

Comment on dynamical theories of the liquid-glass transition

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A nonlinear hydrodynamic model is proposed which reproduces the integral equation of Leutheusser for the density correlation function as the first term in a perturbation expansion. At the transition proposed by this author, our model reduces to a nonlinear oscillator, proving that the transition in this case is an artifact of the approximation.

I. INTRODUCTION

Leutheusser¹ has proposed a theory for the transition from a simple liquid to a glass that proceeds from a nonlinear equation for the density correlation function $C_{\rho\rho}$. The transition is signaled by a divergence in the longitudinal viscosity D and is accompanied by a persistent (i.e., nondecaying) term in $C_{\rho\rho}$. Under these assumptions, the wave-number dependence of $C_{\rho\rho}$ in the hydrodynamic limit effectively vanishes leaving one with an equation for $C_{\rho\rho}(\omega)$ alone, which is solvable analytically at the transition. Reference 2 follows up on this connection with hydrodynamics by proposing a nonlinear fluctuating hydrodynamic theory for the liquid-to-glass transition which reproduces and extends Ref. 1.

In this paper we analyze a slightly different hydrodynamic theory, which yields Leutheusser's equation for $C_{\rho\rho}$ as the first term of a perturbation expansion. At the putative glass transition, for the reasons enunciated by Leutheusser, all wave-number dependence disappears, leaving us with the diagrammatic series for a nonlinear oscillator forced by Gaussian white noise. This equation does not show any nonergodic behavior. This seeming contradiction is resolved by examining higher diagrams and showing them to be inconsistent with the assumed form of the correlation functions at the glass transition. We also comment on the relation of our model to Ref. 2. A fairly careful discussion of the diagrammatic expansion following Ref. 3 is contained in the Appendix, should there be any question about our conclusions.

Our construction cannot logically disqualify Ref. 1 as a model for the glass transition, since there may well be a small expansion parameter in the kinetic theory which leads to the $C_{\rho\rho}$ equation which we do not have. It does suggest that some care needs to be taken in searching for a glass transition in an approximate theory.⁴

II. NONLINEAR HYDRODYNAMICS

Consider the system

$$\dot{\rho} + \nabla \cdot \mathbf{g} = 0, \tag{1a}$$

$$\dot{\mathbf{g}} + \nabla u'(\rho) - D \nabla^2 \mathbf{g} = \boldsymbol{\eta}, \tag{1b}$$

where the white noise $\boldsymbol{\eta}$ obeys

$$\langle \eta_i(x, t) \eta_j(x', t') \rangle = 2D \delta(t - t') \nabla_i \nabla_j \delta(x - x')$$

and ρ and \mathbf{g} represent, respectively, the mass and longitudinal momentum density, and

nal momentum density, and

$$u' = \frac{du}{d\rho} = c^2 \rho + \sum_{n=2}^{\infty} u_n \rho^n. \tag{2}$$

By standard arguments, (1) and (2) imply an equilibrium distribution function for ρ and \mathbf{g} of the form

$$P(\rho, \mathbf{g}) = \exp(-u - \mathbf{g}^2/2). \tag{3}$$

Factors of temperature and a unit of density have been set to 1. All correlations involving ρ have the appropriate factors of $\langle \rho \rangle$ subtracted off.

It will be convenient to define three different functions measuring correlations of the fields. Let $\langle \rho \rho \rangle$ be completely symmetric in the arguments of the two densities (i.e., the anticommutator quantum mechanically) and let $\chi_{\rho\rho}$ be the retarded response function $\delta \langle \rho \rangle / \delta p$, where the infinitesimal "force" p enters (1b) according to $u' \rightarrow u' - \delta p$. Either function defines the retarded correlation $C_{\rho\rho}$ according to

$$C_{\rho\rho}(t, t') + C_{\rho\rho}(t', t) = \langle \rho \rho \rangle(t - t') \tag{4a}$$

or

$$\chi_{\rho\rho}(\omega) - \chi_{\rho\rho}(0) = i\omega C_{\rho\rho}(\omega). \tag{4b}$$

