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Mode-coupling theory of the large long-time tails in the stress-tensor autocorrelation function

T. R. Kirkpatrick
Department of Physics and Astronomy and Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742

J. C. Nieuwoudt
Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742

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A generalized mode-coupling theory that takes into account molecular-scale effects is presented. Thermodynamic as well as dissipative nonlinearities are included. The theory is used to calculate molecular-scale renormalizations or mode-coupling contributions to the zero-wave-number shear viscosity and to the time-dependent stress-tensor autocorrelation function. For a range of times the theory leads to a stress-tensor autocorrelation function that appears to decay as $t^{-3/2}$. The results are in reasonable agreement with computer simulations.

I. INTRODUCTION

Recent simulations[1,2] of molecular dynamics in dense simple classical liquids have shown that the equilibrium stress-tensor autocorrelation function (STCF) decays very slowly for long times. The decay appears to follow a $t^{-3/2}$ law, where t is the time. This functional form can be easily derived from conventional mode-coupling theory[3] but the theoretical coefficient of this long-time tail is approximately 500 times smaller than the observed coefficient.

There are indications[2] that the computer simulations have not yet reached the asymptotic long-time limit where conventional mode coupling is applicable. The velocity autocorrelation function (VACF) is still negative in the time region where most of the data are taken to support a $t^{-3/2}$ tail in the STCF. For these intermediates times it is clear that the VACF has not yet reached its asymptotic positive long-time tail. We also note that although the conventional long-time tails are determined by long-wavelength effects, the intermediate-time behavior of time correlation functions is expected to be determined by intermediate or finite-wave-number effects.

van Beijeren[4] and Kirkpatrick[5] have recently studied intermediate length scale contributions to the STCF. van Beijeren used hard-sphere kinetic theory to obtain an expression for the intermediate length scale contributions to the STCF but he did not evaluate his results. He stressed the importance of retaining what in kinetic theory language is the kinetic part of the intermediate length scale extended hydrodynamic modes. Kirkpatrick also did a kinetic theory analysis but he neglected the kinetic parts of the hydrodynamic modes. It was shown[5] that this is equivalent to using Kadanoff-Swift mode-coupling theory[3,6] at finite wave numbers. Kirkpatrick's final results were easily evaluated and he obtained a STCF that appeared to decay at $t^{-3/2}$ in the time region considered in the simulations. His theoretical results were in qualitative agreement with the computer simulations at the longest times but at shorter times his coefficient was approximately two times too large.[4]

In this paper we use another type of generalized (to include finite-wave-number effects) mode-coupling theory and calculate the frequency-dependent shear viscosity, or STCF. The theory presented here partially accounts for the discrepancy found earlier by Kirkpatrick.

The usual long-time tails are due to the fact that in a fluid the five conserved densities are slowly varying at small wave numbers. The basic idea used here is that in a dense fluid the number-density fluctuations also vary at wave numbers k near where the static structure factor $S(k)$ has its maximum.[7-11] Physically one can interpret this slow relaxation on a molecular scale as being due to structural relaxation. We use nonlinearities and this slowly varying dynamical variable to renormalize the shear viscosity in the usual way.[3]

The theory given here is based on nonlinear generalized fluctuating hydrodynamic equations. It is an improvement over the previous Kadanoff-Swift-type mode-coupling theories because dissipative nonlinearities as well as thermodynamic nonlinearities are taken into account. The effects of dissipative nonlinearities are not included in the Kadanoff-Swift approach. This can be justified when calculating long-wavelength effects. For finite wave numbers, however, we show that there is a mechanism by which they become important and that they can be used to partially account for the discrepancy discussed above. Further, the dissipative nonlinearities can be related to the kinetic parts of the hydrodynamic modes discussed by van Beijeren.[4]

The calculations presented here may also have important implications for the recent dynamical theories of the glass transition.[12-15] This point will be discussed in Sec. IV.

The organization of this paper is as follows. In Sec. II the basic theory used here is outlined. In the linear approximation we first calculate the slowly decaying density fluctuations on a molecular scale. We then use the nonlinearities in our hydrodynamic equations to obtain a formal expression for the renormalized shear viscosity. In Sec. III we give explicit but approximate results for the STCF for hard-sphere fluids. The main approximation is in identifying and evaluating the nonlinear and nonlocal dissipative coupling constant. In Sec. IV we conclude by discussing our results and also by making some additional remarks about the connections to previous theories.

