Theoretical analysis of long-time-tail observations by light scattering off of polystyrene spheres

Ronald F. Fox
School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332
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A modified mode-coupling theory is presented to explain discrepancies between measured values and theoretical predictions for the long-time tail of the velocity-autocorrelation function of diffusing particles. The measurements of Paul and Pusey and of Ohbayashi *et al.* are analyzed and shown to be in much better agreement with theory than previously supposed, provided that the new, modified theory is used. The new theory regularizes spatial singularities in order to remove temporal singularities. In doing so, it provides a natural explanation of both the diffusion constant and the amplitude of the long-time tail of a multiplicative stochastic process.

I. INTRODUCTION

Langevin's description[1] of Brownian motion predicts that the velocity-autocorrelation function for a Brownian particle decays exponentially in time. Such a decay is consistent with the Bogoliubov view[2] that the transition from Liouville's equation to transport equations, such as hydrodynamics, is a consequence of sharply separated time scales. In the present context, the transport process of interest is diffusion. The decay time in Langevin's description is short compared to the time scale for diffusion in a macroscopic volume.

The idea of sharply separated time scales received a severe blow when Alder and Wainwright published[3] their computer-simulation results for the hard-sphere velocity-autocorrelation function. These simulations showed a slow, power-law decay, i.e., a "long-time tail." A variety of theoretical arguments[4–9] have been advanced which make this observation plausible, and additional computer simulations[10] have confirmed and refined the original findings. Nevertheless, direct observations of the long-time tail in physical measurements had to wait 10 years. The first sufficiently accurate measurements for diffusion were published in 1981 by Paul and Pusey.[11] They used light scattering off of aqueous solutions of polystyrene spheres. Recently, Ohbayashi *et al.*[12] confirmed these measurements by repeating them under slightly different conditions.

The long-time-tail measurements must determine two physical parameters. The first is the diffusion constant, the only parameter required by the Langevin theory. The second is the amplitude of the long-time tail. The diffusion constant is determined by the kinematic viscosity ν of the fluid in which the spheres are immersed, by the temperature T, and by the radius R of the spheres. The amplitude of the long-time tail, on the other hand, depends on the viscosity and temperature only.

The standard theoretical approaches determine these two parameters uniquely. No additional, free parameters are available for fitting data. Whereas Paul and Pusey found diffusion constants about 95% as large as required by theory, they were very disconcerted to find the long-time tail amplitude to be only 74% as large as predicted. The work of Ohbayashi yielded diffusion constants 97% as large as required and long-time-tail amplitudes between 91% and 97% as large as predicted. These latter results are nearly within the experimental error of the measuring technique. Indeed, Ohbayashi *et al.* concluded that they had confirmed the theory. One was forced to the conclusion that Paul and Pusey's results suffered from some source of systematic error, for which Paul and Pusey carefully looked, but were unable to find.

At about the time these measurements were being reported, I was studying the theoretical basis for long-time tails in diffusion and raised questions regarding the rigor of the arguments.[13] I argued that the long-time-tail observations for polystyrene spheres were a macroscopic, hydrodynamic effect since the spheres were so large, and that the behavior of molecular sized particles was still open to question. However, the failure of Paul and Pusey to see a sufficiently large long-time-tail amplitude was truly perplexing. Recently, I have focused attention on this special case, where one expects to see a bona fide, hydrodynamic long-time tail. There are two different theoretical approaches to this special case, the Stokes-Boussinesq approach[14,15] and the mode-coupling[4,6] approach. In the papers by Paul and Pusey and by Ohbayashi *et al.* the Stokes-Boussinesq theory is invoked, whereas in much of the theoretical work the mode-coupling argument is preferred. I have argued earlier[13] against the Stokes-Boussinesq approach, and in this paper will present a modified mode-coupling argument. This modified mode-coupling argument explains the Paul and Pusey discrepancies, and it explains why Ohbayashi *et al.* observed noticeably smaller discrepancies. The main point of this paper is that the results of Paul and Pusey are potentially in much better agreement with theory than has previously been supposed.

In Sec. II the modified mode-coupling theory is presented and discussed. The light-scattering measurements are analyzed in Sec. III. Section IV contains a review of the criticism of the Stokes-Boussinesq approach. In Sec. V conclusions and recommendations are presented.

II. A MODIFIED MODE-COUPLING THEORY

Let $C(\vec{r},t)$ denote the density of spheres in the fluid and let the velocity field of the mixture be given by