These relations are consistent by virtue of the fluctuation-dissipation theorem:

$$2 \text{Re} C_{\rho\rho}(\omega) = \langle \rho \rho \rangle(\omega) = \frac{2}{\omega} \text{Im} \chi_{\rho\rho}(\omega). \tag{5}$$

At the linearized level we find from (1)

$$\chi_{\rho\rho} = k^2 / (k^2 c^2 - \omega^2 - iD\omega k^2) \tag{6a}$$

and

$$C_{\rho\rho} = c^{-2} / [-i\omega + k^2 c^2 / (-i\omega + Dk^2)]. \tag{6b}$$

The static response is just c^{-2} .

Consider, following Leutheusser,¹ the large D limit of (6b) with ω fixed. Clearly, $C_{\rho\rho}$ is k independent for $k^2 \geq \omega/D$. We show in the Appendix, diagram by diagram, that provided we impose a cutoff on the internal momentum integrals and incorporate cutoff factors into the coupling constants, (1) and (2) reduce to

$$\begin{aligned} \dot{x} &= p, \\ \dot{p} &= -u' - Dp + \eta, \\ u' &= c^2 x + \sum_{n=2}^{\infty} u_n x^n, \\ \langle \eta \eta \rangle &= 2D \delta(t - t'). \end{aligned} \tag{7}$$

The linear correlation functions read

$$\begin{aligned} \chi_{xx} &= 1/(-\omega^2 + c^2 - iD\omega) , \\ C_{xx} &= c^{-2}/[-i\omega + c^2/(-i\omega + D)] . \end{aligned} \quad (8)$$

The equilibrium distribution follows (3).

The perturbation expansion for (7) involves two self-energies, which are related by the fluctuation-dissipation theorem.³ If we examine $\Sigma_{\hat{p}x}$, which enters the denominator of χ_{xx} (8), then, after removing certain constant terms which renormalize c^2 and an overall factor of ω , we find to order u_3^2, u_4^2 ,

$$D(\omega) = D + 2u_3^2 \mathcal{F}(C_{xx}^2) + 6u_4^2 \mathcal{F}(C_{xx}^3) , \quad (9)$$

with \mathcal{F} denoting the Fourier transform of products of C_{xx} taken in real time. Of course, D is properly retarded.

Equation (9), with $u_4 = 0$ taken together with (8), is precisely Leutheusser's equation (1). Again following Ref. 1, let us imagine that C_{xx} has a piece which relaxes slowly, i.e.,

$$C_{xx} = \frac{fc^{-2}}{-i\omega + \epsilon} , \quad (10)$$

with $0 < f < 1$, $\epsilon \ll 1$. A self-consistent equation for f follows, i.e.,

$$f^2 - f + c^6/(2u_3^2) = 0 , \quad (11)$$

and a "glass" state is obtained for the constant term less than 0.25. It will be observed on dimensional grounds that precisely in this regime the lifetime of the $x \sim 0$ solution becomes of order 1 due to thermal escape over the barrier, i.e., the distribution,

$$P(x) = \exp(-c^2 x^2/2 - u_3 x^3/3) , \quad (12)$$

is unbounded. For this reason we included the u_4 term in (9) which keeps everything finite. A cubic equation for f is obtained in place of (11), which has an acceptable solution for u_3, u_4 large. Of course, if one believes (10) is a valid representation of (7), then a nonconfining potential is not a problem since the motion is not ergodic.

Equation (7) cannot fail to be consistent with the equilibrium distribution (3) or (12). Of course, a nonlinear system subject to a periodic force can mode lock and not explore the available phase space. However, the force in (7) is white and Gaussian. If we integrate over $\Delta t \ll D^{-1}$, c^{-1} then the variance of the force is ($D\Delta t$) and there is always a small probability of a large kick.