II. THEORY

A. Nonlinear generalized hydrodynamic equations

To begin we write down a set of hydrodynamic equations that have the same structure for both small and intermediate [$\equiv k_0$, where $S(k)$ has its maximum] wave numbers. We neglect temperature fluctuations since they play no role in the renormalization discussed below. Further, it is known that they do not play an important role in determining the slowly decaying density fluctuations on a molecular scale.[10,11,16] It is also known that only the number-density fluctuations are slowly varying on a molecular scale.[16] The generalized equations for the number density $n(\mathbf{x},t)$ and the momentum density $\mathbf{g}(\mathbf{x},t)$ are[17,18]

$$\partial_t n(\mathbf{x},t)+\frac{1}{m}\nabla\cdot\mathbf{g}(\mathbf{x},t)=0 \tag{2.1a}$$

and

$$\begin{aligned}\partial_t g_\alpha(x,t)+\frac{\partial}{\partial x_\beta}\frac{g_\alpha(\mathbf{x},t)g_\beta(\mathbf{x},t)}{mn(\mathbf{x},t)}&=-n(\mathbf{x},t)\frac{\partial}{\partial x_\alpha}\frac{\delta F'[n(t)]}{\delta n(\mathbf{x},t)}\\&\quad-\int d\mathbf{x}_1\Gamma_{\alpha\beta}(\mathbf{x},\mathbf{x}_1;n(t))\frac{\delta F}{\delta g_\beta(\mathbf{x}_1,t)}+f_\alpha(\mathbf{x},t)\end{aligned} \tag{2.1b}$$

with $F'[n(t)]$ the free energy for an inhomogeneous equilibrium fluid minus its kinetic-energy contribution,[19]

$$\begin{aligned}\frac{\delta F'[n(t)]}{\delta n(\mathbf{x},t)}=k_BT\Big[&\ln n(\mathbf{x},t)-\int d\mathbf{x}'C(\mathbf{x}-\mathbf{x}')\delta n(\mathbf{x}',t)\\&-\tfrac{1}{2}\int\int d\mathbf{x}'d\mathbf{x}''C_3(\mathbf{x},\mathbf{x}',\mathbf{x}'')\\&\times\delta n(\mathbf{x}',t)\delta n(\mathbf{x}'',t)-\cdots\Big]\,,\end{aligned} \tag{2.1c}$$

and

$$F=\int d\mathbf{x}\frac{g^2(\mathbf{x},t)}{2mn(\mathbf{x},t)}+F'[n(t)]\,, \tag{2.1d}$$

and $f_\alpha(\mathbf{x},t)$ is a Gaussian random force[17] given by the fluctuation dissipation theorem. Here m is the mass of a particle, k_B is Boltzmann's constant, T is the temperature, $\delta n(\mathbf{x},t)=n(\mathbf{x},t)-n_0$, with n_0 the equilibrium density, $C(\mathbf{x}-\mathbf{x}')$ is the equilibrium two-particle direct correlation function, $n_0C(q)=1-1/S(q)$, C_3 is the three-particle direct correlation function, and we have neglected higher-order nonlinearities in Eq. (2.1c).

We next discuss the validity of these equations. We first remark that their form follows from general considerations[17] if temperature fluctuations and non-Markovian effects are neglected. The free energy given by Eq. (2.1c) is the exact expansion of the free energy for an inhomogeneous equilibrium liquid. To complete our equations we need to specify the bare nonlinear dissipative kernel $\Gamma_{\alpha\beta}(\mathbf{x},\mathbf{x}_1;n(t))$. In the long-wavelength limit $\Gamma_{\alpha\beta}$ reduces to the usual combinations of gradients and bare shear and bulk viscosities. For intermediate wave numbers the form of $\Gamma_{\alpha\beta}$ will be more model dependent. We first consider the linear kernel $\Gamma_{\alpha\beta}(\mathbf{x},\mathbf{x}_1;n_0)=\Gamma^0_{\alpha\beta}(\mathbf{x},\mathbf{x}_1)$, or its Fourier transform,

$$\Gamma^0_{\alpha\beta}(\mathbf{k})=\int d\mathbf{x}\,e^{-i\mathbf{k}\cdot\mathbf{x}}\Gamma^0_{\alpha\beta}(\mathbf{x})\,. \tag{2.2}$$