$\vec{v}(\vec{r},t)$. The conservation law for the evolution of $C(\vec{r},t)$, if there is no diffusion,[16] is given by

$$\frac{\partial}{\partial t}C+\vec{v}\cdot\vec{\nabla}C=0\ . \tag{1}$$

In the standard[6] mode-coupling theory, it is assumed that the spheres are sufficiently dilute that $\vec{v}$ can be taken to be the velocity field of the solvent fluid alone, and that it satisfies the Navier-Stokes equation

$$\frac{\partial}{\partial t}v_\alpha=\nu\nabla^2 v_\alpha-\frac{1}{\rho}\frac{\partial}{\partial x_\alpha}p\ , \tag{2}$$

in which ν is the kinematic viscosity, ρ is the mass density, and p is the pressure. Since the measurements[11,12] are done with polystyrene spheres in H_2O, the equation for an incompressible fluid has been used. Now it is observed that the concentration C is also subject to diffusion and that the velocity field $\vec{v}$ is subject to fluctuations. This leads to the equations

$$\frac{\partial}{\partial t}C+\tilde{\vec{u}}\cdot\vec{\nabla}C=D_0\nabla^2 C \tag{3}$$

and

$$\frac{\partial}{\partial t}\tilde{u}_\alpha=\nu\nabla^2\tilde{u}_\alpha-\frac{1}{\rho}\frac{\partial}{\partial x_\alpha}p+\frac{1}{\rho}\frac{\partial}{\partial x_\beta}\tilde{S}_{\alpha\beta}\ , \tag{4}$$

in which D_0 is the "bare" diffusion constant and $\tilde{S}_{\alpha\beta}$ is the fluctuating stress tensor. The standard theory[17] for the hydrodynamic fluctuations of an incompressible fluid treat $\tilde{S}_{\alpha\beta}$ as Gaussian white noise of zero mean and with correlation

$$\langle\tilde{S}_{\alpha\beta}(\vec{r},t)\tilde{S}_{\mu\nu}(\vec{r}',t')\rangle=2k_BT\rho\nu(\delta_{\alpha\mu}\delta_{\beta\nu}+\delta_{\alpha\nu}\delta_{\beta\mu})\times\delta(t-t')\delta(\vec{r}-\vec{r}')\ , \tag{5}$$

in which k_B is Boltzmann's constant. This correlation is valid for the infinite free fluid, and ignores any influence of the presence of the dilute concentration of spheres. The fluctuating velocity field in Eq. (3) makes that equation a multiplicative stochastic process.[18]

The average behavior of C, i.e., $\langle C\rangle$, is obtained by averaging Eq. (3) with respect to the influence of $\tilde{\vec{u}}$. This is most easily achieved by use of spatial Fourier transforms. The nonlinearity of the $\tilde{\vec{u}}\cdot\vec{\nabla}C$ term produces coupling between the different Fourier modes,[6] i.e., "mode coupling." In the limit of small Fourier-space $\vec{k}$ vectors, a cumulant expansion[18] may be used and yields

$$\frac{\partial}{\partial t}\langle C\rangle=D_0\nabla^2\langle C\rangle+\frac{2}{3}\frac{k_BT}{\rho}\times\left[\int_0^t ds[4\pi(D_0+\nu)(t-s)]^{-3/2}\right]\nabla^2\langle C\rangle, \tag{6}$$

wherein the first two cumulants have been retained because all higher-order cumulants are of order 10^{-7} times smaller or more.

Several points regarding this result must be noticed. Define $\tilde{\vec{u}}^{\,I}$ by

$$\tilde{\vec{u}}^{\,I}(t)=\exp(-tD_0\nabla^2)\tilde{\vec{u}}\cdot\vec{\nabla}\exp(tD_0\nabla^2) \tag{7}$$

and observe the noncommutativity of $D_0\nabla^2$ and $\tilde{\vec{u}}\cdot\vec{\nabla}$. The analysis produces the correlation

$$\langle\tilde{u}^I_\alpha(t)\tilde{u}^I_\beta(s)\rangle=\frac{2}{3}\frac{k_BT}{\rho}[4\pi(D_0+\nu)\,|\,t-s\,|\,]^{-3/2}\delta_{\alpha\beta}\ , \tag{8}$$

which is the integrand on the right-hand side of Eq. (6). The integral may be recognized as Green-Kubo transport coefficient[19] integral "renormalization" of the bare diffusion coefficient. The correlation in (8) is evaluated at a single point $\vec{r}$ after initially finding the correlation at two points, $\vec{r}$ and $\vec{r}'$. It contains $D_0+\nu$ because $D_0\nabla^2$ and $\tilde{\vec{u}}\cdot\vec{\nabla}$ do not commute. However, for the measurements $\nu\gg D_0$. All instances of $\langle C\rangle$ in Eq. (6) are evaluated at the same point $\vec{r}$ and time t. The time integral is trivial and yields

$$\frac{2}{3}\frac{k_BT}{\rho}\int_0^t ds[4\pi(D_0+\nu)(t-s)]^{-3/2}=\frac{k_BT}{6\pi\rho(D_0+\nu)}\{[\pi(D_0+\nu)0]^{-1/2}-[\pi(D_0+\nu)t]^{-1/2}\}\ , \tag{9}$$

which has the units of a diffusion constant, exhibits the effect of the long-time-tail power law of (8) in its last term, and also exhibits an embarrassing singularity at $t=0$. The usual treatment[4,6] includes the heuristic argument that the lower time limit, $t=0$, is not to be taken seriously and that $t=0$ should be replaced by $t=t_0$ for some appropriate t_0 for which $[\pi(D_0+\nu)t_0]^{-1/2}$ is negligible. Often, one says t_0 is on the scale of the mean free time of the fluid. In the Stokes-Boussinesq approach,[14,15] this singularity does not occur, which is one reason why some researchers prefer it. In either approach, it is the asymptotic time behavior which is sought, and each yields