When the complete dynamic perturbation series is examined, the "glass" transition for this model appears as just an artifact of the approximation (9). Before doing this, a further simplification is possible which was already apparent in (6b) for large D . Namely, an overdamped oscillator, (7), reduces to just

$$\dot{x} = -\frac{1}{D}u'(x) + \zeta , \quad (13)$$

with

$$\langle \zeta \zeta \rangle = 2D^{-1} \delta(t-t') .$$

Now imagine there is a self-consistent solution (13) in the form

$$\langle xx \rangle = \frac{f}{c^2} e^{-\epsilon|t-t'|} + \frac{(1-f)}{c^2} \delta(t-t') , \quad (14a)$$

$$\chi_{xx} = \frac{f\epsilon}{c^2} e^{-\epsilon(t-t')} \Theta(t-t') + \frac{(1-f)}{c^2} \delta(t-t'-0^+) , \quad (14b)$$

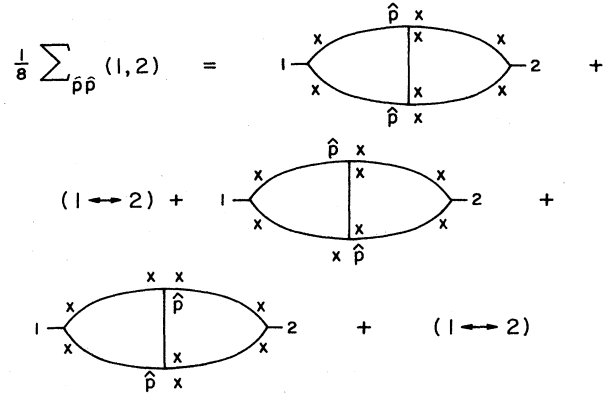


FIG. 1. The three distinct graphics that contribute to $\Sigma_{\hat{p}\hat{p}}$ to order u_3^4 . They all carry a weight of eight, but the first and third possess mirror images (right to left), which are shown as $(1 \leftrightarrow 2)$.

where Θ is the step function, $\epsilon \rightarrow 0$. The δ -function terms are shorthand for the pieces of C or χ which decay rapidly to zero.

Equation (14) is consistent with (10). For instance, by (4b) and for small ω ,

$$\chi_{xx}(\omega) = \frac{i\omega fc^{-2}}{-i\omega + \epsilon} + c^{-2} = \frac{\epsilon fc^{-2}}{-i\omega + \epsilon} + \frac{1-f}{c^2} . \quad (15)$$

One obtains the correct static limit if $\omega \rightarrow 0$ before $\epsilon \rightarrow 0$, but a smaller correlation in the opposite limit. The constant term in (15) is just the weight in frequencies $\gg \epsilon$.

Imagine substituting both the slow and fast terms of (14) into the higher-order diagrams for (13) or (7). [The ansatz (14) applies equally well to (7) if we call χ_{xx}, χ_{xp} ; similarly the graphs in Fig. 1 apply to (13) if the reverse substitution is made.] The pieces of graph involving only the δ functions in χ were retained in Ref. 2 to yield an equation similar to (9) with an unknown but local function of C replacing C^2 and C^3 . All convolutions disappear, since there are as many δ functions as interior integrals over time. The slow pieces of χ cannot be neglected, however, since although they contain an explicit ϵ , the associated time integrals have an effective range of order ϵ^{-1} , provided that only the slow part of $\langle xx \rangle$ is kept. Once again, there are as many interior integrals as factors of χ , so ϵ disappears. Since f is of order 1 at the transition, both pieces of χ must be retained and (9) involves arbitrary convolutions of C . Hence there is no local equation linking $D(t)$ with $C(t)$.

