Hydrodynamic Theory of the Glass Transition

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We demonstrate that the equations of hydrodynamics for a simple compressible fluid, including nonlinearities and thermal fluctuations, display a transition, at sufficiently high densities and low temperatures, to a glass. The theory leads to predictions for the behavior of viscosities, sound speeds, and correlation functions near the transition.

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The equations of hydrodynamics for a simple compressible fluid display a transition at sufficiently high densities and low temperatures to a "phase" with the properties[1] of real glass. A remarkable feature of this transition is that it is *purely dynamical:* All static properties, like thermodynamic derivatives, are regular as one goes through the transition. The shear and bulk viscosities diverge at the glass transition temperature[2] T_G. There is a *discontinuous jump* in the longitudinal sound speed as the temperature T is lowered past T_G. For $T < T_G$, transverse sound waves propagate at arbitrarily low frequencies ω, with a speed whose zero-frequency limit vanishes *discontinuously* at T_G. The density-density correlation function acquires a viscoelastic peak at $\omega = 0$ as $T \rightarrow T_G$, with a width which drops continuously to zero at T_G and stays there for $T \leqslant T_G$.

This behavior of the transverse modes can be interpreted in terms of a shear modulus which vanishes discontinuously at T_G. The viscoelastic response of the system in the large $\omega\tau$ limit, where τ is a characteristic time, shows a nonuniversal power-law behavior in keeping with a vast number of observations in glassy systems.[3] Finally, our theory leads naturally in the glass phase to a yield stress of the order of the shear modulus.

The dynamical mechanism (nonlinear density fluctuations) which leads to this glass transition was recently discovered by Leutheusser and Yip (LY)[4,5] in the kinetic theory of hard spheres. As will become clear below, the origins of their model differ considerably from ours, and their results emerge as a low-order approximation to our more general results.

The equations governing the low-frequency and long-wavelength behavior of an isotropic compressible fluid are those of fluctuating nonlinear hydrodynamics including dissipation and thermal fluctuations. These equations describe the dynamics of the conserved or slow variables in the problem, namely, the mass, momentum, and energy densities ρ, $\mathbf{g}$, and ϵ. Since ϵ plays a secondary role in the development, we shall ignore it in what follows. Results which follow in its inclusion will be given elsewhere. The hydrodynamic equations can be derived by use of standard methods[6] with the usual results

$$\partial\rho/\partial t = \nabla\cdot\mathbf{g}, \tag{1}$$

$$\frac{\partial g_i}{\partial t} + \nabla_j \frac{g_i g_j}{\rho} + \frac{\rho\nabla_i \delta F_U}{\delta\rho} + \nabla_j \sigma_{ij}^D = f_i. \tag{2}$$

Equations (1) and (2) are just the continuity equation expressing conservation of mass and momentum. The second term on the left of (2) is the usual convective term. σ_{ij}^D is the dissipative part of the stress tensor given by

$$\sigma_{ij}^D = -\eta_0(\nabla_i V_j + \nabla_j V_i - \tfrac{2}{3}\delta_{ij}\nabla\cdot\mathbf{V}) - \zeta_0\delta_{ij}\nabla\cdot\mathbf{V}, \tag{3}$$

where η_0 and ζ_0 are the bare[7] shear and bulk viscosities and $\mathbf{V} \equiv \mathbf{g}/\rho$. f_i is a Gaussian noise source whose statistics are related to η_0 and ζ_0 via a fluctuation-dissipation theorem[6] in the conventional fashion. The other term, $\rho\nabla_i\delta F_U/\delta\rho$, involves the "potential" part of the effective free energy $F[\rho, \mathbf{g}]$ which governs the equal-time correlations of the fields ρ and $\mathbf{g}$. Quite generally one can write[8]

$$F[\rho, \mathbf{g}] = \int d^3x\,(g^2/2\rho) + F_U[\rho], \tag{4a}$$

$$F_U[\rho] = \int d^3x\,[f(\rho) + \tfrac{1}{2}C(\nabla\rho)^2 + \ldots], \tag{4b}$$

where f is analytic in ρ with a quadratic minimum at the quiescent density ρ_0, C is the phenomenological parameter, and the ellipses indicate more complicated terms, e.g., higher orders in $\nabla\rho$, cross couplings, etc. In general, in a hydrodynamic theory, one should allow for all terms compatible with symmetry, conservation laws, and overall stability. If one neglects the dependence of $F_U[\rho]$ on the spatial derivatives of ρ, then one easily finds that $\rho\nabla_i\partial F_U/\partial\rho = \nabla_i P[\rho]$, where $P = \rho\partial f/\partial\rho - f$ gives the familiar thermodynamic relationship between the pressure and the free-energy density. Thus we obtain the pressure term in the Navier-Stokes equation. Note that even in the simplest case where f is quadratic, $f = \frac{1}{2}\chi^{-1}(\delta\rho)^2$ with $\delta\rho = \rho - \rho_0$, one generates a nonlinear term in the equation of motion since $P = \rho_0\chi^{-1}\delta\rho + \frac{1}{2}\chi^{-1}(\delta\rho)^2$. This essentially dynamical nonlinearity and related terms are responsible for the glass transition in the theory.