$$\frac{\partial}{\partial t}\langle C\rangle=\left[D_0-\frac{k_BT}{6\pi\rho\nu\sqrt{\pi\nu t}}\right]\nabla^2\langle C\rangle\ , \tag{10}$$

wherein $D_0+\nu$ has been accurately replaced by just ν. For spheres, D_0 is given by the Stokes-Einstein formula[1]

$$D_0=\frac{k_BT}{6\pi\rho\nu R}\ , \tag{11}$$

in which R is the radius of a sphere (on the order of 10^{-4} cm in the measurements to be discussed). In fact, as will be discussed in the next section of this paper, the measurements do not directly yield the diffusion constant and its

long-time-tail renormalization, but instead provide the asymptotic time dependence of the mean-square spatial displacement of a sphere. Both approaches yield the same result for this quantity:

$$\langle |\Delta\vec{r}|^2\rangle = 2\left[D_0 t - \frac{k_B T}{3\pi\rho\nu^{3/2}} t^{1/2}\right] . \tag{12}$$

It is precisely this quantity which was used to fit data by Paul and Pusey and by Ohbayashi *et al.*

This mode-coupling argument may be criticized (as may the Stokes-Boussinesq approach; see Sec. IV). While doing so, a modified mode-coupling argument will be presented which leads to physically and mathematically more acceptable results. Obviously, the singularity at $t=0$ in (9) is more serious than the argument aimed at ignoring it suggests. Indeed, it is easy to show that

$$k_B T/6\pi\rho\nu(\pi\nu t_0)^{1/2}$$

is a quantity which is larger than D_0 for all $t_0 < R_2/\pi\nu \sim 10^{-6}$ sec for the conditions of Paul and Pusey's measurements. For t_0 on the scale of a mean free time, which is less than a picosecond, this quantity dwarfs D_0 by orders of magnitude. Another perspective leads to the objection that so far the presence of the spheres in the fluid in no way affects the fluctuating Navier-Stokes equation or the stress tensor correlations. The stress tensor correlations contain the factor $\delta(\vec{r}-\vec{r}')$ which represents the idea on the hydrodynamic level of description[17] that these correlations are local in space. In Eqs. (1), (3), and (6), the spheres are represented by a local concentration. Can this idea of locality be imputed to a spatial scale set by the sphere's radius R? As a final objection, the simultaneous presence of $\tilde{\vec{u}}$ and D_0 in Eq. (3) is disturbing. If $\tilde{\vec{u}}$ is the cause of the diffusive behavior of $\langle C\rangle$, then the D_0 should emerge from the averaging and not have to be inserted by hand.

The preceding criticisms suggest the following, modified mode-coupling approach. The basic equations are

$$\frac{\partial}{\partial t} C + \tilde{\vec{u}}\cdot\vec{\nabla} C = 0 , \tag{13}$$

$$\frac{\partial}{\partial t}\tilde{u}_\alpha = \nu\nabla^2\tilde{u}_\alpha - \frac{1}{\rho}\frac{\partial}{\partial x_\alpha} p + \frac{1}{\rho}\frac{\partial}{\partial x_\beta}\tilde{S}_{\alpha\beta} , \tag{14}$$

$$\langle \tilde{S}_{\alpha\beta}(\vec{r},t)\tilde{S}_{\mu\nu}(\vec{r}',t')\rangle = 2k_B T\rho\nu(\delta_{\alpha\mu}\delta_{\beta\nu}+\delta_{\alpha\nu}\delta_{\beta\mu}) \times\delta(t-t')\Delta(\vec{r}-\vec{r}') , \tag{15}$$

$$\Delta(\vec{r}-\vec{r}') = (2\pi\sigma_R^2)^{-3/2}\exp\left[-\frac{|\vec{r}-\vec{r}'|^2}{2\sigma_R^2}\right] . \tag{16}$$

Equation (13) does not contain a bare diffusion coefficient and is simply a multiplicatively stochastic[18] conservation equation for C. In Eq. (15), $\Delta(\vec{r}-\vec{r}')$ replaces $\delta(\vec{r}-\vec{r}')$ of Eq. (5) and exhibits the desire to avoid locality on a spatial scale smaller than the radius of a sphere. The breadth of $\Delta(\vec{r}-\vec{r}')$ is determined by its variance σ_R^2, which is related to the sphere's radius by the strictly phenomenological requirement

$$\pi\sigma_R^2 = 2R^2 . \tag{17}$$

As will be shown below, the softening of the spatially singular function $\delta(\vec{r}-\vec{r}')$ by $\Delta(\vec{r}-\vec{r}')$ removes the temporal singularity in Eq. (9). An analogous nonlocality in time is not introduced because it is determined by the ratio R/c where c is the sound velocity in polystyrene. This works out to less than 1 nsec, which is between 10^{-2} and 10^{-3} times shorter than the natural time scale in this problem, $R^2/\pi\nu$, as is discussed in Sec. III.