Whether one regards (14) as an acceptable ansatz depends on interchanging an $\epsilon \rightarrow 0$ limit with the order in the expansion tending to infinity. If this is done then $C(\omega) \sim \omega^{-1}$ implies $D(\omega) \sim \omega^{-1}$ as $\omega \rightarrow 0$ simply on dimensional grounds. This is a dangerous argument, even supposing the coefficient in C and D can be made to work out, as the example of (13) shows. There the small ϵ disappears from the problem entirely by redefining the time scale. There is clearly no dynamical reason why ϵ should tend to zero as other parameters in the model are varied.

III. CONCLUSION

Hydrodynamical theories of the glass transition are not new. For spin glasses, Sompolinsky and Zippelius⁵ used a

relaxational model to elucidate some of the peculiarities of purely static calculations. At the same time, they found it necessary to restate the fluctuation-dissipation relation and to suppose that strictly linear response and the thermodynamics limit are incompatible. Neither property has been investigated in the present model.

Spin and structural glasses are very different in that there are manifestly competing interactions in the former. While there may, in principle, be some vestige of frustration in supercooled liquids if one hypothesizes sufficiently robust local order, a hydrodynamic theory would certainly miss it. One can inquire into the mechanism of a glass transition by considering the simpler problem of localizing a particle in a fixed array of scatterers.⁶ With hard cores, steric effects can obviously lead to localization, but for soft cores or a point test particle we presume classical mechanics yields ergodic motion.⁷ We are unaware of any analog to quantum localization in the manner of Anderson.

We also cannot claim any quantitative correspondence between our model (1)–(3) and a kinetic theory calculation. Clearly, the viscosities and diffusion constants do not involve the potential only through the virial coefficients (i.e., u_n), as (1)–(3) assume.

We do not see, on the other hand, why the model of Ref. 2, being hydrodynamic, is any more plausible a starting point for studying the glass transition than (1)–(3). The convective term in Ref. 2 is only used to rule out consideration of low dimensional systems. We have been unable to derive an analog to their Eq. (8), a local relation between $D(t)$ and $C(t)$, and we doubt that one exists. If instead one merely imagines matching coefficients of ω^{-1} , then almost any field theory is a candidate for a glass transition.

One might take a more phenomenological view, and trust a hydrodynamical theory to give the correct singularity at the transition, even though it does not predict when a transition will occur. One then must contend with the disappearance of all wave-number dependence at the transition that Leutheusser noted. The contribution from various scales is then proportional to their phase-space volume. Wherever one puts the cutoff one has to argue why smaller scales themselves are not glassy. It is these “atomic” scales that one customarily lumps into a bare viscosity which is supposed to be nonsingular. In the present circumstances hydrodynamics suggests small scales “freeze” first. In other terms, the usual renormalization-group notions one invokes to make sense out of fluctuating nonlinear hydrodynamics near a second-order phase transition emphatically do not apply here, since the singularity originates on small scales.

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APPENDIX: DIAGRAMMATIC EXPANSION

We first generate the diagram rules for (7), since their generalization to (1) and (2) is trivial. Two operators \hat{x}, \hat{p}

are introduced, obeying the commutation relations

$$[x, \hat{x}] = 1, \quad [p, \hat{p}] = 1,$$

in terms of which a “Hamiltonian,”

$$\hat{H} = \hat{x}p - D\hat{p}p + \hat{p}\eta - \hat{p}u', \quad (\text{A1})$$

can be written, which permits one to reexpress the equations of motion, (7), as commutators, e.g.,

$$\dot{x} = [x, H], \quad \dot{\hat{x}} = [\hat{x}, H], \text{ etc.}$$

A perturbation expansion is constructed in terms of correlations $\langle xx \rangle$, $\langle xp \rangle$, etc., and formal responses $\langle x\hat{x} \rangle$, \dots , $\langle \hat{x}x \rangle$, \dots , where the first set are retarded and the others advanced. They are all conveniently grouped into a 4×4 matrix propagator.

