

Mode-coupling theory of the glass transition

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The mode-coupling theory of the glass transition recently presented by Leutheusser is generalized so that some of the important wave-number dependence neglected in his theory is taken into account. As a consequence the correlation functions which appear in the theory presented here involve a continuous range of relaxation times rather than the single relaxation time obtained by Leutheusser. However, the important exponents describing the divergence in the shear viscosity and the vanishing of the self-diffusion coefficient are very similar in the two theories.

I. INTRODUCTION

In a recent series of papers, Leutheusser^{1,2} and Leutheusser and Yip³ discussed the glass transition in simple liquids, using a self-consistent mode-coupling theory. They find, for example, that near the glass transition density n_g , the shear viscosity η diverges as $\eta \sim (n_g - n)^{-1.765}$, with n the number density. It should be remarked that this power-law singularity is different than the usually assumed Doolittle form,⁴ but that it is consistent with computer simulations of the hard-sphere glass transition.⁵

Leutheusser bases his analysis on a model whose structure he derives from the mode-coupling theory. Although he states that it is intermediate wave-number phenomena that cause the slowing down of dynamical processes near n_g , he neglects all wave-number dependence in his model equation. As a consequence of this he finds that the time dependence of, e.g., the stress-tensor correlation function is given by a simple exponential. Leutheusser argues that his results can be used to explain recent computer simulation^{6,7} of the stress-tensor correlation function that seem to indicate an algebraic decay with a coefficient much larger than the usual long time tail for this function. More recently⁸ this slowly decaying correlation function has been discussed on the basis of mode-coupling theory generalized to molecular length scales so that structural relaxational effects can be taken into account. In these theories the wave-number dependence plays an important role and it leads to a continuum of relaxation times.

The question then naturally arises whether Leutheusser's results are sensitive to the wave-number coupling and the continuum of relaxation times inherent in any true mode-coupling theory. In this paper this question is addressed. In particular, we extend the mode-coupling theory used previously to discuss the slowly decaying stress-tensor correlation function. The theory is made self-consistent and the resulting nonlinear equation is assumed to describe the glass transition. Retaining what we believe is the important wave-number dependence in the theory we calculate the exponents that describe the divergence in η near n_g and the vanishing of D , the self-diffusion coefficient, near n_g . Although the correlation functions encountered in the theory are con-

siderably different than in Leutheusser's theory, the relevant exponents are changed by less than 10%. This is an important point since it implies that the exponents are insensitive to the approximations made in the two theories.

The organization of this paper is as follows. In Sec. II the basic equations that will be used to describe the glass transition are derived. In Sec. III we calculate exponents describing the divergence in the shear viscosity near n_g , and the vanishing of the self-diffusion coefficient near n_g , and the vanishing of the neutron scattering linewidth near n_g . In Sec. IV this paper is concluded with some remarks.

II. BASIC EQUATIONS

The basic equations used to describe the glass transition can be derived from hydrodynamic mode-coupling theory⁹⁻¹² or from diagrammatic hard-sphere kinetic theory.^{13,14} Since the hydrodynamic theory is the simplest, I will outline that theory here. The basic idea is to recognize that in a dense fluid the dynamics on a molecular length scale slow down appreciably due to the microscopic structure in a dense liquid.¹⁵⁻¹⁸ In particular, it is known that at wave number near k_0 , where the static structure factor has its first maximum, the density-density correlation function (DDCF) decays very slowly even in the absence of mode-coupling effects.^{15,16} It is also known that when mode-coupling effects are taken into account the DDCF becomes even slower, decaying near k_0 .¹⁹ Since mode-coupling effects themselves depend on the DDCF it is this nonlinearity, or feedback mechanism, that we assume leads to the glass transition where the dynamical processes become frozen. Later on we show how the slowing down near k_0 effects the macroscopic, zero frequency, and zero wave number, transport coefficients.