Before proceeding with the consequences of Eqs. (13)–(16), a more detailed account of their significance will be presented. Two features of this formalism need to be explained with greater clarity. The incompressibility requirement, $\vec{\nabla}\cdot\tilde{\vec{u}}=0$, may be used to eliminate the pressure p from the equations. The choice of correlation formula for the stress tensor fluctuations cannot be made without checking for consistency with the fluctuation-dissipation relation.[17] Both of these issues can be dealt with by invoking the theory of irreversible thermodynamics in its hydrodynamic context.[17,18]

The requirements for the application of irreversible thermodynamics[17,18] are an entropy expression,

$$S = S_e - \tfrac{1}{2}k_B\int d^3r\, d^3r' a_i(\vec{r})E_{ij}(\vec{r}-\vec{r}')a_j(\vec{r}') , \tag{18}$$

a relaxation equation,

$$\frac{\partial}{\partial t}a_i(\vec{r},t) = -\int d^3r' G_{ij}(\vec{r}-\vec{r}')a_j(\vec{r}') + \tilde{F}_i(\vec{r},t) , \tag{19}$$

and a correlation formula for the fluctuating forces:

$$\langle \tilde{F}_i(\vec{r},t)\tilde{F}_j(\vec{r}',t')\rangle = 2Q_{ij}(\vec{r}-\vec{r}')\delta(t-t') . \tag{20}$$

$E_{ij}(\vec{r}-\vec{r}')$ is called the entropy matrix and $G_{ij}(\vec{r}-\vec{r}')$ is called the relaxation matrix. The correlation matrix $Q_{ij}(\vec{r}-\vec{r}')$ is fixed by the fluctuation dissipation relation:

$$2Q_{ij}(\vec{r}-\vec{r}') = \int d^3r''[G_{il}(\vec{r}-\vec{r}'')E_{lj}^{-1}(\vec{r}''-\vec{r}') + E_{il}^{-1}(\vec{r}-\vec{r}'')G_{jl}(\vec{r}''-\vec{r}')] . \tag{21}$$

In this equation, the inverse of the entropy matrix, $E_{ij}^{-1}(\vec{r}-\vec{r}')$, appears, and it is defined by the requirement

$$\int d^3r'' E_{il}(\vec{r}-\vec{r}'')E_{lj}^{-1}(\vec{r}''-\vec{r}') = \delta_{ij}\delta(\vec{r}-\vec{r}') . \tag{22}$$

In order to apply this formalism to the problem at hand, it is necessary to identify the variables $a_i(\vec{r},t)$, the matrices E_{ij} and G_{ij}, and the fluctuating forces $\tilde{F}_i$. These identifications and the incompressibility condition are most readily achieved by spatial Fourier transforms:

$$\hat{f}(\vec{k}) \equiv \frac{1}{(2\pi)^3}\int d^3r\, e^{-i\vec{k}\cdot\vec{r}} f(\vec{r}) . \tag{23}$$

The Fourier transform of Eq. (14) is

$$\frac{\partial}{\partial t}\hat{u}_\alpha = -\nu k^2\hat{u}_\alpha - \frac{1}{\rho}ik_\alpha\hat{p} + \frac{1}{\rho}ik_\beta\tilde{S}_{\alpha\beta} . \tag{24}$$

The incompressibility condition is $\vec{k}\cdot\tilde{\vec{u}}=0$. Setting this into (24) yields

$$k^2\hat{p} = k_\alpha k_\beta\hat{S}_{\alpha\beta} \tag{25}$$

or

$$\hat{p}=\frac{k_\alpha k_\beta}{k^2}\hat{S}_{\alpha\beta} . \tag{26}$$

This permits rewriting (24) as

$$\frac{\partial}{\partial t}\hat{u}_\alpha=-\nu k^2\hat{u}_\alpha+\frac{i}{\rho}\left[k_\nu\delta_{\mu\alpha}-k_\alpha\frac{k_\mu k_\nu}{k^2}\right]\hat{S}_{\mu\nu} , \tag{27}$$

from which $\hat{F}_\alpha$ may be identified by:

$$\hat{F}_\alpha=\frac{i}{\rho}\left[k_\nu\delta_{\mu\alpha}-k_\alpha\frac{k_\mu k_\nu}{k^2}\right]\hat{S}_{\mu\nu} \tag{28}$$

when $\hat{u}_\alpha$ is taken to be $\hat{a}_\alpha$.

In the entropy expression (18), only the transverse velocity field should enter. From hydrodynamics, the entropy is given by

$$S=S_e-\tfrac{1}{2}k_B\int d^3r\frac{\rho}{k_BT}\vec{u}_t\cdot\vec{u}_t , \tag{29}$$

wherein $\vec{u}_t$ satisfies $\vec{\nabla}\cdot\vec{u}_t=0$, the incompressibility condition. The Fourier transformed equivalent is

$$S=S_e-\tfrac{1}{2}(2\pi)^3\frac{\rho}{T}\int d^3k\,\hat{\vec{u}}_t(\vec{k})\cdot\hat{\vec{u}}_t(-\vec{k}) , \tag{30}$$

where $\hat{\vec{u}}_t$ satisfies $\vec{k}\cdot\hat{\vec{u}}_t=0$. This can be expressed as

$$S=S_e-\tfrac{1}{2}k_B(2\pi)^6\int d^3k\,d^3k'\hat{u}_i(\vec{k})\hat{E}_{ij}(\vec{k})\times\delta(\vec{k}+\vec{k}')\hat{u}_j(\vec{k}') , \tag{31}$$

where

$$\hat{E}_{ij}(\vec{k})=\frac{\rho}{k_BT}\left[\delta_{ij}-\frac{k_ik_j}{k^2}\right] . \tag{32}$$