In a complete theory of the glass transition we must typically include in the analysis the competition of the supercooled liquid state with the more stable crystalline state and the associated effects of a finite quench rate. This requires the addition of terms to the free energy which reflect the crystalline instability and the treatment of the nonequilibrium problem of a quench at some finite rate from an equilibrium state where the liquid is stable to a state where we expect a glass transition. While it seems possible to carry out such an analysis, it is sensible to first ask if a stationary glasslike state exists if crystallization can be avoided. We address this question specifically in this paper and will return to the more general situation in a later work.

The fluctuations in a stationary state are conveniently studied through an analysis of the spatial Fourier transforms of the time autocorrelation functions. We focus here on the density autocorrelation function

$$C_\rho(\mathbf{q},t) = \langle \delta\rho(-\mathbf{q},0)\delta\rho(\mathbf{q},t)\rangle, \tag{5}$$

and a related analysis follows for the transverse-current autocorrelation function $C_T(\mathbf{q},t)$. The Laplace-transformed quantity

$$C_\rho(\mathbf{q},z) = -i\int_0^{+\infty} dt\, e^{+izt} C_\rho(\mathbf{q},t) \tag{6}$$

has the general representation

$$C_\rho(\mathbf{q},z) = \frac{\chi(\mathbf{q})}{z - c^2q^2[z + iD_L(\mathbf{q},z)q^2]}, \tag{7}$$

where $\chi(\mathbf{q}) = C_\rho(\mathbf{q},t=0)$, c^2 is the isothermal (adiabatic if we include the energy variable) speed of sound, and $\rho_0 D_L(\mathbf{q},z) = \zeta(\mathbf{q},z) + 4\eta(\mathbf{q},z)/3$, where $\eta(\mathbf{q},z)$ and $\zeta(\mathbf{q},z)$ are generalized shear and bulk viscosities. In the absence of nonlinearities in the equations of motion, $\eta(\mathbf{q},z) = \eta_0$ and $\zeta(\mathbf{q},z) = \zeta_0$, and we obtain the usual[9] mode structure for simple fluids. The glass transition is caused by the effects of nonlinearities on the effective transport coefficients.

Using renormalized perturbation theory[10] we can develop a systematic perturbation-theory analysis of these equations in powers of k_BT. For dimension $d \leqslant 2$ the convective nonlinearities lead to strong fluctuations which cause a breakdown in conventional hydrodynamics. Our analysis therefore will be restricted to $d > 2$ where the convective and various other nonlinear interactions in our "loop" expansion lead to no qualitative changes in $D_L(\mathbf{q},z)$ and $\eta(\mathbf{q},z)$ and their contributions can be absorbed into D_L^0 and η^0. The details of the graphical analysis will be given elsewhere. A key point is that for low temperatures the vertex in the equation of motion proportional to $(\delta\rho)^2$ and higher powers of $\delta\rho$ forces $D_L(\mathbf{q},z)$ to grow sufficiently large for small z that $\phi(z) = C_\rho(\mathbf{q},z)/\chi(\mathbf{q}) = [z + id^{-1}(z)]^{-1}$, with $d(z) = D_L(\mathbf{q},z)/c^2$, becomes large and essentially independent of $\mathbf{q}$. (We assume here that we work with wave numbers sufficiently small so that we can replace the static structure factor with its $\mathbf{q}=0$ value.) Consequently $\phi(z)$ becomes sharply peaked near $z=0$. This result can then be used to simplify Feynman graphs at arbitrary order which have vertex insertions from the density nonlinearities.

One finds that internal propagators can be essentially shrunk to δ functions in time which in turn leads to the nonlinear integral equation

$$d(z) = d_0 + \int_0^{+\infty} dt\, e^{+izt} H(\phi(t)), \tag{8}$$

and an analogous equation for $\eta(\mathbf{q},z) = \eta(z)$. $H(x)$ is analytic in x with a power series that begins at $O(x^2)$. Leutheusser[4] solved a special case of (8). Our method of solution of the general equation is quite similar to his.