Interactions come solely from the term $\hat{p}u'$ in (A1). The only nonvanishing self-energies are $\Sigma_{p\hat{x}}$, $\Sigma_{x\hat{p}} (= \Sigma_{\hat{p}x}^*)$, and $\Sigma_{\hat{p}\hat{p}}$ which are, respectively, retarded, advanced, and symmetric in time. The simplest way to express G in terms of Σ is to observe that $\Sigma_{\hat{p}x}$ and $\Sigma_{x\hat{p}}$ always occur in combination with c^2 in G^{-1} , while $\Sigma_{\hat{p}\hat{p}}$ naturally adds to $\langle \eta\eta \rangle$. Thus,

$$\begin{aligned} \langle x\hat{x} \rangle &= (-i\omega + D) / (-\omega^2 + c^2 - iD\omega - \Sigma_{\hat{p}x}), \\ \langle p\hat{x} \rangle &= -i\omega \langle x\hat{x} \rangle - 1, \\ \langle x\hat{p} \rangle &= 1 / (-\omega^2 + c^2 - iD\omega - \Sigma_{\hat{p}x}), \\ \langle p\hat{p} \rangle &= -i\omega \langle x\hat{p} \rangle, \\ \langle xx \rangle &= (2D + \Sigma_{\hat{p}\hat{p}}) |\langle x\hat{p} \rangle|^2. \end{aligned} \quad (\text{A2})$$

The remaining functions can be found by using $-i\omega x = p$.

The physical response function χ_{xx} we introduced above is computed by adding an infinitesimal force to u' in (7), i.e., the equilibrium distribution should become

$$\mathcal{P} \sim \exp(-c^2 x^2 / 2 + fx + \dots).$$

We then add $\hat{p}f$ to \hat{H} and prove

$$\chi_{xx} = \langle x\hat{p} \rangle. \quad (\text{A3})$$

Since our diagrammatic expansion is not restricted to equilibrium problems, the fluctuation-dissipation relation is not obvious. Thus it must be shown that

$$\langle xx \rangle = \frac{2}{\omega} \text{Im} \langle x\hat{p} \rangle, \quad (\text{A4a})$$

or

$$2 \text{Im}(\Sigma_{\hat{p}x}) = \omega \Sigma_{\hat{p}\hat{p}}. \quad (\text{A4b})$$

The diagram rules for $\Sigma(G)$ obey the usual combinatorics, thus to $\mathcal{O}(u_n^2)$, ignoring “Hartree” terms,

$$\Sigma_{\hat{p}x}(u') = nn! u_n^2 \langle xx \rangle^{n-1} \langle x\hat{p} \rangle, \quad (\text{A5a})$$

$$\Sigma_{\hat{p}\hat{p}}(u') = n! u_n^2 \langle xx \rangle^n. \quad (\text{A5b})$$

To verify (A4b) we write

$$\begin{aligned} 2 \text{Im}[\Sigma_{\hat{p}x}(\omega)] \\ = n(n!) u_n^2 \int (\omega - \Sigma_l \omega_l) \langle xx \rangle (\omega - \Sigma_l \omega_l) \prod_{i=1}^{n-1} \langle xx \rangle(\omega_i); \end{aligned} \quad (\text{A6})$$

when the frequency integrals are symmetrized using

$\omega_n = \omega - \sum_{i=1}^{n-1} \omega_i$, the explicit frequency dependence reduces to ω/n . Q.E.D.

Equation (9) follows from either the numerator of $\langle xx \rangle$ or the denominator of $\langle x\hat{p} \rangle$. In the former instance one has to write (A5b) as an advanced and retarded piece using (4a). To work from $\Sigma_{\hat{p}x}$, use (4b) to reexpress $\langle x\hat{p} \rangle(\omega) = \langle x\hat{p} \rangle(0) + i\omega C_{xx}(\omega)$. The constant piece in (A5a) adds to c^2 , while in the remainder we use (4a) to write

$$\begin{aligned} & \int i(\omega - \Sigma_i \omega_i) C_{xx}(\omega - \Sigma_i \omega_i) \prod_{i=1}^{n-1} \langle xx \rangle(\omega_i) \\ &= \frac{i\omega}{n} \int C_{xx}(\omega - \Sigma_i \omega_i) \prod_{i=1}^{n-1} C_{xx}(\omega_i) . \end{aligned}$$

The external ω_i/n factor arises just as in the reduction of (A6).

