Metastability, Mode Coupling and the Glass Transition

Gene F. Mazenko and Joonhyun Yeo

*The James Franck Institute and Department of Physics
The University of Chicago
5640 S. Ellis Avenue, Chicago, Illinois 60637*

Abstract

Mode coupling theory (MCT) has been successful in explaining the observed sequence of time relaxations in dense fluids. Previous expositions of this theory showing this sequence have required the existence of an ideal glass transition temperature $T_0$. Recent experiments show no evidence of $T_0$. We show here how the theory can be reformulated, in a fundamental way, such that one retains this sequence of relaxation behaviors but with a smooth temperature dependence and without any indication of $T_0$. The key ingredient in the reformulation is the inclusion of the metastable nature of the glass transition problem through a coupling of the mass density to the defect density. A main result of our theory is that the exponents governing the sequence of time relaxations are weak functions of the temperature in contrast to the results from conventional MCT.
I. INTRODUCTION

We show here how the condition of metastability in the glass transition problem can be used to establish the conditions necessary for a theoretical understanding of the experimentally observed elaborate sequence of time relaxation behaviors [1] spread over many decades in time. This time sequence was originally predicted by mode coupling theory (MCT) [2,3]. We find a smooth temperature dependence for the relaxation without any evidence of an ideal glass transition temperature as hypothesized in conventional MCT.

The mode coupling theory for the kinetics near the glass transition predicts [4] a sequence of time behaviors which has received substantial verification through a steadily improving series of experiments in dense liquids [5–7]. This sequence, shown schematically in Fig.1 for the density-density auto correlation function, begins, after those times associated with any fast microscopic processes, with a power-law regime $f + A_1 t^{-a}$. For times $t \simeq \tau_\alpha$ there is a cross over to the so-called von Schweidler regime where the correlation function decays as $f - A_2 t^b$. For times $t > \tau_\alpha$ one moves into the earliest stages of the primary or $\alpha$ relaxation which can be characterized by a stretched exponential behavior $A_3 \exp(-(t/\tau)^\beta)$. There may then be a very long-time crossover to a final Debye or exponential decay regime. Within MCT the coefficients $A_1, A_2$ and $A_3$ are parameters which depend on details of the model but the exponents $a$ and $b$ are related by a general nonlinear relationship [4] (discussed below) for which there is some experimental verification [7]. For certain simplified models [4,8] there is definite relationship between the exponent $b$ and the stretching exponent $\beta$. This relationship has been less well studied both theoretically and experimentally. The prediction of this sequence of time behaviors, which has substantial experimental support, must be considered a substantial achievement.

Problems with MCT [9] begin when one considers the temperature dependence generated by the conventional assumption [4] that there is an ideal glass transition temperature $T_0$ above and below which the dynamics are dramatically different. Indeed according to conventional MCT the von Schweidler and $\alpha$-relaxation regimes are confined to the temper-
atures $T > T_0$. This sharp temperature dependence, as pointed out by Kim and Mazenko [8], is in disagreement with the high quality experiments of Dixon et al. [10]. Furthermore, and again in disagreement with experiment, the conventional MCT finds that the sequence of relaxations must be confined to temperatures near $T_0$ and that the associated exponents $a, b$ and $\beta$ should be temperature independent. The assumption in conventional MCT is similar to that associated with critical slowing down near a second order phase transition. Experimentally this picture does not hold. Dixon et al. [10] find that the stretching exponent $\beta$ is weakly temperature dependent and that the qualitative relaxational behavior is the same for all temperatures spread around any reasonable choice for $T_0$. As pointed out by Kim and Mazenko, [8] the data of Ref. 10 gives that $(1 + b)/(1 + \beta)$ is temperature independent. Since $\beta$ is temperature dependent the exponent $b$ must also be temperature dependent. If the general MCT nonlinear relationship between $a$ and $b$ [4,21] holds, then $a$ must also be temperature dependent. MCT theory has even less to say about the remarkable scaling behavior found by Nagel and coworkers [10]. Kim and Mazenko [8] have shown that this scaling can be made compatible with MCT but at the expense of imposing additional ad hoc constraints on the theory.

