# Absence of a Sharp Glass Transition in Mode Coupling Theory

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A self-consistent mode coupling model for supercooled fluids is derived from fluctuating nonlinear hydrodynamics (extended to short wavelengths) with attention to detailed balance constraints. The sharp glass transition predicted by mode coupling models based only on pressure nonlinearities does not occur here. Instead, the long time asymptotic behavior of the density autocorrelation function is determined by additional nonlinearities imposed by the detailed balance constraints.

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The experimentally observed transition of a supercooled fluid to an amorphous solid is generically referred to as a glass transition. A most appealing signature of such a transition would be the divergence of a characteristic time for structural relaxation at a precise critical temperature or pressure. An order parameter for structural relaxation is the time dependent mass density autocorrelation function, $\langle \delta\rho(\mathbf{r},t)\delta\rho(\mathbf{r}',0)\rangle$, in the metastable supercooled fluid state. At high temperatures this function decays to zero for long times, representing configurational relaxation to the metastable fluid state. However, if there is a diverging structural relaxation time below some critical temperature, then spontaneous fluctuations would remain finite for infinite times ("broken ergodicity" or complete structural arrest).

A mechanism for structural arrest was identified eight years ago [1,2] and associated with the glass transition. The underlying theoretical model and subsequent versions are generally referred to as mode coupling models [3]. In recent years the predictions of such models, particularly scaling laws valid asymptotically close to the transition point, have been compared with a number of spectroscopic experiments [4] and satisfactory agreement is observed in many cases. However, the theory predicts an ideal glass transition for simple atomic systems at a temperature for which computer simulation results are still decaying; also, the most recent comparisons of these models with experiment show significant deviations from complete structural arrest [5]. These considerations suggest that the mode coupling effects are relevant but that the sharp singularity is not correct. Evidently, some assumptions of the original mode coupling model fail close to the predicted transition where a new asymptotic dynamics appears. Only two possibilities for improved mode coupling theories have been suggested thus far, one based on kinetic theory [6] and the other based on fluctuating Navier-Stokes equations [7]. Each entails plausible but uncontrolled approximations and the results are quite different in the long wavelength regime where both can be compared. In spite of its successes, the current status of mode coupling theory and the detailed form of this theory for long times remains inconclusive and contradictory.

In this Letter we present new quantitative results that show the important role played by detailed balance conditions in controlling complete structural arrest in mode coupling theory. Our objective is to construct and analyze a mode coupling model that retains *both* the physical mechanism associated with structural arrest (density nonlinearities) and the mathematical structure imposed by the underlying microscopic dynamics (detailed balance). There are three parts to the analysis. The first is a description of fluctuating hydrodynamics (Langevin equations) extended to short wavelengths, to account for mode coupling effects at all length scales. These equations are identified in a form that makes explicit certain "detailed balance" conditions. The second part of our analysis concerns approximations to the equations. The mode coupling mechanism for the ideal glass transition is associated with the nonlinear dependence of the pressure on the mass density. A primary observation of our work is that detailed balance places strong constraints on the form of the Langevin equations: Consideration of density nonlinearities due to the pressure in the equation for the momentum field requires specific density-momentum field bilinearities in the continuity equation as well. These additional bilinearities imposed by detailed balance eliminate the structural arrest predicted by mode coupling theories with only the pressure nonlinearities. In addition, we exploit an exact relationship between correlation functions and response functions by considering a Gaussian stationary state. The result of these two parts of the analysis is an action with cubic order nonlinearity, providing a nontrivial theoretical description of density fluctuations that includes manifestly the mode coupling mechanism of interest and a proper stationary state.


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At this point questions can be posed in a controlled and precise fashion. Is there an ideal glass transition? If not, what is the mechanism responsible for asymptotic structural relaxation? In what respect is the theory with an ideal transition approximately correct? We answer these questions within the context of renormalized perturbation theory, which is the third part of our analysis: a determination of the closed equations for the density autocorrelation function to one loop order. Our primary result is that there is no ideal glass transition; instead, the asymptotic dynamics is determined from the density-momentum field bilinearities imposed by detailed balance. However, there appear to be intermediate time scales for which the original mode coupling models are approximately correct. These results are consistent with the schematic scenario of Refs. [5] and [6]; our contribution is to identify the origin of this new asymptotic dynamics as due to detailed balance, and to express this in terms of microscopic parameters.