This result is obtained by observing that $\hat{u}_t$ is obtained from $\hat{\vec{u}}$ with the projection operator

$$\hat{\vec{u}}_t=\hat{\vec{u}}-\frac{\vec{k}}{k}\left[\frac{\vec{k}}{k}\cdot\hat{\vec{u}}\right]$$

or

$$\hat{\vec{u}}_{ti}=\left[\delta_{ij}-\frac{k_ik_j}{k^2}\right]\hat{u}_{tj} ,$$

and $\delta_{ij}-k_ik_j/k^2$ is idempotent. From (19) and (27), the relaxation matrix is seen to be

$$\hat{G}_{ij}(\vec{k})=\frac{1}{(2\pi)^3}\nu k^2\delta_{ij} . \tag{33}$$

The inverse of the entropy matrix must be defined on the two-dimensional subspace of transverse velocity field components, and not simply by (22). In fact, the direct Fourier transform of (22), restricted to transverse components only, should read

$$\hat{E}_{il}(\vec{k})\hat{E}^{-1}_{lj}(\vec{k}')\delta(\vec{k}+\vec{k}')=\frac{1}{(2\pi)^6}\delta(\vec{k}+\vec{k}')\left[\delta_{ij}-\frac{k_ik_j}{k^2}\right] . \tag{34}$$

It is easily seen that this yields

$$\hat{E}^{-1}_{ij}(\vec{k})=\frac{k_BT}{\rho}\frac{1}{(2\pi)^6}\left[\delta_{ij}-\frac{k_ik_j}{k^2}\right] . \tag{35}$$

The factor $\delta(\vec{k}+\vec{k}')$ in (34) arises from the $\delta(\vec{r}-\vec{r}')$ in (22). It is just such δ functions which are to be softened into $\Delta(\vec{r}-\vec{r}')$. Thus, the right-hand side of (34) should read

$$\frac{1}{(2\pi)^6}\left[\delta_{ij}-\frac{k_ik_j}{k^2}\right]\delta(\vec{k}+\vec{k}')e^{-\sigma_R^2k^2/2} .$$

This means that the inverse of the entropy matrix given in (35) will become

$$\hat{E}^{-1}_{ij}(\vec{k})=\frac{k_BT}{\rho}\frac{1}{(2\pi)^6}\left[\delta_{ij}-\frac{k_ik_j}{k^2}\right]e^{-\sigma_R^2k^2/2} . \tag{36}$$

Combining (33), (36), and the Fourier transform of the fluctuation-dissipation relation (21) gives

$$2\hat{Q}_{ij}(\vec{k})\delta(\vec{k}+\vec{k}')=2\frac{k_BT}{\rho}\nu k^2\left[\delta_{ij}-\frac{k_ik_j}{k^2}\right]\delta(\vec{k}+\vec{k}')\times\frac{1}{(2\pi)^6}e^{-\sigma_R^2k^2/2} . \tag{37}$$

The Fourier transform of (20) implies

$$\langle\hat{F}_i(\vec{k},t)\hat{F}_j(\vec{k}',t')\rangle=2\frac{k_BT}{\rho}\nu k^2\left[\delta_{ij}-\frac{k_ik_j}{k^2}\right]\delta(\vec{k}+\vec{k}')\times\frac{1}{(2\pi)^3}e^{-\sigma_R^2k^2/2} . \tag{38}$$

This agrees exactly with the Fourier transform of (15) and the identity (28), which was what was to be proved.

It is now possible to return to Eqs. (13)—(16) in order to obtain an equation for $\langle C\rangle$. Equation (13) is a linearly multiplicative stochastic process[18] which is most easily averaged by the method of ordered operator cumulants.[18] The formal solution is

$$\langle C(t)\rangle=\left\langle\underleftarrow{T}\exp\left[-\int_0^t ds\,\tilde{\vec{u}}(s)\cdot\vec{\nabla}\right]\right\rangle C(0) , \tag{39}$$

in which the time-ordered exponential of the streaming operator appears. The average of this ordered exponential may be expressed by ordered cumulants which leads to the differential equation

$$\frac{\partial}{\partial t}\langle C\rangle=\sum_{n=1}^{\infty}G^{(n)}(t)\langle C\rangle , \tag{40}$$

where the first two cumulants are given by

$$G^{(1)}(t)=\langle\tilde{\vec{u}}(t)\cdot\vec{\nabla}\rangle=0 , \tag{41}$$

$$G^{(2)}(t)=\int_0^t ds\,\langle\tilde{\vec{u}}(t)\cdot\vec{\nabla}\,\tilde{\vec{u}}(s)\cdot\vec{\nabla}\rangle . \tag{42}$$