For wavelengths on the order of a molecular diameter σ (or $k\simeq k_0$) we expect $\Gamma^0_{\alpha\beta}(\mathbf{k})/mn_0$ to be only weakly k dependent and on the order of τ^{-1}, with τ the mean free time between collisions, which is very small for liquid-state densities. This follows since on this scale fluid momentum approximately behaves as tagged-particle momentum and acts as though it were not a conserved quantity. In wave-number space we expect $\mathbf{g}(\mathbf{k},\mathbf{t})$ to approximately satisfy a relaxation-type equation. For our explicit calculations we consider only hard-sphere fluids. For this case, a very simple and accurate (for the densities we consider) calculation for $\Gamma^0_{\alpha\beta}(\mathbf{k})$ near k_0 can be performed[10,11] with the result

$$\frac{\hat{\mathbf{k}}\cdot\underline{\Gamma}^{(0)}(\mathbf{k})\cdot\hat{\mathbf{k}}}{mn_0}=\gamma(k)=\frac{2}{3t_E}[1-j_0(k\sigma)+2j_2(k\sigma)]\,, \tag{2.3}$$

for the longitudinal viscosity. Here $\hat{\mathbf{k}}=\mathbf{k}/|\mathbf{k}|$ is a unit vector in the direction of $\mathbf{k}$, t_E is the Enskog mean free time between collisions, σ is the hard-sphere diameter, and j_l is the spherical Bessel function of order l. A similar expression can be given for the generalized transverse viscosity[11] but it will not be needed here. We note that Eq. (2.3) is consistent with the general arguments given above. The nonlinear part of $\Gamma_{\alpha\beta}$ will be discussed below.

For future use we next calculate the number density and longitudinal momentum density time correlation functions near k_0 in the linear approximation. Later we show how these correlation functions determine the dominant mode-coupling contributions to the zero-wave-number shear viscosity. The Fourier transform of the linearized Eqs. (2.1) at intermediate wave number are

$$\partial_t\delta n(\mathbf{k},t)+\frac{ik}{m}g_l(\mathbf{k},t)=0 \tag{2.4a}$$

and

$$\partial_t g_l(\mathbf{k},t)=-\frac{ik\,\delta n(\mathbf{k},t)}{\beta S(k)}-\gamma(k)g_l(\mathbf{k},t)+f_l(\mathbf{k},t)\,. \tag{2.4b}$$

Here $g_l(\mathbf{k})=\hat{\mathbf{k}}\cdot g(\mathbf{k})$ is the longitudinal momentum density, $\beta^{-1}=k_BT$, and f_l is the longitudinal Langevin force. Multiplying these equations by $\delta n(-\mathbf{k})$, averaging, and neglecting $\partial_t\langle g_l(\mathbf{k},t)\delta n(-\mathbf{k})\rangle$, which is negligible for long times, yields

$$\frac{1}{\Omega}\langle \delta n(\mathbf{k},t)\delta_n(-\mathbf{k})\rangle = C_{nn}(k,t)$$

$$= n_0 S(k)\exp[-\omega(k)t] \; , \qquad (2.5a)$$

with $\omega(k)$ the equilibrium relaxation rate[8,11] for equilibrium density fluctuations near k_0,

$$\omega(k) = \frac{k^2}{\beta m S(k)\gamma(k)} \; , \qquad (2.5b)$$

and Ω is the volume of the fluid. Note that $\omega(k)$ is small near k_0 since $S(k)$ has a maximum there and because $\gamma(k)$ is large, i.e., density fluctuations are slowly decaying near k_0. Equation (2.5b) is a valid representation for $\omega(k)$ for only a restricted range of k values.[11] For a representation of this slow relaxation rate that is valid for essentially all wave numbers we refer elsewhere.[9,11] Equation (2.5a) and the continuity equation imply that longitudinal momentum time correlation functions also have a slow component near k_0 that are given by

$$\frac{1}{\Omega}\langle g_l(\mathbf{k},t)\delta n^*(\mathbf{k})\rangle = -\frac{im}{k}\omega(k)C_{nn}(k,t) \; , \qquad (2.6a)$$

$$\frac{1}{\Omega}\langle g_l(\mathbf{k},t)g_l^*(\mathbf{k})\rangle = -\left[\frac{m\omega(k)}{k}\right]^2 C_{nn}(k,t) \; . \qquad (2.6b)$$

It is important to remark that although Eqs. (2.6) are small [they are multiplied by $\omega(k)$] we give a mechanism below by which they become important.