Fluctuating hydrodynamic equations and their origins in nonequilibrium statistical mechanics have been discussed elsewhere [8]. Here, we consider only the mass and momentum density equations and neglect any effects associated with temperature fluctuations. The stochastic equations we consider are given by

$$\frac{\partial}{\partial t}a_\alpha(\mathbf{r},t)+K_\alpha(\mathbf{r}|[a(t)])=\xi_\alpha(\mathbf{r},t)\,, \tag{1}$$

$$\langle\xi_\alpha(\mathbf{r},t)\xi_\beta(\mathbf{r}',t')\rangle=2k_BT\Gamma_{\alpha\beta}(\mathbf{r}-\mathbf{r}')\delta(t-t')\,, \tag{2}$$

where $a_0(\mathbf{r},t)=\rho(\mathbf{r},t)$ is the mass density and $a_i(\mathbf{r},t)=g_i(\mathbf{r},t)$ are components of the momentum density (here and below Greek indices have the range 0–3 while Latin indices have the range 1–3). The nonlinear functions $K_\alpha(\mathbf{r}|[a(t)])$ characterize the deterministic equations, and $\xi_\alpha(\mathbf{r},t)$ is a random force representing Gaussian white noise with zero average. The "noise matrix" is symmetric, $\Gamma_{\alpha\beta}(\mathbf{r}-\mathbf{r}')=\Gamma_{\beta\alpha}(\mathbf{r}'-\mathbf{r})$, and explicitly given by $\Gamma_{\alpha\beta}=0$ for $\alpha$ or $\beta=0$ and $\Gamma_{ij}(\mathbf{r})=-\partial_{ij}\gamma^L(r)-(\delta_{ij}\nabla^2-\partial_{ij})\gamma^T(r)$, where $\gamma^L$ and $\gamma^T$ are two scalar viscosity kernels. Detailed balance conditions associated with microscopic time reversal symmetry lead to a canonical form for $K_\alpha(\mathbf{r}|[a(t)])$ [9]:

$$K_\alpha(\mathbf{r}|[a])=\int d\mathbf{r}'[R_{\alpha\beta}(\mathbf{r},\mathbf{r}'|[a])+\Gamma_{\alpha\beta}(\mathbf{r}-\mathbf{r}')]\frac{\delta F[a]}{\delta a_\beta(\mathbf{r}')}\,, \tag{3}$$

$$F[a]=\frac{1}{2}\int d\mathbf{r}\frac{a_i(\mathbf{r})a_i(\mathbf{r})}{a_0(\mathbf{r})}+F'[a_0]\,. \tag{4}$$

Here $F[a]$ is a "free energy" that is related to the stationary probability density according to $P[a]\propto\exp(-F[a]/k_BT)$. The first term represents the kinetic energy and the second term, $F'[a_0]$, is the free energy functional of the fluid locally at rest depending only on the mass density and containing all information on the static structure of the system. Finally, the matrix $R$ in (3) is antisymmetric, $R_{\alpha\beta}(\mathbf{r},\mathbf{r}'|[a])=-R_{\beta\alpha}(\mathbf{r}',\mathbf{r}|[a])$, and represents the reversible (Euler) dynamics,

$$\begin{aligned}&R_{00}(\mathbf{r},\mathbf{r}'|[a])=0\,,\\ &R_{0i}(\mathbf{r},\mathbf{r}'|[a])=\partial_i a_0(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')=-R_{i0}(\mathbf{r}',\mathbf{r}|[a])\,,\\ &R_{ij}(\mathbf{r},\mathbf{r}'|[a])=\partial_j a_i(\mathbf{r},t)\delta(\mathbf{r}-\mathbf{r}')+a_j(\mathbf{r},t)\partial_i\delta(\mathbf{r}-\mathbf{r}')\,.\end{aligned} \tag{5}$$

We will refer to any Langevin equation of the form (3), with matrices $R$ and $\Gamma$ having the aforementioned symmetry properties, as satisfying detailed balance conditions. Equations (1)–(5) provide a closed set of stochastic Langevin equations from which the density fluctuations can be determined.

A formal path integral solution to these equations can be given in terms of the action [10]

$$A\{a,\hat{a}\}=\int_{-\infty}^{\infty}dt\int d\mathbf{r}\,\hat{a}_\alpha(\mathbf{r},t)\left(\frac{\partial}{\partial t}a_\alpha(\mathbf{r},t)+K_\alpha(\mathbf{r}|[a(t)])-k_BT\int d\mathbf{r}'\Gamma_{\alpha\beta}(\mathbf{r}-\mathbf{r}')\hat{a}_\beta(\mathbf{r}',t)\right). \tag{6}$$

In practice, this field-theoretical formalism [11] is useful when the action is of polynomial order or when a small parameter is available for ordering a perturbation expansion. There are two serious technical problems in the present case: (1) The action is not of polynomial order due to dependences on $1/\rho(\mathbf{r},t)$ arising from the free energy (4), and expansions in $\delta\rho(\mathbf{r},t)$ do not preserve detailed balance order by order. (2) The equations for the correlation functions are coupled to those for a second set, the response functions, leading to an intractable complexity of nonlinear integro-differential equations for eight fields even at one loop order.