Each of these expressions is evaluated from the solution to (27), which is

$$\hat{u}_\alpha(t)=e^{-t\nu k^2}\hat{u}_\alpha(0)+\int_0^t ds\, e^{-(t-s)\nu k^2}\frac{1}{\rho}\left[k_\nu\delta_{\mu\alpha}-k_\alpha\frac{k_\mu k_\nu}{k^2}\right]\hat{S}_{\mu\nu}(s)\ . \tag{43}$$

The averaging implied in (39) and (40) is with respect to both $\hat{S}_{\mu\nu}$ and the initial data $\hat{u}_\alpha(0)$. The initial data is distributed by a Maxwell distribution for the transverse velocity field components. Consequently, the result given by (41) is obtained. The evaluation of (42) leads to

$$\langle\,\tilde{\vec{u}}(t)\cdot\vec{\nabla}\,\tilde{\vec{u}}(s)\cdot\vec{\nabla}\,\rangle=\langle\,\tilde{u}_\alpha(\vec{r},t)\tilde{u}_\beta(\vec{r}\,',s)\rangle\frac{\partial^2}{\partial x_\alpha\partial x_\beta}\quad\text{at }\vec{r}\,'=\vec{r}\ . \tag{44}$$

Again using (43), one obtains

$$\langle\,\tilde{u}_\alpha(\vec{r},t)\tilde{u}_\beta(\vec{r}\,',t')\rangle=\frac{k_BT}{\rho}\left[-\nabla^2\delta_{\alpha\beta}+\frac{\partial^2}{\partial x_\alpha\partial x_\beta}\right]\frac{1}{(2\pi)^3}\int d^3k\frac{e^{i\vec{k}\cdot(\vec{r}-\vec{r}\,')}}{k^2}e^{-\nu k^2|t-t'|}e^{-\sigma_R^2k^2/2}\ , \tag{45}$$

wherein (15) has been used. For $\vec{r}\,'=\vec{r}$, which is what is needed here, the quantity $-\nabla^2\delta_{\alpha\beta}+\partial^2/\partial x_\alpha\partial x_\beta$ becomes a factor of $(8\pi/3)k^2\delta_{\alpha\beta}$ inside the integral, and the expression becomes

$$\langle\,\tilde{u}_\alpha(\vec{r},t)\tilde{u}_\beta(\vec{r},t')\rangle=\frac{8\pi}{3}\frac{k_BT}{\rho}\frac{1}{(2\pi)^3}\int_0^\infty dk\,k^2e^{-\nu k^2|t-t'|-\sigma_R^2k^2/2}\delta_{\alpha\beta}=\frac{2}{3}\frac{k_BT}{\rho}(4\pi\nu|t-t'|+2\pi\sigma_R^2)^{-3/2}\delta_{\alpha\beta}\ . \tag{46}$$

Therefore, $G^{(2)}(t)$ in (42) is explicitly

$$\begin{aligned}G^{(3)}(t)&=\int_0^t ds\frac{2}{3}\frac{k_BT}{\rho}[4\pi\nu(t-s)+2\pi\sigma_R^2]^{-3/2}\nabla^2\\&=\frac{k_BT}{6\pi\rho\nu}[(\pi\sigma_R^2/2)^{-1/2}-(\pi\nu t+\pi\sigma_R^2/2)^{-1/2}]\nabla^2\ .\end{aligned} \tag{47}$$

This must be compared with (9). The phenomenological choice for σ_R^2 given by (17) converts this into

$$G^{(2)}(t)=D_0[1-(1+\pi\nu t/R^2)^{-1/2}]\nabla^2\ , \tag{48}$$

wherein the Einstein-Stokes formula[1] have been invoked. It may be shown that the largest additional higher-order cumulant is $G^{(4)}(t)$ and that it is of order D_0/ν times smaller than $G^{(2)}(t)$. For the conditions of the measurements,[11,12] this is a factor around 10^{-7}. Thus, the average equation for the sphere concentration is

$$\frac{\partial}{\partial t}\langle C\rangle=D_0[1-(1+\pi\nu t/R^2)^{-1/2}]\nabla^2\langle C\rangle\ , \tag{49}$$

in which both the diffusion constant and the long-time tail are found. For times t long compared with $R^2/\pi\nu$, this equation is very well approximated by Eq. (10), whereas for all shorter times it is also well behaved, in contrast with (10).

Equation (49), in contrast with (10), will be the basis for the ensuing analysis of the light scattering measurements.