A perfectly natural definition[11] of a glass is a system where $\phi(t) \rightarrow$ const for long times. We therefore assume in the glass phase that the solution of the coupled set of equations for d and ϕ is of the form

$$\phi(t) = h + \phi_\nu(t)\ , \tag{9a}$$

or, equivalently,

$$d(z) = ih(1-h)^{-1}z^{-1} + d_\nu(z) \tag{9b}$$

and a similar expression for $\eta(z)$, where for long times or small frequencies ϕ_ν and d_ν are small compared to the leading terms. Inserting (9a) into the equations for ϕ and d and expanding in powers of $\phi_\nu(t)$, we find that $\phi_\nu(t) \sim t^{-\gamma}$ at the transition; furthermore, one obtains an equation with terms diverging as z^{-1}, $z^{-1+\gamma}$, and $z^{-1+2\gamma}$ for small z. The condition that the coefficients of these terms vanish at the transition gives the three equations

$$(1+H)h = H, \tag{10a}$$

$$1 + H = (1-h)H', \tag{10b}$$

and

$$H'\Gamma^2(1-\gamma) = (1-h)H''\Gamma(1-2\gamma)/2, \tag{10c}$$

where the argument of H is h and Γ is the gamma function. In the glass phase, $\phi_v(t)$ decays exponentially,[12] and h is determined by (10a).

Our basic results are that (i) Eq. (8) holds for some function H, and (ii) Eqs. (10) determine T_G as a function of the other parameters in the theory, the value of h at T_G, and the exponent γ.

In general, H will depend on the precise form of the effective free energy and hence will be system dependent. As a result, so will T_G, h_c, and γ. Whether a given system has a solution for $T_G > 0$ is not accessible in our hydrodynamic model. This will depend on certain microscopic properties of the system. However, if the system does form a glass and can avoid crystallization, then this theory should describe the nature of that transition. That is, it is characterized by a phase boundary $T_G = T_G(\rho, C, \ldots)$, an infinite-time limit of the density-density correlation function h, and an exponent γ with ramifications to be discussed below.

It should be pointed out that there are no compelling mathematical reasons for truncating the function H at a finite order in the loop expansion since the series is not expected to be convergent. On the other hand, the excellent results of Ref. 5 for the freezing packing fraction of hard spheres and our results (see below and Ref. 13) for the growth of the viscosity as $T \rightarrow T_G$ as compared with computer simulations indicate that power-series approximations for $H(\phi)$ may be useful.

Analyzing coupled sets of equations derived[14] in an approximate kinetic theory, LY arrived at (8) but with[15] $H(\phi) = 4\lambda\phi^2$. Using this form for $H(h)$ in (10), one obtains $\lambda_c = 1$, $h_c = \frac{1}{2}$, and $\gamma = 0.395\ldots$ at the transition. It is easy to see from our results that these values are modified by higher-order corrections. In a model where f is purely quadratic, including contributions up to order ϕ^3 in H, and solving the set of Eqs. (10), one[16] obtains $\lambda_c = 0.55\ldots$, $h_c = 0.59\ldots$, and $\gamma = 0.385\ldots$. Thus the value of γ shows a certain robustness, but this may be spurious. We emphasize that our basic conclusions are not tied to these estimates for λ_c, h_c, and γ.

Notice that the value of h at T_G is nonzero. The behavior of the transport coefficients on either side of the transitions, when expressed in terms of γ, is the same as in LY, except that γ is nonuniversal. Introducing $\epsilon = |T - T_G|$, we find[13] that $\mathrm{Re}\,d(0,T)$ and $\mathrm{Re}\,\eta(0,T)$ go as $\epsilon^{-\mu}$ for $T > T_G$ and $\epsilon^{-\mu'}$ for $T < T_G$, while both $\mathrm{Re}\,d(z,T_G)$ and $\mathrm{Re}\,\eta(z,T_G)$ diverge as $z^{\gamma-1}$, where $\mu = (1+\gamma)/2\gamma$, $\mu' = \mu - 1$, and $0 < \gamma < \frac{1}{2}$. Since $\mathrm{Re}\,\eta(z) \sim z^{\gamma-1}$ near the transition, one obtains the result that for $\omega\tau$ (τ being a characteristic time scale) large the viscoelastic response of the system scales with a power law $(\omega\tau)^{\gamma-1}$ as observed[3] in many glassy systems.

The structure of the time Fourier transforms $C_\rho(\mathbf{q},\omega)$ and $C_T(\mathbf{q},\omega)$ which follow from our results is particularly rich and will be discussed elsewhere. We note here that the longitudinal sound speeds jump from c in the liquid to $c/(1-h)^{1/2}$ in the glass, while the transverse speeds jump from 0.

Our hydrodynamic theory is very general. It does not start with any particular microscopic model (say, hard spheres or tetrahedrally coordinated silicon) but is valid quite generally for *any* compressible fluid system, by construction, since the corresponding equations include all terms allowed by the symmetries[17] and conservation laws of the simple fluid. The sole limitation of such an approach is its inability to answer questions that involve a precise knowledge of the numerical values in those equations.