These problems are addressed in the following manner. Approximations are restricted to retain *both* the nonlinear mass density dependence associated with the ideal transition (arising from the pressure term $R_{i0}\delta F'/\delta a_0$) to quadratic order, *and* the above structure imposed by detailed balance (the term $R_{0i}\partial F/\delta a_i$). Furthermore, the problem with coupling to response functions is solved by using a Gaussian approximation to the stationary state in which case there are exact "fluctuation-dissipation" relations expressing the response functions in terms of the correlation functions [12]. In the equilibrium fluid state the free energy has a minimum with $\mathbf{g}=0$ and a uniform average density $\rho_0$. We assume this fluid branch persists as a local minimum in the metastable state and restrict our attention to states near this minimum,

$$F[a]\to\frac{1}{2\rho_0}\int d\mathbf{r}\,\mathbf{g}^2(\mathbf{r})+\frac{1}{2m\beta\rho_0}\int d\mathbf{r}\,d\mathbf{r}'[\delta(\mathbf{r}-\mathbf{r}')-nc(|\mathbf{r}-\mathbf{r}'|)]\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')\,, \tag{7}$$

where $m$ is the mass per particle, $n=\rho_0/m$ is the average density, and $c(r)$ is the direct correlation function of the fluid at density $\rho_0$. Furthermore, in the interest of simplicity, we retain only the density dependence of $R_{\alpha\beta}$, thus setting $R_{ij}\to 0$. With no further approximations, the resulting action has a cubic order nonlinearity, satisfies detailed balance, and has a Gaussian stationary state.

We note that this expansion of the free energy about the minimum at $\mathbf{g}=0$ breaks Galilean invariance and hence the resulting approximate hydrodynamic equations are valid only in the rest frame. It is well known that without exact Galilean invariance the mass flux is no longer exactly equal to the momentum density. Consequently, the approximate continuity equation has additional nonlinearities reflecting this change in the mass flux; their form is fixed by the detailed balance conditions. Of course, global conservation of particle number is preserved.

It is now a straightforward but lengthy exercise to obtain a closed set of equations for the correlation functions using the method of [11]. In this Letter we quote only the results. It is convenient to use a Fourier representation of the correlation functions. Separating the momentum into longitudinal and transverse components allows reduction of these correlation functions to four dimensionless scalar functions determined from $C_{\alpha\beta}(\mathbf{k},t)\equiv V^{-1}\times\langle\delta a_\alpha(\mathbf{k},t)\delta a_\beta(-\mathbf{k},0)\rangle$:

$$
\begin{aligned}
C_0(k,t)&\equiv\frac{1}{m\rho_0 S(k)}C_{00}(\mathbf{k},t)\,,\\
C_1(k,t)&\equiv -i\frac{1}{\rho_0}\left[\frac{\beta}{mS(k)}\right]^{1/2}\hat{k}_j C_{j0}(\mathbf{k},t)\,,\\
C_2(k,t)&\equiv\frac{\beta}{\rho_0}\hat{k}_i\hat{k}_j C_{ij}(\mathbf{k},t)\,,\\
C_3(k,t)&\equiv\frac{\beta}{\rho_0}(\delta_{ij}-\hat{k}_i\hat{k}_j)C_{ij}(\mathbf{k},t)\,,
\end{aligned}
\tag{8}
$$

where $S(k)$ is the static structure factor. The Dyson equations for $C_\alpha$ are expressed most compactly in terms of the dimensionless Laplace transforms, $\tilde{C}_\alpha(k,z^*)=\Omega(k)\int dt\, e^{-zt}C_\alpha(k,t)$ where $\Omega(k)\equiv k[mS(k)/k_BT]^{-1/2}$ and $z^*\equiv z/\Omega(k)$. Then,

$$
\tilde{C}_0(k,z^*)=\left(z^*+\tilde{M}_0(k,z^*)+\frac{[1-\tilde{M}_1(k,z^*)]^2}{z^*+\sigma^L(k)+\tilde{M}_2(k,z)}\right)^{-1}\,,
\tag{9}
$$