To proceed, I first define a normalized DDCF, Φ_{kz} , for wave numbers k and Laplace transform variable z by

$$\Phi_{kz} = \int_0^\infty dt e^{-zt} \frac{1}{ns(k)\Omega} \left\langle \sum_i e^{-ik \cdot r_i} \sum_j e^{ik \cdot r_j(t)} \right\rangle, \quad (1)$$

where Ω is the volume of the fluid, $s(k)$ is the static structure factor, \mathbf{r}_i is the position of the i th particle, and the angular brackets denote a grand canonical ensemble average. Using the number and momentum conservation laws^{10,18}—here we neglect temperature fluctuations which are known to be small on molecular length scales²⁰—we easily obtain that Φ_{kz} is given by

$$\Phi_{kz} = \frac{1}{z + k^2/\beta ms(k)[z + k^2 D_l(k, z)]} \quad (2)$$

Here m is the mass of the particles, $\beta = (k_B T)^{-1}$ with k_B Boltzmann's constant and T the temperature, and $D_l(k, z)$ is the generalized, k and z dependent, longitudinal viscosity.

Next an approximate expression for $D_l(k, z)$ is obtained. We write

$$k^2 D_l(k, z) = \gamma(k, z) + \Sigma(k, z) \quad (3a)$$

Here $\gamma(k, z)$ is the bare contribution to $k^2 D_l(k, z)$, where mode-coupling effects are neglected and $\Sigma(k, z)$ is the mode-coupling contribution to $k^2 D_l(k, z)$ which itself depends on Φ_{kz} . For $\gamma(k, z)$ we use the short-time approximation for the longitudinal viscosity for particles interacting through a hard-sphere potential. It will be seen in the following that the behavior of the fluid near the glass transition is not sensitive to the particular model used for $\gamma(k, z)$. For hard spheres I obtain²¹

$$\gamma(k, z) = \gamma(k) = \frac{2}{3t_E} [1 - j_0(k\sigma) + 2j_2(k\sigma)] \quad (3b)$$

$$\Sigma(kz) = \int_{c-i\infty}^{c+i\infty} \frac{dz_1}{2\pi i} \int_0^\infty dq \int_{-1}^{+1} d\mu V(q, k, \mu) \frac{1}{\{z_1 + [\Omega^2(q_+)]/\Gamma(q_+, z_1)\} \{z - z_1 + [\Omega^2(q_-)]/\Gamma(q_-, z - z_1)\}} \quad (5a)$$

where c defines the contour of the z_1 integral and

$$q_\pm = (q^2 \pm kq\mu + k^2/4)^{1/2} \quad (5b)$$

$V(q, k, \mu)$ is a vertex function that is determined from wave-number-dependent mode-coupling amplitudes and it is given by

$$V(q, k, \mu) = \frac{q^2 k^2 s(q_+) s(q_-)}{2n(2\pi)^2 \beta m} \left[\left[\frac{1}{2} + \frac{q\mu}{k} \right] nc(q_+) + \left[\frac{1}{2} - \frac{q\mu}{k} \right] nc(q_-) + n^2 c(q, k, \mu) \right]^2 \quad (5c)$$

In Eq. (5c), $c(q)$ is the direct correlation function and $c(\mathbf{q}_-, \mathbf{q}_+) \equiv c(q, k, \mu)$ is the three-particle direct correlation function. This same result can also be derived from kinetic theory.¹⁴

III. CALCULATION OF EXPONENTS

Since this section is lengthy we first give an outline of its content. First Eqs. (4) and (5) are simplified so that an

with t_E the Enskog mean free time, σ the hard-sphere diameter, and j_l the spherical Bessel function of order l . Before giving $\Sigma(k, z)$, I use that we are interested in the long-time or small- z behavior of the DDCF and I replace Eq. (2) by

$$\Phi_{kz} = \frac{1}{z + \Omega^2(k)/[\gamma(k) + \Sigma(k, z)]} \equiv \frac{1}{z + \Omega(k)^2/\Gamma(k, z)} \quad (4a)$$

with

$$\Omega^2(k) \equiv \frac{k^2}{\beta ms(k)} \quad (4b)$$

and

$$\Gamma(k, z) \equiv \gamma(k) + \Sigma(k, z) \quad (4c)$$

This is especially appropriate near n_g since $\Gamma(k, z)$ will be shown to diverge in the limit $n \rightarrow n_g$. Finally, it should be remarked that if I neglect Σ in Eq. (4) and use Eq. (3), then I obtain a representation for Φ_{kz} almost identical to that obtained before by de Schepper and Cohen¹⁶ on the basis of kinetic theory. In their language, $\Omega^2(k)/\gamma(k)$ is the extended heat-mode eigenvalue which follows here from very simple considerations.