A closed equation for C_{xx} to arbitrary order in $u'(x)$ follows from $\langle x\hat{p} \rangle$ in (A2) and (A3) with $i\omega C_{xx} = \langle x\hat{p} \rangle(\omega) - \langle x\hat{p} \rangle(0)$;

$$[-\omega^2 - i\omega D + \tilde{c}^2 - i\omega \delta D(\omega)] C_{xx} = \text{I.H.} , \quad (\text{A7})$$

where $\delta D = \mathcal{F}(\Theta(t-t') \Sigma_{\hat{p}\hat{p}}(t-t'))$ picks out the retarded piece of $\Sigma_{\hat{p}\hat{p}}$ as explained above, and the inhomogeneous term (I.H.) results from the elimination of $\langle x\hat{p} \rangle(\omega)$. The renormalized static susceptibility is denoted by \tilde{c}^{-2} , and I.H. just enforces the boundary conditions on C_{xx} , i.e., $C_{xx}(0) = \tilde{c}^{-2}$, $dC_{xx}(0)/dt = 0$.

To examine the self-energy to higher order (e.g., Fig. 1) in the "glass" limit we found it easier to retain $\Sigma(\langle xx \rangle, \langle x\hat{p} \rangle)$ and use (14) in place of (10). Clearly, in $\Sigma_{\hat{p}\hat{p}}$, every interior vertex brings in one \hat{p} and hence one $\langle x\hat{p} \rangle$ line as well as one time integral.

The reduction from (7) to (13) is also easy to see in the

large D limit. For $\langle x\hat{p} \rangle$ in (A2), we have

$$\langle x\hat{p} \rangle \approx \frac{D^{-1}}{-i\omega + c^2/D} ,$$

and we identify $\epsilon = c^2/D$ and reduce the weight by f to recover (14b). The diagrams for (13) are generated from

$$\hat{H} = -\frac{1}{D} \hat{x} u'(x) = \hat{x} \zeta .$$

There is no "Jacobian term" if we are careful about the order of \hat{x} and u' . In Σ for (7), $\langle x\hat{p} \rangle$ is replaced by $\langle x\hat{x} \rangle$.

There is a natural correspondence between (1a) and (1b) as a function of wave number and (7). Specifically,

$$X = \rho, \quad P = -ik \cdot g, \quad \eta = k^2 \eta ,$$

$$C^2 = k^2 c^2, \quad D = k^2 D, \quad U_n = k^2 u_n ,$$

where capitals on the left-hand sides are used to rewrite (1) in the form of (7). To verify the fluctuation-dissipation relation, observe that

$$\chi_{\rho\rho}(k, \omega) = k^2 \langle X\hat{P} \rangle .$$

Furthermore, all the k dependence on the vertices is associated with \hat{P} and thus always occurs in the combination $k^2 \langle X\hat{P} \rangle$. Therefore, $\Sigma(\chi_{\rho\rho}, \langle \rho\rho \rangle)$ is identical to what one would obtain from (7) using the analogous variables. Note that the exterior factors of k work out properly, a k^2 from $\Sigma_{\hat{p}x}$ to be combined with $-D\nabla^2$ in (1b) and a k^4 from $\Sigma_{\hat{p}\hat{p}}$ to add to $2Dk^4$ in the numerator of $\langle PP \rangle$. Equation (9) remains unchanged save for a convolution in wave number since (4a) and (4b), which relate $\chi_{\rho\rho}$ and $\langle \rho\rho \rangle$ to $C_{\rho\rho}$, are identical to the corresponding relations for (7) with x replacing ρ .

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