Our work here is to show how the MCT theory can be reformulated so as to be compatible with one's intuition that the substantial observed slowing down results from the fluid system becoming metastable for temperatures below the melting temperature. The strong temperature dependence in the system goes into the $\tau$ parameters which characterize the various frequency behaviors. It appears [11] that these relaxation times show a power-law behavior as a function of temperature for higher temperatures but one expects such quantities to show an Arrhenius or Vogel-Fulcher temperature dependence for sufficiently low temperatures.

Our analysis is based on a model that involves a number of simplifying assumptions. While most our final results are model dependent, our final conclusions may be quite general. The model we use is that due to Das and Mazenko [12], who developed fluctuating nonlinear hydrodynamics for the mass density $\rho$ coupled to the momentum density $g$, extended to
include a coupling to an additional variable $n$ which we associate with vacancy diffusion in the system. In the crystal we would be forced to include this variable, along with the Nambu-Goldstone modes corresponding to transverse phonons, in a rigorous treatment of the hydrodynamics of such systems [13]. Here we assume that it is sensible to define such a variable in the dense but disordered state [14]. One can think of this in terms of treating an order parameter in the disordered state. We will not need a microscopic definition of this variable. We assume that $n$ is a diffusive variable with a diffusion coefficient $\Gamma_v$. It is reasonable to assume that the time scale associated with $n$ is very long, since one expects that defects must surmount an activation barrier in order to move. Thus we also assume that the driving effective free energy for $n$ is a double well potential with the metastable defects associated with the higher energy well. We assume that the tunneling out of this well is facilitated by a coupling of $n$ to the mass density in the effective free energy. We find self-consistently that the stretched dynamics can be associated with a defect potential with a very small activation barrier and a weak coupling between $n$ and $\rho$. We show for the model we study that the vanishing of the barrier and the development of an inflexion point in the potential is a necessary condition for the slowing down observed experimentally. Apparently the system must build up the potential in which $n$ moves. We also see that the notion of a ‘below’ the transition is not well defined from this point of view.

II. THE MODEL

The model we start with is the standard set of equations of fluctuating nonlinear hydrodynamics for the set of variable $\rho, g$ and $n$. We assume that $\rho$ and $n$ have the usual Poisson brackets of a scalar field with $g$ and that the bare diffusion coefficients are just the bare shear and bulk viscosities $\eta_0$ and $\zeta_0$ for $g$ and a bare diffusion coefficient $\Gamma_v$ for $n$. The dynamics of this set is then driven by an effective free energy of the form:

$$F = \int d^3x \frac{g^2(x)}{2\rho(x)} + F_U,$$  \hspace{1cm} (1)
where the leading term is the kinetic energy which follows from Galilean invariance. The term $F_U$ contains the dependence on $\rho$ and $n$ and will be discussed in detail below. The associated Langevin equations of motion are given then by

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \mathbf{g}$$

(2)

$$\frac{\partial g_i}{\partial t} = -\rho \nabla_i \frac{\delta F_U}{\delta \rho} - n \nabla_i \frac{\delta F_U}{\delta n} - \sum_j \nabla_j (\rho V_i V_j) - \sum_j L_{ij} V_j + \Theta_i$$

(3)

$$\frac{\partial n}{\partial t} = - \sum_i \nabla_i (n V_i) + \Gamma_v \nabla^2 \frac{\delta F}{\delta n} + \Xi,$$

(4)

where $\mathbf{V} = \mathbf{g}/\rho$ and $L_{ij}(x) = -\eta_0 \left( \frac{1}{3} \nabla_i \nabla_j + \delta_{ij} \nabla^2 \right) - \zeta_0 \nabla_i \nabla_j$. The bare longitudinal viscosity is defined by $\Gamma_0 = \zeta_0 + \frac{4}{3} \eta_0$. $\Theta_i$ and $\Xi$ in (3) and (4) are gaussian noises with variance depending on $L_{ij}$ and $\Gamma_v$. To complete the specification of our model we must specify the potential $F_U$. Our simple choice is

$$F_U = \int d^3x \left[ \frac{1}{2} (\delta \rho)^2 + B (\delta \rho) n + h(n) \right],$$