B. Renormalization of the shear viscosity by molecular scale mode-coupling effects

Here we obtain a formal expression for the renormalization of the shear viscosity due to the slow decay of density fluctuations near k_0 and the nonlinearities in Eq. (2.1). We first remark that the convective terms, $\sim g^2$, will not be important. Near k_0 momentum fluctuations either are rapidly decaying or are small [cf. Eq. (2.6)]. Physically this is probably obvious: convection is difficult in a dense fluid. The density nonlinearities in the generalized pressure on the right-hand side of Eq. (2.1b) will play an important role. In fact, we show below that if these are the only nonlinearities retained then one obtains a result identical to that obtained before by Kirkpatrick.[5] Another important nonlinearity is from the expansion of the dissipative kernel $\Gamma_{\alpha\beta}$,

$$\Gamma_{\alpha\beta}(\mathbf{x},\mathbf{x}_1;n(t))$$

$$\simeq \Gamma^0_{\alpha\beta}(\mathbf{x}-\mathbf{x}_1) + \int d\mathbf{x}_2 \left.\frac{\delta\Gamma_{\alpha\beta}(\mathbf{x},\mathbf{x}_1;n(t))}{\delta n(\mathbf{x}_2,t)}\right|_{\text{eq}} \delta n(\mathbf{x}_2,t) \; . \qquad (2.7)$$

One might think that the resulting nonlinearity could be neglected since it involves a momentum fluctuation. However, if we use the estimate $\delta\Gamma_{\alpha\beta}/\delta n \sim O(\Gamma^0_{\alpha\beta}) \sim O([\omega(k)]^{-1})$, we see that this term can have a large coefficient such that when it multiplies Eq. (2.6) the net result is a term of order one, or of the same order as the nonlinearities from the generalized pressure. Below we confirm this estimate with a model hard-sphere calculation.

Denoting the relevant quadratic nonlinearities in Eq. (2.1b) by $I_\alpha^{\text{NL}}(\mathbf{x},t)$, one obtains

$$I_\alpha^{\text{NL}}(\mathbf{x},t) = k_B T \int d\mathbf{x}_1 \int d\mathbf{x}_2 \left[\frac{\partial C(\mathbf{x}-\mathbf{x}_1)}{\partial x_\alpha}\delta(\mathbf{x}-\mathbf{x}_2) + \frac{1}{2}\frac{\partial}{\partial x_\alpha}C_3(\mathbf{x},\mathbf{x}_1,\mathbf{x}_2)\right]\delta n(\mathbf{x}_1,t)\delta n(\mathbf{x}_2,t)$$

$$-\frac{1}{mn_0}\int d\mathbf{x}_1 \int d\mathbf{x}_2 \left.\frac{\delta\Gamma_{\alpha\beta}(\mathbf{x},\mathbf{x}_2;n(t))}{\delta n(\mathbf{x}_1,t)}\right|_{\text{eq}} \delta n(\mathbf{x}_1,t)g_\beta(\mathbf{x}_2,t) + \frac{1}{mn_0^2}\int d\mathbf{x}_1 \Gamma^0_{\alpha\beta}(\mathbf{x}-\mathbf{x}_1)g_\beta(\mathbf{x}_1,t)\delta n(\mathbf{x}_1,t) \; . \qquad (2.8)$$

The last term in Eq. (2.8) will not renormalize the zero-wave-number shear viscosity since it is of $O(k^2)$ and can be easily shown to lead to terms of $O(k^3)$ in the long-wavelength hydrodynamic equations. For finite-k effects it will also be important. The other two terms in Eq. (2.8) are of $O(k)$. Here k is the external wave number for the long-wavelength fluctuation we wish to consider.

With the formal identification of the relevant nonlinearities the renormalization or mode-coupling contribution to the zero-wave-number frequency-dependent shear velocity $\eta(\omega)$ can be calculated in the standard way.[20-22] We are interested in the molecular scale (for the intermediate wave vectors) contributions so that we shall use Eq. (2.5a) for the density-density correlation function. Further, since we are interested in the slow components we will replace momentum fluctuations by their longitudinal components and use Eq. (2.6). After a standard calculation we find that the dominant molecular scale mode-coupling contribution to $\eta(\omega)$ [$\equiv \eta_{\text{mc}}(\omega)$] is given by

$$\eta_{\text{mc}}(\omega) = -\frac{n_0^2 k_B T}{2k^2}\int_0^\infty dt\, e^{i\omega t}\int \frac{d\mathbf{k}_1}{(2\pi)^3}\int \frac{d\mathbf{k}_2}{(2\pi)^3} S(k_1)S(k_2)e^{-[\omega(k_1)+\omega(k_2)]t}\hat{k}^i_\alpha \hat{k}^i_\beta$$

$$\times \int d(\mathbf{x}-\mathbf{x}')\int d\mathbf{x}_1 \int d\mathbf{x}_2 \int d\mathbf{x}_3 \int d\mathbf{x}_4 e^{-i\mathbf{k}\cdot(\mathbf{x}-\mathbf{x}')+i\mathbf{k}_1\cdot(\mathbf{x}_1-\mathbf{x}_4)+i\mathbf{k}_2\cdot(\mathbf{x}_2-\mathbf{x}_3)}$$