$$
\tilde{C}_1(k,z^*)=[1-\tilde{M}_1(k,z^*)][z^*+\sigma^L(k)+\tilde{M}_2(k,z^*)]^{-1}\tilde{C}_0(k,z^*)\,,
\tag{10}
$$

$$
\tilde{C}_2(k,z^*)=[z^*+\tilde{M}_0(k,z^*)][z^*+\sigma^L(k)+\tilde{M}_2(k,z^*)]^{-1}\tilde{C}_0(k,z^*)\,,
\tag{11}
$$

$$
\tilde{C}_3(k,z^*)=[z^*+\sigma^T(k)+\tilde{M}_3(k,z^*)]^{-1}\,,
\tag{12}
$$

and $\sigma^{L,T}(k)\equiv[k^2/\rho_0\Omega(ik)]\int dr\, e^{i\mathbf{k}\cdot\mathbf{r}}\gamma^{L,T}(r)$. The self-energies determined from renormalized perturbation theory to one loop order are bilinear functionals of the correlation functions, of the form

$$
\tilde{M}_\alpha(k,z^*)=(2\pi)^{-3}\Omega^{-1}\int_0^\infty dt\, e^{-zt}\int d\mathbf{q}\,\Lambda_{\alpha\beta\gamma}(\mathbf{k};\mathbf{q},\mathbf{k}-\mathbf{q})C_\beta(q,t)C_\gamma(|\mathbf{k}-\mathbf{q}|,t)\,.
\tag{13}
$$

A summation over $\beta$ and $\gamma$ is implied. The coupling kernels have the symmetry, $\Lambda_{\alpha\beta\gamma}(\mathbf{k};\mathbf{q}_1,\mathbf{q}_2)=\Lambda_{\alpha\gamma\beta}(\mathbf{k};\mathbf{q}_2,\mathbf{q}_1)$, and are given by

$$
\begin{aligned}
\Lambda_{002}(\mathbf{k};\mathbf{q},\mathbf{p})&=\frac{1}{2}\frac{S(q)}{S(k)}\hat{p}_i\hat{p}_j U_i^{(2)}(\mathbf{q},\mathbf{p})U_j^{(2)}(\mathbf{q},\mathbf{p})\,,\\
\Lambda_{003}(\mathbf{k};\mathbf{q},\mathbf{p})&=\frac{1}{2}\frac{S(q)}{S(k)}(\delta_{ij}-\hat{p}_i\hat{p}_j)U_i^{(2)}(\mathbf{q},\mathbf{p})U_j^{(2)}(\mathbf{q},\mathbf{p})\,,\\
\Lambda_{011}(\mathbf{k};\mathbf{q},\mathbf{p})&=-\frac{\sqrt{S(q)S(p)}}{S(k)}\hat{q}_i\hat{p}_j U_i^{(2)}(\mathbf{q},\mathbf{p})U_j^{(2)}(\mathbf{q},\mathbf{p})\,,\\
\Lambda_{101}(\mathbf{k};\mathbf{q},\mathbf{p})&=\frac{1}{2}\frac{S(q)\sqrt{S(p)}}{\sqrt{S(k)}}\hat{k}_i\hat{p}_j U_i^{(1)}(\mathbf{q},\mathbf{p})U_j^{(2)}(\mathbf{q},\mathbf{p})\,,\\
\Lambda_{200}(\mathbf{k};\mathbf{q},\mathbf{p})&=\frac{1}{2}S(q)S(p)\hat{k}_i\hat{k}_j U_i^{(1)}(\mathbf{q},\mathbf{p})U_j^{(1)}(\mathbf{q},\mathbf{p})\,,\\
\Lambda_{300}(\mathbf{k};\mathbf{q},\mathbf{p})&=\frac{1}{4}S(q)S(p)(\delta_{ij}-\hat{k}_i\hat{k}_j)U_i^{(1)}(\mathbf{q},\mathbf{p})U_j^{(1)}(\mathbf{q},\mathbf{p})\,.
\end{aligned}
\tag{14}
$$

The elements not displayed are either zero or follow from the symmetry quoted above. Moreover, the vertices $U_i^{(1,2)}$ are defined by $U_i^{(1)}(\mathbf{q},\mathbf{p})=U_i(\mathbf{q},\mathbf{p})+U_i^{(2)}(\mathbf{q},\mathbf{p})$, $U_i^{(2)}(\mathbf{q},\mathbf{p})=(\rho_0/k_BT)^{-1/2}(q_i+p_i)$, $U_i(\mathbf{q},\mathbf{p})\equiv-(\rho_0k_BT/m^2)^{1/2}[q_ic(q)+p_ic(p)]$. The Dyson equations (9)–(12) and the self-energy equations (13) provide a closed set of equations to determine the correlation functions and are the main results of this paper.