(5)

where $\delta \rho = \rho - \rho_0$ and the defect potential is given by

$$h(n) = \epsilon \bar{n}^4 \left[ \frac{1}{3} \left( \frac{n}{\bar{n}} \right)^4 - \frac{1}{3} (2 - \sigma) \left( \frac{n}{\bar{n}} \right)^3 + \frac{1}{2} (1 - \sigma) \left( \frac{n}{\bar{n}} \right)^2 \right],$$

(6)

where $\bar{n}$ is an average defect density in the metastable well in the absence of any coupling to $\rho$ and $\epsilon$ gives an over all scale for the potential and $\sigma$ measures the ‘distance’ from an inflexion point in the potential, or equivalently, the barrier height. In order to keep the analysis as simple as possible, we will assume in (5) a very simple form for the density-dependent part of $F_U$ which corresponds to a wavenumber independent structure factor. A closely related approximation is that the correlation function can be factored into a wavenumber dependent part and a frequency dependent part [19]. This assumption works better than one might initially guess because, to a first approximation, the slowing down influences all wavenumbers. This is not a long wavelength or hydrodynamic approximation.

The way in which one can include the energy variable in the problem has been discussed by Kim and Mazenko [15], but we neglect any such coupling here. The technical problems of treating the nonlinearities in this model using perturbative field theoretical methods [16]
has been discussed by Das and Mazenko \[12\] and clarified by Mazenko and Yeo \[17\]. The details of this analysis will be discussed elsewhere \[18\]. Here we briefly summarize the nature of the calculation and focus on the results.

For the general set of equations described above with the assumption of the factorization of wavenumber and frequency dependent parts, one can show that the Laplace-Fourier transform of the density-density correlation function can be written in the general form

\[ C_{\rho\rho}(z) = \phi(z) = \frac{z + i\Gamma(z)}{z^2 - \Omega_0^2 + i\Gamma(z)[z + i\gamma(z)]}, \quad (7) \]

where \( \Omega_0 \) is a microscopic ‘phonon’ frequency, \( \gamma(z) \) is a long-time Das-Mazenko cutoff, and \( \Gamma(z) \) is the renormalized or physical longitudinal viscosity. Using the methods of Das and Mazenko \[12\] one can calculate \( \gamma \) and \( \Gamma \) in perturbation theory for almost any choice for the driving free energy. With this background and the assumption that current correlations decay much faster than \( \rho \) correlations, Das et al. \[20\] indicated that the physical viscosity can be written in the general form

\[ \Gamma(z) = \Gamma_0 + \Omega_0^2 \int_0^\infty dt \ e^{izt} H(\phi(t)), \quad (8) \]

where the mode coupling kernel can be written in the form

\[ H(\phi(t)) = \sum_{n=1}^N c_n \phi^n(t). \quad (9) \]

The MCT analysis is carried out in terms of the coefficients \( c_n \). In the original Leutheussar model \[2\] one had only the parameter \( c_2 \). Das et al. \[20\] showed how the development could be generalized to include an arbitrary set of parameters. We follow here the presentation of Kim and Mazenko \[8\]. A significant step forward was made by Götze \[21\] who realized that if one included a linear \( (c_1) \) term in \( H \) then the von Schweidler and stretching behavior results. He included such a term on phenomenological grounds. Kim \[22\] showed how such a term can be generated by coupling the mass density to an additional slower variable in the problem. One can also obtain the von Schweidler form and stretching, and effectively generate a \( c_1 \) term, if one includes the wavenumber in the analysis. This
has the physical interpretation that some band of wavenumbers is slower than others and stretches the faster modes. Some evidence for this picture was found in the simulations of Valls and Mazenko [23] and the mode coupling calculations of Fuchs et al. [24]. Unfortunately an analytical treatment of these effects are not available. By including the wavenumber dependence in the development, as in the calculation of Das [25], one can include such effects. Here we focus on the wavenumber independent model.