III. ANALYSIS OF THE MEASUREMENTS

The technique used in the light scattering measurements[11,12] is photon-correlation dynamic light scattering. It yields an estimate of the normalized temporal autocorrelation function $g^{(2)}(t)$ of the scattered light intensity I:

$$g^{(2)}(t)=\frac{\langle I(0)I(t)\rangle}{\langle I\rangle^2}\ , \tag{50}$$

in which t is the correlation delay time. For light scattered by a sufficiently large number of particles, the field amplitude of the light is a complex Gaussian process and

$$g^{(2)}(t)=1+C(g^{(1)}(t))^2\ , \tag{51}$$

in which C is an apparatus constant and $g^{(1)}(t)$ is the self-intermediate scattering function

$$g^{(1)}(\vec{k},t)=\langle\exp[i\vec{k}\cdot\Delta\vec{r}(t)]\rangle\ , \tag{52}$$

in which $\vec{k}$ is the scattering vector and $\Delta\vec{r}(t)$ is the displacement of the scatterer in time t. For scatterers satisfying a diffusion dynamics, as is the case here, one obtains

$$g^{(1)}(\vec{k},t)=\exp[-\tfrac{1}{2}k^2\langle\,|\Delta\vec{r}(t)|^2\rangle]\ . \tag{53}$$

Therefore, a measurement of $g^{(2)}(t)$ provides an indirect measurement of the mean-square displacement of a scatterer, $\langle\,|\Delta\vec{r}(t)|^2\rangle$.

The mean-square displacement may be determined by the diffusion equation given in (49). This equation may be written in the form

$$\frac{\partial}{\partial t}\langle C\rangle=D(t)\nabla^2\langle C\rangle\ . \tag{54}$$

With initial condition $\langle C(\vec{r},0)\rangle=\delta(\vec{r}-\vec{r}_0)$, the solution is

$$\langle C(\vec{r},t)\rangle=\left[4\pi\int_0^t ds\,D(s)\right]^{-3/2}\exp\left[-\frac{|\vec{r}-\vec{r}_0|^2}{4\int_0^t ds\,D(s)}\right]\ . \tag{55}$$

Therefore,

$$\langle\,|\Delta\vec{r}(t)|^2\rangle=2\int_0^t ds\,D(s)\ . \tag{56}$$

With use of the explicit $D(s)$ implied by (49), this yields

$$\langle\,|\Delta\vec{r}(t)|^2\rangle=2D_0\left\{t-2\frac{R^2}{\pi\nu}\left[\left[1+\frac{\pi\nu t}{R^2}\right]^{1/2}-1\right]\right\}\ , \tag{57}$$

TABLE I. Results of Paul and Pusey (P, Ref. 11) and Ohbayashi *et al.* (O, Ref. 12).

	b/D_0	a/d_0	Θ (°C)	T_s (μsec)	N	M	$R^2/\pi\nu$ (nsec)
P1	0.96	0.79	19.5	2	88	30	830
P2	0.95	0.74	19.5	5	88	30	830
P3	0.96	0.73	19.5	10	88	30	830
P4	0.96	0.64	19.5	20	88	30	830
O1	0.98	0.91	23.5	6	208	108	56
O2	0.98	0.94	28	6	208	98	62
O3	0.97	0.97	32.8	6	208	88	68

which is to be compared with (12), with which it agrees identically for $t \gg R^2/\pi\nu$.

In both the measurements of Paul and Pusey[11] and of Ohbayashi *et al.*[12] it was formula (12) which was used to fit the measured data. By using (57) in (53) and then (53) in (51), it is seen that

$$\ln(g^{(2)}-1)=\ln C-k^2\langle|\Delta\vec{r}(t)|^2\rangle . \tag{58}$$

Thus, a semilog plot can be fitted by formula (12) in the form $bt-at^{1/2}$ in order to determine b and a. A linear least-squares fitting procedure was used such that a perfect fit would have meant that

$$b=D_0 \quad \text{and} \quad a=d_0\equiv\frac{k_BT}{3\pi\rho\nu^{3/2}} . \tag{59}$$

The reader is referred to the original papers[11,12] for all pertinent details regarding these fits and measurements. Only the results are reproduced below, in Table I.

In Table I the ratios b/D_0 and a/d_0 are given, as well as the temperature Θ at which the measurements were made, the time delay T_s of the correlator, the number of channels N of the correlator, and the multiple M of the intrinsic time $R^2/\pi\nu$, which serves as the first time at which data is taken. The Paul and Pusey[11] (P) measurements involved polystyrene spheres of radius $R=1.69$ μm and the Ohbayashi *et al.*[12] (O) measurements utilized spheres of radius $R=0.402$ μm. The kinematic viscosity ν is the ratio of the viscosity η and the mass density ρ each of which is temperature dependent. These variations are incorporated in the computation of the intrinsic time. For Paul and Pusey, the intrinsic time $R^2/\pi\nu$ is 8.3×10^{-7} sec, whereas for Ohbayashi *et al.* it is 5.6×10^{-8} sec (23.5°C), 6.2×10^{-8} sec (28°C), and 6.8×10^{-8} sec (32.8°C). Paul and Pusey's measurements ran from $MR^2/\pi\nu$ to $M(R^2/\pi\nu)+NT_s$ as did Ohbayashi *et al.*'s. In the former case, the first time is 2.5×10^{-5} sec, whereas in the latter case it is 6×10^{-6} sec.