$$\times V_\alpha(\mathbf{x},\mathbf{x}_1,\mathbf{x}_2)V^\dagger_\beta(\mathbf{x}',\mathbf{x}_3,\mathbf{x}_4) \qquad (2.9a)$$

with

$$V_\alpha(\mathbf{x},\mathbf{x}_1,\mathbf{x}_2)=\frac{\partial C(\mathbf{x}-\mathbf{x}_1)}{\partial x_\alpha}\delta(\mathbf{x}-\mathbf{x}_2)+\frac{\partial C(\mathbf{x}-\mathbf{x}_2)}{\partial x_\alpha}\delta(\mathbf{x}-\mathbf{x}_1)+n_0\frac{\partial}{\partial x_\alpha}C_3(\mathbf{x},\mathbf{x}_1,\mathbf{x}_2)$$
$$+i\beta\frac{\omega(k_2)}{n_0k_2}\hat{k}_{2\nu}\frac{\delta\Gamma_{\alpha\nu}(\mathbf{x},\mathbf{x}_2)}{\delta n(\mathbf{x}_1,t)}+i\beta\frac{\omega(k_1)}{n_0k_1}\hat{k}_{1\nu}\frac{\delta\Gamma_{\alpha\nu}(\mathbf{x},\mathbf{x}_1)}{\delta n(\mathbf{x}_2,t)} \tag{2.9b}$$

and with $V_\beta^\dagger$ given by V_β except the first three terms are multiplied by -1. In Eq. (2.9a) $\hat{\mathbf{k}}^i$ is a unit vector orthogonal to $\hat{\mathbf{k}}$ and the limit $k\to 0$ is to be taken. Further, in giving Eq. (2.9a) we have included only the lowest-order or two-mode contribution to $\eta_{\rm mc}(\omega)$.

III. RESULTS FOR HARD-SPHERE FLUIDS

In order to evaluate Eq. (2.9a) we need expressions for the functional derivatives in Eq. (2.9b). In the Appendix we obtain approximate expressions for these vertex functions for hard-sphere fluids. Unfortunately they involve three-particle equilibrium correlation functions which are not known. To make further progress we use the Kirkwood superposition approximation to express these correlation functions in terms of accurately known two-particle functions. Using Eqs. (A3), (A5), and (A6) in Eq. (2.9) and then taking the limit $k\to 0$ yields

$$\eta_{\rm mc}(\omega)=\int_0^\infty dt\, e^{i\omega t}\rho_\eta(t) \tag{3.1}$$

with

$$\rho_\eta(t)=\frac{k_BT\sigma^2}{60\pi^2}\int_0^\infty dk\,\frac{k^4}{S^2(k)}A^2(k)\exp[-2\omega(k)t]\,, \tag{3.2a}$$

where

$$A(k)=\frac{\partial S(k)}{\partial k\sigma}+\frac{4\beta m\omega(k)}{k^2t_E}S^2(k)[j_1(k\sigma)-3j_2(k\sigma)/k\sigma]$$
$$+\frac{\beta m\omega(k)S(k)}{2\pi^2k^2t_E}[4I_2(k\sigma)-I_3(k\sigma)]\,. \tag{3.2b}$$

The second and third terms in Eq. (3.2b) are due to the dissipative nonlinearity and were neglected previously.[5] From Eqs. (2.3) and (2.5b) it is easily seen that they are the same order as the first term in Eq. (3.2b). I_2 and I_3 in Eq. (3.2b) are the integrals given by Eqs. (A6a) and (A6b). Finally, we remark that the wave-number integral in Eq. (3.2a) should be restricted to regions in wave-number space where $\omega(k)$ is the slowest decaying extended hydrodynamic mode[9–11] $(2<k\sigma<20)$. We have verified that the contribution to $\rho_\eta(t)$ for wave numbers outside this region are negligible.

To evaluate $\rho_\eta(t)$ we use the Percus-Yevick representation[23] (with the Verlet-Weiss correction) for the static structure factor and simple numerical integration techniques. In Fig. 1 we graph

$$\tilde{\rho}_\eta(t)=\frac{\rho_\eta(t)t_E}{\eta_E} \tag{3.3}$$

as a function of $t^*=t/t_E$ at the reduced hard-sphere density $n\sigma^3=0.88$. The line is from the numerical evaluation of Eq. (3.2). The error bars denote the typical spread in data points in the computer simulations of Erpenbeck and Wood.[2] From Fig. 1 one see that the theory is in reasonable agreement with the computer experiments. Examining the experimental data in detail one finds that at the shortest times the theoretical result tends to be too large while at the longest times the theoretical result tends to be too small. Because of this the apparent agreement between theory and experiment in Fig. 1 may be accidental. It might also be due to the large spread in data points in the computer simulations. Further, it must be stressed that we have used several approximations to obtain our theoretical result. We can conclude, however, that the theory is in qualitative agreement with the simulations. Finally, we remark that if our result for $\tilde{\rho}_\eta(t)$ is plotted versus $(t^*)^{-3/2}$ then a reasonably straight line is obtained in the time region considered in the simulations. For $t\to\infty$ the decay of Eq. (3.2a) is much faster than $t^{-3/2}$.