The mode-coupling contribution to the longitudinal viscosity, $\Sigma(k, z)$, can be calculated in the standard way.⁹⁻¹² Using that is is density fluctuations that decay the slowest near n_g we easily obtain

analytic treatment of the glass transition is possible. Then an equation for n_g is obtained by assuming that at the glass transition there is localized behavior.²² When such a solution first occurs then we identify this point with the glass transition and obtain an equation for n_g . After this, the corrections to the leading singularity at n_g will be calculated. Later on these corrections will determine the scaling form for $\Gamma(z)$ when $n < n_g$.

Next densities below the glass transition are considered. By using a simple scaling ansatz and the results of the calculation at n_g we determine the singular behavior of $\Gamma(k, z)$ for $n \rightarrow n_g$ near $k \simeq k_0$. Finally, we show how the singularities near k_0 determine the singularities in the macroscopic transport coefficients near n_g .

Equations (4) and (5) give a highly nonlinear equation for $\Sigma(k, z)$ which is not easily solved. To proceed we make a number of approximations that enable us to extract the singular behavior of $\Sigma(k, z)$ at and near n_g . We first replace $\Gamma(k)$ and $\Gamma(q_\pm)$ in Eqs. (4) and (5) by $\Gamma(k_0)$. This approximation is motivated by the fact that it is the wave-number dependence in Ω^2 that is important in producing the de Gennes minimum¹⁵⁻¹⁷ observed in neutron scattering in dense fluids for wave numbers around k_0 . We then obtain

$$\Gamma(k_0, z) \equiv \Gamma(z) = \gamma(k_0) + \int_{c-i\infty}^{c+i\infty} \frac{dz_1}{2\pi i} \int_0^\infty dq \int_{-1}^{+1} d\mu \frac{V(q, k_0, \mu)}{\{z_1 + [\Omega^2(q_+)] / [\Gamma(z_1)]\} \{z - z_1 + [\Omega^2(q_-)] / [\Gamma(z - z_1)]\}} \quad (6)$$

with $q_\pm = q^2 \pm k_0 q \mu + k_0^2 / 4$.

This is the most important simplification since the unknown, Γ , no longer depends on wave number. The next approximation uses that the largest contribution to the integrals in Eq. (6) for small z comes from the region where $q \simeq q_0 = \sqrt{3}/2 k_0$ and μ is close to zero. Using that $V(q_0, k_0, \mu)$ has a maximum²³ at $\mu = 0$, we approximate Eq. (6) by²⁴

$$\begin{aligned} \Gamma(z) &\simeq \gamma(k_0) + \int_{c-i\infty}^{c+i\infty} \frac{dz_1}{2\pi i} \int_0^\infty dq \frac{\bar{V}(q_0, k_0)}{\{z_1 + [\Omega^2(\sqrt{q^2 + k_0^2}/4)] / [\Gamma(z_1)]\} \{z - z_1 + [\Omega^2(\sqrt{q^2 + k_0^2}/4)] / [\Gamma(z - z_1)]\}} \\ &\simeq \gamma(k_0) + \frac{2}{\sqrt{3}} \bar{V} \left[\frac{\sqrt{3}}{2} k_0, k_0 \right] \int_{c-i\infty}^{c+i\infty} \frac{dz_1}{2\pi i} \int_{-\infty}^{+\infty} dx \frac{1}{\{z_1 + [\Omega^2(k_0)] / [\Gamma(z_1)] + [x^2 \Omega^{2''}(k_0)] / [2\Gamma(z_1)]\}} \\ &\quad \times \frac{1}{\{z - z_1 + [\Omega^2(k_0)] / [\Gamma(z - z_1)] + [x^2 \Omega^{2''}(k_0)] / [2\Gamma(z - z_1)]\}} \end{aligned} \quad (7a)$$