The Das-Mazenko cutoff appearing in (7) generates an exponential decay when it kicks in. We assume that the basic mechanism introduced by Sjögren [26] and discussed by Kim and Mazenko [8] shifts the values of $\gamma$ to very small values. We assume for the rest of the discussion here, over the range of time scales we discuss, that this cutoff can be set to zero.

If there was no coupling of $\rho$ to $n$ then our calculation is equivalent to that carried out by Das et al. [20] and in more detail by Das and Mazenko [12] and no linear term in $H(t)$ is produced. The results in this case are equivalent to the Leutheusser model [2] which has no stretching and no von Schweidler regime. The basic idea for introducing a $c_1$ term in the analysis, as discussed by Kim [22] and us elsewhere [18], is that the perturbation theory expansion for $\Gamma$ will generate terms involving quadratic and higher order products of correlation functions. The correlation functions involving a current decay faster and those involving the vacancies slower than the density. Thus the vacancy-vacancy correlation function $C_{nn}$ can be taken as a constant over the time range where the density-density correlation function $C_{\rho \rho}$ is stretched [27]. Thus, for example, the quadratic form $C_{nn}C_{\rho \rho}$ can be replaced by a constant times $C_{\rho \rho}$ and generates an effective linear term in $H$.

Metastability enters the problem since there is a significant time period over which the defects are trapped in a metastable state with some average density $\bar{n}$. We restrict our perturbation analysis to this time regime. A key aspect of our analysis is that because $n$ is coupled to $\rho$ the stationary value of $\bar{n}$ depends on the local value of $\rho$ determined by looking for the metastable minimum of $F$ which is given by

$$n^* = \bar{n}[1 - \frac{x}{\sigma y} \frac{\delta \rho}{\rho_0} - \left(\frac{1 + \sigma}{\sigma}\right) \left(\frac{x}{\sigma y}\right)^2 \left(\frac{\delta \rho}{\rho_0}\right)^2 + \ldots]$$ (10)
where we have the dimensionless parameters $x = B\rho_0\bar{n}/A\rho_0^2$ (a measure of the coupling between $\rho$ and $n$) and $y = \epsilon\bar{n}/A\rho_0^2$. Our procedure is then to expand $n$ about $n^*$ in the Langevin equations and then carry out perturbation theory in the nonlinear terms keeping terms up to $N = 2$ in the mode coupling kernel. Self-consistently we find substantial slowing of the dynamics in the cases where $x$ and $\sigma$ are very small. The smallness of $\sigma$ corresponds to a low barrier in $h(n)$ while small $x$ means that the potential is not greatly distorted by fluctuations in $\rho$. The limit in which we obtain self-consistency is where $x = C\sigma^2$ with $C$ of $0(1)$. We then obtain, eliminating $x$ in terms of $C$ and $\sigma$ for small $\sigma$, that

\[ c_1 = \xi[ -8(y + C) - 4(C^2/y + 3y + 8C)\sigma] + O(\sigma^2) \]  
\[ c_2 = \xi[ 1 + 4y + 2(3y + 2C)\sigma] + O(\sigma^2), \]  

where the formal expansion parameter $\xi = k_B T \Lambda^3/(6\pi^2 A\rho_0^2)$ and $\Lambda$ is a short-distance cut-off. The terms $c_3, c_4, \cdots$ are available if one goes to higher order in perturbation theory.

We now demand that the parameters characterizing the defect well and the coupling are chosen to give the slow dynamics observed experimentally. This involves the mathematical machinery developed by MCT [4,21] but interpreted differently [8]. This analysis can be stated rather generally. If we define

\[ \sigma_0 = (1 - f)V(f) \]  
\[ \sigma_1 = (1 - f)^2V'(f) \]  
\[ \lambda = \frac{1}{2}(1 - f)^3H''(f), \]  

where $V(f) = H(f) - f/(1 - f)$ and $f$ has the physical interpretation as the metastable value of $\phi$ evaluated for the critical conditions $\sigma_0 = \sigma_1 = 0$ which characterize the slow dynamics. In this case it can be shown that the decay exponents $a$ and $b$ are given by [21]

\[ \frac{\Gamma(1 - a)}{\Gamma(1 - 2a)} = \lambda = \frac{\Gamma(1 + b)}{\Gamma(1 + 2b)} \]  