IV. DISCUSSION

In this paper we have used a generalized mode-coupling theory that takes into account molecular scale effects and computed molecular scale renormalizations of the zero-wave-number viscosity and the STCF. These mode-coupling contributions are in addition to the long-wavelength contributions usually computed. We have shown that these molecular scale effects can lead to an apparent long-time tail in the STCF. Our results are orders of magnitude larger than the usual long-wavelength con-

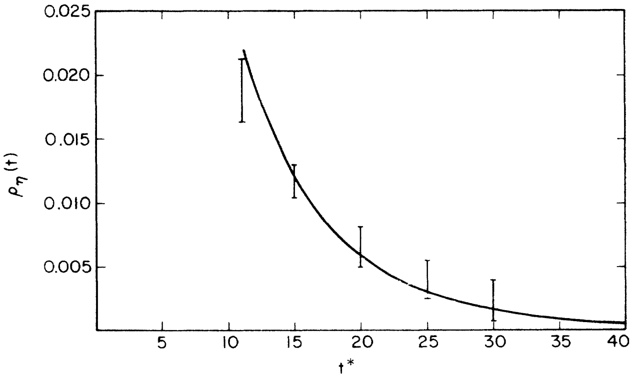

FIG. 1. $\tilde{\rho}_\eta(t)$ as a function of $t^*=t/t_E$. The line is from the numerical evaluation of Eq. (3.2). The error bars denote the typical spread in data points in the computer simulations of Ref. 2.

tributions and are in reasonable agreement with computer simulations. Physically, the importance of density fluctuations indicates that we are taking into account some of the important structural relaxation effects that are present in a dense fluid.

One of the main aims of this paper was to point out the importance of including dissipative nonlinearities as well as thermodynamic nonlinearities in calculating finite-wave-number mode-coupling effects. The dissipative nonlinearities were shown to partially account for the discrepancy found earlier by Kirkpatrick.[5]

We have made several severe approximations in our theory. The most important are those used in the Appendix. We have used approximate short-time arguments to obtain the nonlinear and nonlocal dissipative terms in our hydrodynamic equations. Part of this contribution depends on three-particle equilibrium correlation functions, and to calculate the effects of these terms on the STCF we have used the Kirkwood superposition approximation. These three-particle contributions turn out to be relatively small which might indicate that our results are not too sensitive to this approximation. A more complete kinetic theory calculation that removes these approximations is being performed by van Beijeren and co-workers. Another source of error is the two-mode (or non-self-consistent one-loop) approximation used here. Only for asymptotically long-wavelength contributions can this be justified. In the theory given here this approximation is an uncontrolled one. Nevertheless, our final results are in reasonable agreement with the computer simulations.

We conclude with a number of remarks.

(1) Throughout we have used a hydrodynamiclike description even at wave numbers on the order of an inverse molecular diameter. The validity of this is assured, at high densities, by the fact that the mean free path in a dense liquid is much smaller than a molecular diameter. Since hydrodynamics applies for wave numbers up to an inverse mean free path, it certainly applies for wave numbers on the order of σ^{-1}.

(2) Some time ago Kawasaki[24] argued that thermodynamic and dissipative nonlinearities led to contributions to the transport coefficients of different signs. His general arguments seem in conflict with our explicit results given by Eqs. (3.1) and (3.2). To understand this apparent paradox we note that Eq. (3.2) is valid only for a restricted range of times and breaks down at short times. This is due to the fact that in obtaining Eq. (2.9) we have replaced a momentum-momentum correlation function by only its slowly decaying component. It is not hard to show that the purely dissipative contribution to $\rho_\eta(t)$ given by Eq. (3.2) is valid only when the inequality (here $k=k_0$)

$$\frac{\omega(k)}{\gamma(k)}e^{-\omega(k)t} > e^{-\gamma(k)t}$$

is satisfied. For the times we consider, $t > 10t_E$, this inequality is satisfied but at shorter times ($t \lesssim 10t_E$) the inequality is violated and our approximation becomes invalid. At these shorter times the purely dissipative nonlinear contribution to $\rho_\eta(t)$ is negative.

