the delta function in (5a) introduces an auxiliary variable  $\delta \hat{n}$ .  $Z$  can be written as

$$Z = \int D[\delta n] D\left[\frac{\delta \hat{n}}{2\pi}\right] \Delta(\delta n) \exp\left(-i \int dx_1 \delta \hat{n}(x_1) \frac{\delta \beta F}{\delta(\delta n(x_1))} - \beta F\right). \quad (5b)$$

Equation (5b) defines a probability measure  $\mathcal{P}[\delta n, \delta \hat{n}]$  for the fields  $\delta n$  and  $\delta \hat{n}$ . In usual phase transition problems  $\mathcal{P}[\delta n]$  is a delta function at the unique (or, more generally, at all globally symmetry-related) equilibrium state(s) of the system. However, in general, equations (5) are capable of describing a large number of symmetry-unrelated states that are statistically distributed.

We have connected the static approach to the dynamical approach as follows. There are three two-point propagators associated with  $\mathcal{P}[\delta n, \delta \hat{n}]$ , namely

$$\begin{aligned} R(x_1, x_2) &= \langle i \delta \hat{n}(x_1) \delta n(x_2) \rangle & P(x_1, x_2) &= \langle i \delta \hat{n}(x_1) i \delta \hat{n}(x_2) \rangle \\ Q(x_1, x_2) &= \langle \delta n(x_1) \delta n(x_2) \rangle \end{aligned}$$

where the angle brackets denote an average with weight  $\mathcal{P}$ . The function  $R$  is the density linear response function and the function  $Q$  is the square average of a density order parameter. In order to have consistency with the dynamical approach,  $Q$  should turn out to equal  $q_{EA}$ . We next solve for the propagators in (6) using approximations

<sup>†</sup> For a discussion of states in disordered magnetic systems, see [8].

similar to those used in the dynamical approach. To define a perturbation expansion for  $R$ ,  $P$  and  $Q$  we assume that the field  $H$  in (1) is a small Gaussian random field which statistically breaks the symmetry of the liquid phase to a glassy phase. The random field  $H(x)$  serves as an external coupling term conjugate to the Edwards–Anderson order parameter which characterises the glassy phase. Thus,  $H(x)$  breaks the symmetry between the liquid and the glassy states in much the same way as an external magnetic field breaks the symmetry between  $+m$  and  $-m$  phases of a ferromagnet. The variance of  $H(x)$  is set to zero at the end of the calculation. Carrying out a self-consistent perturbation expansion [11], using the fact that  $g_3$  and  $g_4$  are small and setting the random field strength equal to zero at the end of the calculation yields closed equations for  $R$ ,  $P$  and  $Q$ . In  $k$  space these equations are

$$R(k) = -P(k) = n_0 S(k) - Q(k) \quad (6a)$$

and

$$Q(k) = R(k) \left( 2g_3^2 \int_{k_1} Q(k - k_1) Q(k_1) \right) n_0 S(k). \quad (6b)$$

Comparing (6) with (3) and (4) shows that  $Q(k) = q(k)$  is the glassy-state Edwards–Anderson order parameter and that the static and dynamic approaches are consistent with each other. Equation (6a) indicates that the density susceptibility (compressibility) satisfies the Fischer relation [4] in the glassy phase. In giving (6), we explicitly considered random solutions by requiring  $V^{-1} \int dx \delta n(x) \rightarrow 0$ , where  $V$  is the volume, even though the square (spatial) average of  $\delta n$  is non-zero. Also note that equations (6) imply that the static structure factor,  $S(k)$ , is continuous across the ordering transition temperature,  $T_A$ , even though  $q(k)$  is discontinuous at  $T_A$ .

We note that the manipulations leading to (6) are formally very similar to those used for mean-field spin-glass (SG) models [4, 12–15] where randomness occurs in the starting Hamiltonian. Physically the STG theory presented here is similar to mean-field SG because the term in the square brackets in (6b) represents a self-generated static random noise which is analogous to the static randomness in SG models. In the dynamical approach to the STG problem this term arises from the correlation of the renormalised random Langevin force which has a static component in the glassy phase due to frozen density fluctuations. Finally, we mention that to obtain (6) we used an infinitesimal Gaussian random field to set up the perturbation theory. Although this field was eventually set equal to zero its introduction forces us to use replica methods. In obtaining (6) we used a replica symmetry breaking scheme that assumed only self-overlap of the metastable glassy states. This point and why this procedure is needed to connect static and dynamical theories will be discussed in detail elsewhere [7].