In the present case where we include only $c_1$ and $c_2$ the critical conditions $\sigma_1 = 0$ can be used to eliminate the parameter $f$ in equations (13-15) to obtain for small $\sigma_0$, 

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Comparing (17) and (18) with (11) and (12) we obtain, assuming \( \sigma_0 \simeq \sigma \), four equations which can be solved to give \( C \), \( y \) and \( \lambda \) as functions of \( \xi \) given by

\[
C = \frac{1}{4}(1 - \frac{2\lambda + 1}{2\lambda^3})
\]

\[
y = \frac{1}{4}(\frac{1}{\xi\lambda} - 1)
\]

and we have the implicit equation for \( \lambda \) as a function of \( \xi \) given by

\[
\xi = \frac{1}{\lambda^2}\left\{1 - \frac{3(2\lambda - 1)}{2[7 + 2\lambda + \sqrt{4\lambda^2 + 22\lambda + 91}]}\right\}.
\]

We can also express \( \sigma \) in terms of \( \sigma_0 \) and \( \xi \):

\[
\sigma = -\frac{3}{2[3y + 2C]\xi\lambda(1 - \lambda)^2}\sigma_0.
\]

For \( \frac{1}{2} < \lambda < 1 \), \( \sigma \) and \( \sigma_0 \) have the same sign. However, as can be seen from (6), only the absolute value \( |\sigma| \) matters in determining the critical condition, since the potential \( h(n) \) is ‘symmetric’ around \( \sigma = 0 \) in the sense that both \( \sigma > 0 \) and \( \sigma < 0 \) cases represent a double-well potential.

**III. DISCUSSION AND CONCLUSION**

Using the results of the previous section, we can express the exponents \( a \) and \( b \) and the amplitude \( f \) as weak functions of temperature, \( \xi \), as shown in Fig. 2. Note that we have been able, except for the temperature dependence of \( \sigma \), to determine the form of the potential \( h(n) \) and its coupling to \( \rho \) as a function of temperature as represented by the parameter \( \xi \). At this stage it looks worthwhile to try and determine \( \sigma \) experimentally.

Our analysis here has focused on the time regime prior to the \( \alpha \)-relaxation and we have not yet addressed the question of the scaling found by Dixon et al. [10]. Our detailed results
giving $a$, $b$ and $f$ as functions of $\xi$ are model dependent and since our model is over-simplified should not be expected to apply to experiments in detail. However it is possible that our basic picture that $a$, $b$ and $f$ are weak functions of temperature and that the parameter $\sigma$ controls the slowing down may prove to be robust.

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[27] This separation of times scales between the density and the vacancy variables result if the coupling $b$ between $\rho$ and $n$ and $\sigma$ are very small and satisfy a certain limit which
will be obtained in the following discussion. In this limit, the density-vacancy correlation function $C_{\rho n}$ is a linear combination of $C_{\rho \rho}$ and $C_{nn}$.

[28] The form of the potential $h(n)$ is invariant under $\bar{n} \to \bar{n}' \equiv (1 - \sigma)\bar{n}$ and $\sigma \to \sigma' \equiv -\sigma/(1 - \sigma)$. Thus $h(n)$ with $\bar{n}$ and $\sigma < 0$ is the same double-well potential as the one with $\bar{n}'$ and $\sigma' > 0$. 
FIGURES

FIG. 1. A schematic plot of the sequence of relaxation behaviors predicted by MCT; (a) power-law decay relaxation $f + A_1 t^{-a}$; (b) von-Schweidler relaxation $f - A_2 t^b$; (c) primary relaxation $A_3 e^{-(t/\tau)^\beta}$; and (d) exponential relaxation $e^{-\gamma t}$.

FIG. 2. The exponent parameters $a$, $b$ and the metastability parameter $f$ as functions of the temperature represented by $\xi$. The condition $\frac{1}{2} < \lambda < 1$ restricts the range of $\xi$ to $0.93 < \xi < 4$. 