Finally, we emphasize the ideal nature of the stationary state we have explored. Except for systems with extremely rapid quench rates and complete suppression of crystallizations, one expects that there will be kinetic effects, such as vacancy diffusion and metastability, which can cut off the sharp nature of the state we discuss here. We believe, however, that our model is a convenient starting point for investigating the inclusion of these effects.

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[1] For a review see G. S. Grest and M. H. Cohen, in *Advances in Chemical Physics,* edited by I. Prigogine and S. Rice (Wiley, New York, 1981), Vol. 48.

[2] The relation of the transition temperature T_G, defined below, to various glass transition temperatures defined in the literature is not obvious. The effects of finite quench rates must be included before the connection can be clarified.

[3] See, for example, A. K. Jonscher, Nature **267**, 673 (1977); K. L. Ngai, Comments Solid State Phys. **9**, 127 (1979). Our results seem to be compatible with the Davidson-Cole form [D. W. Davidson and R. H. Cole, J. Chem. Phys. **19**, 1484 (1951)] for the response of the system.

[4] E. Leutheusser, Phys. Rev. A **29**, 2765 (1984); E. Leutheusser and S. Yip, to be published. We refer to these collectively as LY.

[5] After this work was completed the work of U. Bengtzelius, W. Götze, and A. Sjölander, unpublished, was brought to our attention. This work is very similar to that of Ref. 4, but the authors treat the effects of local structure more carefully. Of particular relevance is that they obtain a packing fraction for a hard-sphere glass transition of 0.516. This compares favorably with the computer simulation results of 0.52 [L. V. Woodcock, J. Chem. Soc. Faraday Trans. 2, **73**, 11 (1977)] and 0.56 [L. V. Woodcock and C. A. Angell, Phys. Rev. Lett. **47**, 1129 (1981)].

[6] S. Ma and G. F. Mazenko, Phys. Rev. B **11**, 4077 (1975); G. Mazenko, S. Ramaswamy, and J. Toner, Phys. Rev. A **28**, 1618 (1983).

[7] These "background" transport coefficients may have a substantial nonsingular temperature dependence at T_G not coming from the anharmonic effects driving the glass transition.

[8] J. Langer and L. Turski, Phys. Rev. A **8**, 3230 (1973).

[9] D. Forster, *Hydrodynamic Fluctuations, Broken Symmetry, and Correlation Functions* (Benjamin, Reading, Mass., 1975).

[10] P. C. Martin, E. Siggia, and H. Rose, Phys. Rev. A **8**, 423 (1973). One can also use the methods developed in Ref. 6.

[11] This is reminiscent of the order parameter introduced by S. A. Edwards and P. Anderson, J. Phys. F **5**, 965 (1975).

[12] The convective nonlinearities convert this into the famous $t^{-d/2}$ long-time tail decay in d dimensions. See D. Forster, D. Nelson, and M. Stephen, Phys. Rev. A **16**, 732 (1977).

[13] Our predictions that the viscosities diverge as a power law do not agree with the Vogel-Fulcher law [H. Vogel, Phys. Z **22**, 645 (1921); G. S. Fulcher, J. Am. Ceram. Soc. **8**, 339 (1925)] whose relevance has recently been emphasized in the interesting paper by R. G. Palmer, D. L. Stein, E. Abrahams, and P. W. Anderson, to be published. It appears that the simulations and data of L. V. Woodcock and C. A. Angell [Phys. Rev. Lett. **47**, 1129 (1981)] for the density behavior of the self-diffusion coefficient, which is inversely proportional to the viscosity, can equally well be fitted by a power law $(\rho_c - \rho)^x$. Our best fit to their data gives an $x = 1.86$. It is encouraging, though not definitive, that we obtain $x = \mu = (1+\gamma)/2\gamma \sim 1.80$ using our second-order estimate for γ. Experimentally, the problem of preparing the system in a quasistationary state as one gets close to T_G makes it difficult to resolve this question.

[14] J. R. Dorfman and E. G. D. Cohen, Phys. Rev. A **6**, 2247 (1972); G. F. Mazenko, Phys. Rev. A **9**, 360 (1974).

[15] The parameter λ is a function of temperature and density and other material parameters and in principle can be inverted to give $T_G = T_G(\rho, \ldots)$. While it is to possible to determine the dependence of λ on these parameters within a hydrodynamic theory, one can see, however, that it depends on an integral over the static structure factor and therefore is sensitive to the size and location of its maximum. Thus one expects λ to increase monotonically as the density increases. See Ref. 5.

[16] S. Das and G. Mazenko, unpublished.

[17] When additional hydrodynamic variables appear, for reasons of broken symmetry the analysis must be extended to include them. See, for example, S. Ramaswamy and J. Toner, Phys. Rev. Lett. **53**, 447 (1984).