with

$$\bar{V}(q, k_0) = \int_{-1}^{+1} d\mu V(q, k_0, \mu), \quad (7b)$$

and we have used that $\Omega^2(q)$ has a strong minimum around k_0 . The x integral in Eq. (7a) is elementary,

$$\begin{aligned} \Gamma(z) &= \gamma(k_0) + \frac{4\pi}{\sqrt{6}} \frac{\bar{V} \left[\frac{\sqrt{3}}{2} k_0, k_0 \right]}{[\Omega^{2''}(k_0)]^{1/2}} \int_{c-i\infty}^{c+i\infty} \frac{dz_1}{2\pi i} \frac{\Gamma(z_1) \Gamma(z - z_1)}{[(z - z_1) \Gamma(z - z_1) - z_1 \Gamma(z_1)]} \\ &\quad \times \frac{1}{[\Omega^2(k_0) + z_1 \Gamma(z_1)]^{1/2}} \left[1 - \left[1 + \frac{(z - z_1) \Gamma(z - z_1) - z_1 \Gamma(z_1)}{\Omega^2(k_0) + z_1 \Gamma(z_1)} \right]^{-1/2} \right]. \end{aligned} \quad (8)$$

The structure of Eq. (8) is now simple enough for us to analytically derive the singular behavior of $\Gamma(z \rightarrow 0)$ at n_g , obtain an implicit equation for n_g , and derive an exponent for the divergence in $\Gamma(z = 0)$ as $n \rightarrow n_g$.

A. At the glass transition

To motivate the approximate solution to Eq. (8) at n_g , we note that at the glass transition localized behavior²² can be expected. This implies that $\Gamma(z)$ should have the form

$$\Gamma(z) = \frac{a}{z} + \Gamma_v(z) \quad (9)$$

with $z\Gamma_v(z) \rightarrow 0$ for $z \rightarrow 0$. This form also follows mathematically from Eq. (8). If we insert Eq. (9) into Eq. (4a) then we see that at n_g part of Φ_{kz} will not decay in time and the dynamic structure factor will have a delta function peak. Inserting Eq. (9) into Eq. (8) we can systematically solve Eq. (8) by treating $z\Gamma_v(z)$ as small. To zeroth order in Γ_v , we obtain

$$\frac{a}{z} = \frac{2\pi}{\sqrt{6}} \frac{\bar{V} \left[\frac{\sqrt{3}}{2} k_0, k_0 \right]}{[\Omega^{2''}(k_0)]^{1/2}} \frac{a^2}{[a + \Omega^2(k_0)]^{3/2}}$$

$$\times \int_{c-i\infty}^{c+i\infty} \frac{dz_1}{2\pi i} \frac{1}{z_1(z - z_1)}, \quad (10)$$

which yields an equation for a since Eq. (9) is a physical solution only when a is real and positive. We can use Eq. (10) to obtain an equation for n_g . The implicit equation for n_g is straightforwardly found to be given by

$$\frac{2\pi}{\sqrt{6}} \frac{\bar{V} \left[\frac{\sqrt{3}}{2} k_0, k_0; n_g \right]}{[\Omega^{2''}(k_0; n_g)]^{1/2}} = \frac{\sqrt{27}}{2} [\Omega^2(k_0; n_g)]^{1/2}, \quad (11a)$$

and at n_g , $a (\equiv a_g)$ is given by

$$a_g = 2\Omega^2(k_0; n_g). \quad (11b)$$

The leading behavior of the less singular term, $\Gamma_v(z)$, can be determined by expanding Eq. (8) to second order in Γ_v . The first-order terms on the right-hand and left-hand sides cancel as they must. The resulting equation for $\Gamma_v(z)$ is