(3) Although the formalism used in Sec. II is valid for any liquid all of our explicit results were for hard-sphere fluids. We argued that the form of the linear dissipative coefficient should be roughly the same for all simple liquids at wave numbers near k_0. However, the form of the nonlinear dissipative vertex function seems much more difficult to determine. As a consequence of this the theory used here is difficult to apply to more general liquids.

(4) In the recent[12–15] dynamical theories of the glass transition the effects of dissipative nonlinearities were neglected. It is not clear that this can be justified. First, we note that the second and third terms in Eq. (2.8) were neglected in these theories. In principle both of these nonlinearities should have been retained. We believe that the second one is of more importance. In the long-wavelength version of these theories, this nonlinearity would have the form

$$\frac{\partial\eta_B}{\partial n}\delta n(\mathbf{k}-\mathbf{q},t)g_l(\mathbf{q},t) ,$$

with $\mathbf{k}$ ($\mathbf{q}$) the external (internal) wave number and η_B the bare shear viscosity. The above-mentioned calculations are all self-consistent one-loop calculations which effectively replace $g_l(\mathbf{q},t)$ by $\eta^{-1}\delta n(\mathbf{q},t)$, with η the full shear viscosity. These theories then look for solutions where η diverges at a critical glass transition density. In such an approach the above nonlinearity vanishes since it is $\sim\eta^{-1}(\partial\eta_B/\partial n)$. However, it is easy to imagine that a vertex renormalization could change this to $\eta^{-1}(\partial\eta/\partial n)=\partial\ln\eta/\partial n$ which would lead to a singular vertex function if η is a singular function of density. Such terms would actually dominate those retained.[12–15] If this type of nonlinearity is effectively present then it would probably modify the singularities found in the current theories.[12–15] The same argument can be used for the third term in Eq. (2.8). The resulting vertex is not a singular function but it is of $O(1)$.

(5) In Sec. I we mentioned that the effects of dissipative nonlinearities are not included in a Kadanoff-Swift mode-coupling theory. Further, we noted that the Kadanoff-Swift approach was identical to a kinetic theory analysis where kinetic parts of the hydrodynamic modes are neglected. Although we have not yet verified it in detail, it appears that the dissipative nonlinearities included here are in principle equivalent to retaining the kinetic parts of the hydrodynamic modes in a kinetic theory approach.[4,25] This is known to be true for the Lorentz gas.[26]

(6) Elsewhere we will present a similar phenomenological theory for the intermediate-time behavior of the velocity autocorrelation function.

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APPENDIX

To generate the dissipative nonlinear vertex functions in Eq. (2.9b) we consider a hard-sphere fluid and use short-time approximations. Such approximations are known[11] to be qualitatively correct in describing linear transport at finite (near k_0) wave numbers in dense hard-sphere fluids. We also remark that the same nonlinearities can be obtained directly from the revised Enskog kinetic equation for hard spheres. Since we are interested in nonlinear terms in the momentum equation we consider

$$\partial_t \langle g_\alpha(\mathbf{x}) \rangle_{F(t)} = \langle \mathscr{L}_+ g_\alpha(\mathbf{x}) \rangle_{F(t)} \, . \tag{A1}$$

Here $F(t)$ is an N-particle nonequilibrium distribution function at time t, $g_\alpha(\mathbf{x})$ is the microscopic momentum density, $\mathscr{L}_+$ is the forward streaming pseudo-Liouville operator for hard-sphere particles,[27] and the angular brackets denote a phase-space average with distribution function $F(t)$. The right-hand side of Eq. (A1) can be easily expressed in terms of one- and two-particle nonequilibrium distribution functions.

The short-time approximation mentioned above is implemented by assuming that the initial N-particle distribution function is a Γ-space local equilibrium distribution function and at a short time later it is still of local equilibrium form. This implies that the two-particle distribution function is $(1=\mathbf{R}_1,\mathbf{V}_1)$

$$f_2(1,2,t) = f_l(1t) f_l(2t) G_2(\mathbf{x}_1,\mathbf{x}_2;n(t)) \, , \tag{A2a}$$

with f_l the local equilibrium one-particle distribution,

$$f_l(1,t) = n(x_1,t) \left[\frac{\beta m}{2\pi} \right]^{3/2} \exp \left[-\frac{m\beta}{2} [\mathbf{V}_1 - \mathbf{u}(x_1,t)]^2 \right] \tag{A2b}$$