The mode coupling effects arise from two quadratic nonlinearities of the Langevin equation. The first, with vertex $U_i^{(1)}$, is due to quadratic density dependence of the pressure in the momentum equation while the second, with vertex $U_i^{(2)}$, is a density-momentum bilinearity in the density equation required by detailed balance, as indicated above Eq. (7). The first nonlinearitity is expected to provide the physical origin of possible structural arrest due to density mode coupling, so we consider first neglecting all contributions from $U_i^{(2)}$. In this case the self-energies $\tilde{M}_0$ and $\tilde{M}_1$ vanish, $U_i^{(1)}\to U_i$, and the equations of Ref. [2] are regained. In particular, for temperatures below a critical value, the amplitude $\Lambda_{200}$ is sufficiently large that $\tilde{M}_2(k,z^*)$ acquires a pole at $z^*=0$ and, con-

sequently, $\tilde{C}_0(k,z^*)$ also has such a pole. This corresponds to complete structural arrest and is the signature of an ideal glass transition.

More generally, the full set of equations including the nonlinearities due to detailed balance *does not* lead to an ideal glass transition. Qualitatively, as $z^* \to 0$, $\tilde{M}_0(k, z^*)$ and $\tilde{M}_1(k,z^*)$ do not diverge since they are determined from density-momentum correlation functions which decay even if there is structural arrest. Conversely, $\tilde{M}_2(k,z^*)$ is becoming large. Thus for very small $z^*$, $\tilde{C}_0(k,z^*)$ has a simple pole located approximately at $z^* = -\tilde{M}_0(k,0)$. However, the ideal glass transition (pole at $z^*=0$) is now precluded by the fact that $\tilde{M}_0(k,0)\neq 0$. Instead of leading to structural arrest the correlation function behaves asymptotically as $C_0(k,t) \sim \exp[-\tilde{M}_0(k,0)t^*]$, with $t^* = \Omega(k)t$.

Several final comments are offered as a summary of the current work.

(1) A model Langevin equation has been proposed here on the basis of retaining the density mode coupling mechanism, detailed balance conditions, and a quadratic free energy functional. Within the context of this model and one loop perturbation theory, we find no ideal glass transition although the mode coupling mechanism associated with $U_i^{(1)}$ can generate large relaxation times. The ideal transition of the simple mode coupling theory is regained if the nonlinearity associated with $U_i^{(2)}$ is neglected. Since detailed balance conditions prohibit such neglect in general, we conclude that a finite mode coupling theory requires attention to these conditions.

(2) The approximation of a quadratic free energy functional provides a "fluctuation-dissipation relation" that allows exact elimination of response functions in terms of correlation functions [12]. Even at one loop order perturbation theory, the formalism becomes intractable without this simplification (unless additional uncontrolled approximations are introduced).

(3) It is possible that a number of features of the simple mode coupling model with $U_i^{(2)}=0$ may be approximately correct. The scenario has been described in Refs. [5] and [6], where it is assumed that the ultimate decay of the correlation functions has a very large time scale (small $\tilde{M}_0$) so that the simple mode coupling model applies for a range of intermediate times. To explore this possibility, we have estimated the self-energies using a model structure factor and find that the amplitude of $\tilde{M}_2$ is more than an order of magnitude larger than the other self-energies. This is consistent with the above scenario envisioned in Refs. [5] and [6], and explored numerically recently using $\tilde{M}_0$ as an adjustable parameter (the first work of Ref. [5]).

(4) Previous studies of finite mode coupling models [6,7] lead to qualitatively similar results. The mode coupling theory of Ref. [6] is obtained from a formal kinetic theory, projected onto density and momentum fields. The resulting asymptotic behavior is similar to (10) with an important qualitative difference at long wavelengths. Both the result obtained here and that of Ref. [7] predict asymptotic diffusive decay at long times, while that of Ref. [6] is exponential at long wavelengths. Hence the existing finite mode coupling theories are *not* equivalent.

(5) In Refs. [5] and [6] the asymptotic dynamics due to $\tilde{M}_0$ has been called "hopping dynamics" and associated with activated processes. This terminology is used in several different contexts—either single particle transitions between localized sites, or system transitions between different local free energy minima. None of the existing finite mode coupling models entails hopping in this latter sense; all assume implicitly or explicitly (as here) expansions about a single fluid-type free energy minimum.

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