$$\frac{8}{5} z \Gamma_v^2(z) = \int_{c-i\infty}^{c+i\infty} \frac{dz_1}{2\pi i} \Gamma_v(z_1) \Gamma_v(z - z_1), \quad (12a)$$

which has a solution of the form,

$$\Gamma_v(z) = \frac{A}{z^{1-\alpha}}. \quad (12b)$$

Inserting Eq. (12b) into Eq. (12a) yields an equation for α given by

$$\frac{8}{5}\hat{\Gamma}^2(1-\alpha)=\hat{\Gamma}(1-2\alpha), \quad (12c)$$

with $\hat{\Gamma}(x)$ the gamma function of order x . Equation (12c) is a transcendental equation which can be solved,

$$\alpha \simeq 0.36. \quad (12d)$$

Using Eqs. (9)–(12) in Eq. (4a) yields the DDCF at n_g when k is near k_0 ,

$$\Phi_{kz} = \frac{1}{z\{1+[k^2s(k_0)]/[2k_0^2s(k)]\}} + O\left[\frac{1}{z^{1-\alpha}}\right]. \quad (13)$$

B. Below the glass transition ($n < n_g$)

To solve Eq. (8) for $n < n_g$, a scaling assumption will be used. Since at n_g , $\Gamma(z)$ consists of a most singular (s) and a less singular (v) contribution, our scaling assumption is

$$\begin{aligned} \Gamma(z) &= \frac{1}{z}d_s(\delta/z) + \frac{1}{z^{1-\alpha}}\tilde{d}_v(s/z) \\ &= \frac{1}{z}d_s(\delta/z) + s^{\alpha-1}d_v(z/s). \end{aligned} \quad (14a)$$

Here δ and $s \rightarrow 0$ as $n \rightarrow n_g$ and

$$d_s(0) = a_g, \quad \tilde{d}_v(0) = A. \quad (14b)$$

Furthermore, we expect $\delta \ll s$ as $n \rightarrow n_g$ since at high frequencies the most singular part of Γ should rapidly approach its value at n_g since on short-time scales the undercooled liquid is glasslike. This will also follow mathematically. It should also be remarked that the simple pole form for the most singular part of Γ assumed by Leutheusser^{1,2} can easily be shown not to be consistent with Eq. (8). Finally, it should be remarked that δ^{-1} and s^{-1} are not relaxation times but rather time scales for the continuum of relaxation times inherent in any mode-coupling theory.

$$X_{(3)} \sim O\left[s^{2\alpha-2} \int_{c-i\infty}^{c+i\infty} \frac{dz_1}{2\pi i} d_v(z_1/s) d_v((z-z_1)/s), s^{\alpha-2} \delta d_v(z/s)\right]. \quad (18)$$

Scaling z (and z_1) with s we see that $X_{(3)}$ and $X_{(1)}$ correctly scale and that $X_{(2)}$ is negligible if

$$s \simeq \epsilon^{1/2\alpha} = (n_g - n)^{1/2\alpha} \simeq (n_g - n)^{1.39} \quad (19a)$$

and

$$\delta \sim \epsilon^{(1+\alpha)/2\alpha} = (n_g - n)^{(1+\alpha)/2\alpha} \simeq (n_g - n)^{1.89}. \quad (19b)$$

In the next section it will be shown that δ determines the singularity in the zero frequency viscosity and diffusion coefficient as $n \rightarrow n_g$.

In this section we use Eq. (14a) in Eq. (8) and determine the exponents which describe how δ and s vanish as $n \rightarrow n_g$. The basic idea is to use Eq. (14) in Eq. (8) for values of z such that

$$\delta \ll |z| \ll s^{1-\alpha}, \quad (15a)$$

so that we can write

$$\begin{aligned} \Gamma(z) &\cong \frac{d_s(0)}{z} + \frac{\delta}{z^2} d'_s(0) + s^{\alpha-1} d_v \left[\frac{z}{s} \right] \\ &= \frac{a_g}{z} + \frac{\delta}{z^2} d'_s(0) + s^{\alpha-1} d_v \left[\frac{z}{s} \right]. \end{aligned} \quad (15b)$$

With this assumed scaling form, Eq. (8) will be shown to lead to values for δ and s .