with $\mathbf{u}$ the macroscopic flow velocity. G_2 in Eq. (A2a) is the configurational part of the two-particle distribution function for an inhomogeneous equilibrium fluid at density $n(\mathbf{x},t)$. With Eqs. (A2) in the right-hand side of Eq. (A1) the vertex $\delta\Gamma_{\alpha\beta}/\delta n$ can be identified by expanding Eq. (A1) in powers of $\delta n(\mathbf{x},t)$ and $g_\beta(\mathbf{x},t) = mn(\mathbf{x},t) u_\beta(\mathbf{x},t)$. We obtain[28]

$$\frac{1}{mn_0} \frac{\delta\Gamma_{\alpha\beta}(\mathbf{x},\mathbf{x}_2;n(t))}{\delta n(\mathbf{x}_1,t)} = \frac{1}{2\pi n_0 t_E} \int d\hat{\sigma}\, \hat{\sigma}_\alpha \hat{\sigma}_\beta \left[\delta(\mathbf{x}-\mathbf{x}_2)\delta(\mathbf{x}-\mathbf{x}_1-\sigma\hat{\sigma}) - \delta(\mathbf{x}-\mathbf{x}_1)\delta(\mathbf{x}-\mathbf{x}_2-\sigma\hat{\sigma}) \right.$$
$$\left. + \frac{n_0}{g(\sigma)} \delta(\mathbf{x}-\mathbf{x}_2) H_3(\mathbf{x},\mathbf{x}_2-\sigma\hat{\sigma} \mid \mathbf{x}_1) - \frac{n_0}{g(\sigma)} \delta(\mathbf{x}-\mathbf{x}_2-\sigma\hat{\sigma}) H_3(\mathbf{x},\mathbf{x}_2 \mid \mathbf{x}_1) \right] \tag{A3a}$$

with

$$H_3(\mathbf{x},\mathbf{x}_2 \mid \mathbf{x}_1) = \left. \frac{\delta G_2(\mathbf{x},\mathbf{x}_2;n(t))}{\delta n(\mathbf{x}_1,t)} \right|_{\text{eq}} \, , \tag{A3b}$$

and $t_E = \sqrt{\beta m \pi}/4\pi n \sigma^2 g(\sigma)$, and $g(\sigma)$ is the radial distribution function at contact, and $\hat{\sigma}$ is a unit vector. Note that $\delta\Gamma/\delta n$ is large, $\sim t_E^{-1}$, in agreement with the estimate given below Eq. (2.7).

$H_3(\mathbf{x},\mathbf{x}-\hat{\sigma}\sigma \mid x_1) \equiv H(\mathbf{x}-\mathbf{x}_1-\hat{\sigma}\sigma,\mathbf{x}-\mathbf{x}_1)$ can be expressed in terms of equilibrium distribution functions as

$$H(\mathbf{x}-\hat{\sigma}\sigma,\mathbf{x}) = h_3(\sigma, \lvert \mathbf{x}-\sigma\hat{\sigma} \rvert, x) - C(\lvert \mathbf{x}-\sigma\hat{\sigma} \rvert)[g(\sigma)-1] - C(x)[g(\sigma)-1]$$
$$- n_0 \int d\mathbf{x}' h_3(\sigma, \lvert \mathbf{x}-\sigma\hat{\sigma}-x' \rvert, \lvert x-x' \rvert) C(x') \, , \tag{A4}$$

with h_3 the three-particle cluster function in the cluster expansion of the three-particle equilibrium distribution function. The Kirkwood superposition approximation for H is given by

$$H(\mathbf{x}-\hat{\sigma}\sigma,\mathbf{x}) = g(\sigma) \int \frac{d\mathbf{q}_1}{(2\pi)^3} \int \frac{d\mathbf{q}_2}{(2\pi)^3} e^{i\mathbf{q}_1\cdot(\mathbf{x}-\hat{\sigma}\sigma)+i\mathbf{q}_2\cdot\mathbf{x}} \times \frac{h_2(q_1)h_2(q_2)}{S(\lvert \mathbf{q}_1+\mathbf{q}_2 \rvert)} \tag{A5}$$

with $S(q) = 1 + nh_2(q)$.

To obtain Eq. (3.2b) from Eqs. (2.9), (A3), and (A5) we have defined the integrals

$$I_2(q\sigma) = n_0 \int_0^\infty dl\, l^2 h_2(l) \frac{j_2(l\sigma)}{l\sigma} \times \int_{-1}^{+1} d\mu\, \mu h_2((q^2+l^2-2ql\mu)^{1/2}) \tag{A6a}$$

and

$$I_3(q\sigma) = n_0 \int_0^\infty dl\, l^2 h_2(l) j_3(l\sigma) \times \int_{-1}^{+1} d\mu (3\mu^3-\mu) \times h_2((q^2+l^2-2ql\mu)^{1/2}) \, . \tag{A6b}$$

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