We next discuss the physical significance of the temperature  $T_A$  [13–15]. With (5a) we can define two (in general) distinct free energies [10]. The usual canonical free energy,  $F_c$ , is just the logarithm of  $Z$ . The second free energy is the average free energy,  $\bar{F}$ , computed with weight  $\exp(-\beta F_s)/Z$ . Direct calculation gives  $F_c = F_L$  and  $\bar{F} > F_c$  and  $\delta \bar{F} / \delta Q(x_1) = 0$  leads to (6) as the equation of state. Here  $F_L$  is the liquid-state free energy which does not depend on the order parameter  $Q(k)$ . The inequality  $F_c \neq \bar{F}$  can occur if and only if the states leading to (6) are metastable and there are an extensive number of these states [16]. Since  $\bar{F} > F_c$ , it follows that at  $T_A$  the liquid—within our perturbative calculations—freezes into a metastable glass that

is stabilised by an exponentially large solution degeneracy [15]. Within our approximate calculation  $F_c$  is not a physically meaningful free energy because it contains an entropic term that is a measure of states that are not probed in the timescale in which our calculations are valid.

As stressed above, our calculations are controlled in a perturbative sense. However, in an exact non-perturbative theory we would not expect a sharp freezing at  $T_A$  [13]. By the law of large numbers an exponentially large number of metastable states will have a Gaussian distribution of free energies. In a volume of  $O(L^d)$ , two states will typically differ in free energy by an amount of  $O(\pm L^{d/2})$ . The states here are therefore similar to those relevant in the random-field Ising model [8]. Using this and non-perturbing droplet-like arguments we argue elsewhere [7] that  $T_A$  is a temperature below which the long-time dynamics is governed by activated transport as finite domains in the liquid change from one metastable state to another, resulting in structural relaxation. In this picture the solution degeneracy discussed above plays the role of the configurational entropy in the entropy theory of the glass transition of Gibbs and Di Marzio [17] and for  $t \rightarrow \infty$  the canonical free energy,  $F_c$ , is the only physical free energy.

Following this idea we can within our model identify an ideal structural glass transition temperature. We define a Kauzmann temperature [1, 13],  $T_K$ , as the temperature where the configurational entropy becomes non-extensive. We find  $0 < \tau(T = T_K) < \tau(T = T_A)$ . Physically, we expect that below  $T_K$  there are still an extensive number of free-energy metastable states but that the barriers between these states and those we consider are too large to be relevant for any meaningful transport. The difference between  $\bar{F}$  and  $F_c$ , namely the configurational entropy, is the driving force for activated transportation  $T < T_A$ . Thus one expects exponentially divergent relaxation times as  $T \rightarrow T_K$  according to standard droplet arguments. This is in accord with experiments in viscous liquids where relaxation times are often fitted to a Vogel-Fulcher law [1].

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## References

- [1] Jäckle J 1986 *Rep. Prog. Phys.* **49** 171
- [2] Singh Y, Stoessel J P and Wolynes P G 1985 *Phys. Rev. Lett.* **54** 1059  
Wolynes P G 1985 *J. Non-Cryst. Solids* **75** 443
- [3] Munakata T 1977 *J. Phys. Soc. Japan* **43** 1723  
de Schepper I M, Cohen E G D and Zuilhof M J 1984 *Phys. Lett.* **101A** 399  
Kirkpatrick T R 1985 *Phys. Rev. A* **32** 3130
- [4] Binder K and Young A P 1986 *Rev. Mod. Phys.* **58** 801
- [5] Götze W 1986 *Proc. Nato Advanced Study Institute on Amorphous and Liquid Materials* ed E Lüscheu, G Jacucci and G Fitsch (Dordrecht: Reidel)
- [6] Siggia E D 1985 *Phys. Rev. A* **32** 3135
- [7] Kirkpatrick T R and Thirumalai D 1989 in preparation
- [8] Huse D A and Fisher D S 1987 *J. Phys. A: Math. Gen.* **20** L997  
Fisher D S and Huse D A 1987 *J. Phys. A: Math. Gen.* **20** L1005
- [9] Amit D J 1984 *Field theory, the Renormalization Group, and Critical Phenomena* (Singapore: World Scientific)
- [10] De Dominicis C and Young A P 1983 *J. Phys. A: Math. Gen.* **16** 2063
- [11] De Dominicis C 1980 *Phys. Rep.* **67** 37

- [12] Kirkpatrick T R and Thirumalai D 1987 *Phys. Rev. Lett.* **58** 2091; 1987 *Phys. Rev. B* **36** 5388; 1988 *Phys. Rev. B* **37** 5342
- [13] Kirkpatrick T R and Wolynes P G 1987 *Phys. Rev. B* **36** 8552
- [14] Thirumalai D and Kirkpatrick T R 1988 *Phys. Rev. B* **38** 4881
- [15] Kirkpatrick T R and Thirumalai D 1988 *Phys. Rev. A* **37** xxxx
- [16] van Enter A C D and van Hemmen J L 1984 *Phys. Rev. A* **29** 355
- [17] Gibbs J H and Di Marzio E A 1958 *J. Chem. Phys.* **28** 373