Inserting Eq. (15b) in Eq. (8) and expanding terms to $O(\delta, d_v^2)$ yields an equation from which we can determine δ and s . Since the equation is rather lengthy we will not reproduce here but only discuss its structure. If we denote the terms which are independent of δ and d_v by $X_{(1)}$ then we find that they are of order

$$X_{(1)} \sim O\left[\frac{\epsilon}{z}\right] \quad (16a)$$

with

$$\epsilon = n_g - n. \quad (16b)$$

This follows, since these terms precisely cancel at n_g and if we expand \bar{V} , etc., around n_g then we obtain Eq. (16). If we denote the terms of $O(\delta d_v^0, d_v)$ by $X_{(2)}$, then we obtain

$$X_{(2)} \sim O\left[\frac{\delta \epsilon}{z^2}, s^{\alpha-1} \epsilon d_v(z/s)\right]. \quad (17)$$

The ϵ arises as for term $X_{(1)}$ since these terms also cancel at n_g . We shall show below that term $X_{(2)}$ is negligible. The terms of $O(\delta d_v, d_v^2)$ are denoted by $X_{(3)}$ and to leading order in ϵ they are of the form

C. Macroscopic transport coefficients

Here we show how the singularity in Γ leads to a singularity in, for example, the zero-frequency shear viscosity. The basic idea is that through mode coupling, the effects that occur on one length scale, here k_0^{-1} , couple back and effect phenomena on all length scales. That is, η has contributions from all length scales. For example, the relevant mode-coupling contribution to the shear viscosity can be written

$$\eta = \eta_B + \int_0^\infty dq \int_{-1}^{+1} d\mu V_\eta(q, \mu) \lim_{z \rightarrow 0} \int_{c-i\infty}^{c+i\infty} \frac{dz_1}{2\pi i} \frac{1}{[z_1 + \Omega^2(q)/\Gamma(z_1)][z - z_1 + \Omega^2(q)/\Gamma(z - z_1)]}. \quad (20)$$

Here $V_\eta(q, \mu)$ is the positive definite shear viscosity vertex function that is given elsewhere,^{8,11} η_B is the bare viscosity, and we have used that the most important mode coupling is coupling to density fluctuations since they are singular as $n \rightarrow n_g$. Using Eqs. (14) and (19) in Eq. (20) and scaling z_1 with δ yields

$$\eta \sim \frac{1}{\delta} \text{ as } n \rightarrow n_g. \quad (21)$$

Similarly one can show

$$D \sim \delta \text{ as } n \rightarrow n_g. \quad (22)$$

IV. DISCUSSION

We conclude this paper with a few remarks.

(1) In this paper we have taken into account some of the wave-number dependence Leutheusser neglected in his theory of the glass transition. Although the correlation functions in the two theories are qualitatively different—in the theory presented here there is a continuous range of relaxation times—the important exponents describing the singularities in the transport coefficients are very similar, i.e., the difference in the exponents is less than 10%. This implies that the actual exponents may not be too sensitive to the approximation made in calculating them.

It should be stressed, however, that the description of the glass transition is not universal as in critical phenomena and will in general be sensitive to the type of approximations made. Physically this is obvious since the basic phenomena that cause the glass transition take place on a molecular length scale and not on the very long length scale typical for critical phenomena where universal behavior is expected.

Finally, we mention that the vertex functions that appear in the theory presented here are different than those referenced by Leutheusser.¹ This point has been discussed elsewhere.⁸

(2) The theory of the glass transition presented here is probably only correct for simple liquids—which usually do not form glasses in the laboratory²⁵—where translational diffusion plays the dominant role. In glass forming molecular liquids one anticipates that fluctuations in the orientational order slow down long before fluctuations in the translational order. It would be of interest to capture the essence of this orientational order in some kind of self-consistent mode-coupling theory.

(3) There are computer simulations⁵ of, for example, a

hard-sphere fluid near its glass transition. In these simulations the ratio D/D_E has been measured, where D_E is the Enskog self-diffusion coefficient. The extraction of a reliable critical exponent is difficult since the theory presented here and by Leutheusser is only valid when $D/D_E \ll 1$, where only a limited amount of computer data is available. However, if one fits the decrease in D/D_E to a power law decrease than for small values of D/D_E an exponent between 1.5 and 2 is found to be consistent²⁶ with the computer data.

We also mention here that there have been computer simulations^{27,28} of the linewidth of the dynamic structure factor in undercooled liquids at wave numbers close to k_0 . It is found that the linewidth appears to be a decreasing function that is linear in $(n^* - n)$, where n^* is some physically irrelevant density that does *not* correspond to the glass transition density. This indicates that these simulations are not yet in the region close enough to n_g for the theory presented here to be valid. This is consistent with the fact that Eq. (4a) with Σ set equal to zero leads—over a limited density range—to a linear decreasing function of density for the neutron scattering linewidth near k_0 that extrapolates to zero also at a physically irrelevant density.²⁹

(4) It should be remarked that [cf. Eq. (4)] $\Omega^2(k)/\Gamma(k, z)$ is not a soft mode in the sense discussed some time ago by several authors.^{17,30} The slowing down of dynamical processes near k_0 is a general consequence that all dynamical processes are slowing down as $n \rightarrow n_g$. We take the point of view here that since $\Omega^2(k)/\Gamma(k)$ around k_0 is already almost a soft mode, the general slowing down as $n \rightarrow n_g$ is most effectively coupled to wave numbers near k_0 . This is confirmed¹⁹ by a perturbative solution of Eq. (5a).

(5) The theory of the glass transition for simple liquids presented here is a purely dynamical transition with equilibrium correlation functions playing only a minor role. In this sense the transition is very similar to the Anderson transition³¹ where the relevant order parameter is essentially the diffusion coefficient.

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- ²¹To derive Eq. (3b) one should use the collision operators that generate hard-sphere dynamics. See M. H. Ernst, J. R. Dorfman, W. Hogey, and J. M. J. van Leeuwen, *Physica* **45**, 127 (1969).
- ²²By localized behavior we mean that the DDCF does not decay in time and in real space a density fluctuation is localized in space.
- ²³To verify this I have used the Kirkwood superposition approximation for $c(q, k, \mu)$ and the Percus-Yerick representation for $c(q)$. I would like to thank J. Niewoudt for his assistance with this check.
- ²⁴The logic used here is that we have a two-dimensional integral over a product of two functions, the propagators and $V(q, k_0, \mu)$, both of which have maximums at $q = q_0$ and $\mu = 0$. We then simplify the two-dimensional integral to a product of one-dimensional integrals by using that the propagators are peaked about $q = q_0$ to replace $V(q, k_0, \mu)$ by $V(q_0, k_0, \mu)$, and that $V(q_0, k_0, \mu)$ has a maximum at $\mu = 0$ to replace the propagators by their value at $\mu = 0$. By considering simple model integrals one can convince oneself that this is not an unreasonable approximation.
- ²⁵See, for example, C. A. Angell, J. H. R. Clarke, and L. V. Woodcock, *Adv. Chem. Phys.* **48**, 398 (1981).
- ²⁶A best fit to the available experimental data yields an exponent of 1.86. R. Zwanzig (private communication).
- ²⁷R. D. Mountain, *Phys. Rev. A* **26**, 2859 (1982).
- ²⁸R. D. Mountain and P. K. Basu, *Phys. Rev. A* **28**, 370 (1983).
- ²⁹See also, I. M. de Schepper, E. G. D. Cohen, and M. J. Zuilhot, *Phys. Lett.* **101A**, 399 (1984).
- ³⁰T. Schneider, R. Brout, H. Thomas, and J. Feder, *Phys. Rev. Lett.* **25**, 1423 (1970); T. Schneider, *Phys. Rev. A* **3**, 2145 (1971).
- ³¹For a review of Anderson localization, see *Anderson Localization*, edited by Y. Nagoaka and H. Fukugoma (Springer, Berlin, 1982).