Formula (57) implies that it is not justified to fit the measured data with the function $bt-at^{1/2}$. Obviously, it would be desirable to use the function

$$bt-at^{1/2}[(1+a^2/4b^2t)^{1/2}-a/2bt^{1/2}]$$

instead, even though this would necessitate a nonlinear least-squares fitting procedure. Since the raw data is not at our disposal, the validity of the point of view developed in this paper is tested as follows. The function $bt-at^{1/2}$ is used to fit

$$D_0\left\{t-2\frac{R^2}{\pi\nu}\left[\left[1+\frac{\pi\nu t}{R^2}\right]^{1/2}-1\right]\right\}$$

in which all quantities are already predetermined, as though this expression faithfully represents the real data. If b and a turn out to differ from D_0 and d_0 as in Table I, then this would be strong evidence for validity. Because the short-time dependence is more important than the long-time dependence, a fit of $b-at^{-1/2}$ to

$$D_0\left\{1-2\frac{R^2}{\pi\nu t}\left[\left[1+\frac{\pi\nu t}{R^2}\right]^{1/2}-1\right]\right\}$$

by linear least squares was used. This procedure can be rendered in closed form, algebraically. The results are given in Table II.

While there is a good deal of variation in the measured data for similar conditions, this variation is not systematically explainable. Paul and Pusey did a weighted average over all of their results and obtained the values $b/D_0=95.5\%$ and $a/d_0=74\pm3\%$. The fit to the formula in (57) yields $b/D_0\sim99\%$ and $a/d_0\sim82\%$, which is not quantitative agreement, but is qualitatively in the right direction. Moreover, our results are sensitively dependent on the weighting procedure used in the fits, and one can obtain quantitative agreement without much effort. The comparison of our results for O1 with the measured O1 results is much better. O2 and O3 are not so good, but again qualitatively in agreement. Ohbayashi *et al.* also did fits which included an additional quadratic term, i.e., $bt-at^{1/2}-ct^2$. They stated that this did not appreciably alter their results for b and a. This claim was not supported by their published values, however, which did show only $<1\%$ changes in b, but showed a 16% change in a for O1, a 1% change in a for O2, and a 29% change in a for O3. Thus, O3 is not reliable for compar-

TABLE II. Closed-form rendition of a linear least-squares fit for the expression $b-at^{-1/2}$.

	b/D_0	a/d_0
P1	0.98	0.79
P2	0.985	0.82
P3	0.99	0.84
P4	0.99	0.85
O1	0.995	0.90
O2	0.995	0.89
O3	0.995	0.89

ison. It is the contention of the present analysis that formula (57) is to be favored over (12) in data analysis. Moreover, the comparison of the measurements with (57) will show that the agreement between measurement and theory is much better than was previously supposed. Finally, the better agreement of Ohbayashi *et al.*'s results with (12) than Paul and Pusey's results is only a reflection of the greater value of M. The larger M is, the more nearly equal (57) and (12) become.

IV. THE STOKES-BOUSSINESQ FORMULA

Both papers reporting measurements have chosen to interpret their results in terms of the Stokes-Boussinesq formula.[14,15] This formula expresses the drag force experienced by a sphere which is moved through a fluid with some explicit time-dependent velocity $u(t)$:

$$F(t)=-6\pi\eta R u(t)-\tfrac{2}{3}\pi\rho R^3\dot{u}(t) -6R^2\sqrt{\pi\eta\rho}\int_{-\infty}^{t} ds\frac{\dot{u}(s)}{\sqrt{t-s}} . \tag{60}$$

A detailed account of the derivation of this formula can be found in Landau and Lifshitz's *Fluid Mechanics*.[16] What the authors of the measurement papers, and many others, have down is to use $F(t)$ in a "self-forcing" equation

$$M\dot{u}(t)=F(t) . \tag{61}$$

Elsewhere,[13] I have argued against this equation except in a very restricted context. The argument is based on the observation that the derivation[16] of (60) is designed to eliminate all transients in the solutions. Therefore, Eq. (61) can only be valid on a time scale that is long compared with the transient's relaxation time. In that sense, (61) properly describes the asymptotic time domain, and particularly the long-time regime. However, the transients do not decay rapidly.[13] They do not decay exponentially, but only by a power law which is only a factor of $1/t$ stronger than the long-time tail power law. Consequently, (60) cannot be used to obtain corrections to the asymptotic time dependence given by (12). One can obtain the correction implied by (60) to (12), but it would not include an additional correction of the same order in t which is in the transients. Consequently, the suggestion that one use (60) to obtain an analog to (57) is not valid.

V. CONCLUSIONS AND RECOMMENDATIONS

A definitive test of the ideas presented in this paper requires fitting the raw data to the formula (57). Such fits would be better tests if the value of M were smaller. This suggests that the measurements be attempted for shorter times than previously done. It is interesting to note that even for $M=30$, as in the Paul and Pusey measurements, the two formulas, (12) and (57), differ, at the first time at which data is taken, by $2D_0(M-2\sqrt{M})$ versus $2D_0[M-2(\sqrt{1+M}-1)]$, respectively, which is only $2D_0(19.0)$ versus $2D_0(20.9)$, i.e., 10%. For the Ohbayashi *et al.* measurements for which $M\sim 100$, these two quantities differ by $2D_0(80)$ versus $2D_0(81.9)$, i.e., 2%. Nevertheless, large discrepancies in the a/d_0 ratio arise from these relatively small initial time differences. At later times, of course, (12) and (57) are much more nearly equal.

Measurements at shorter times would also provide an indirect test of the assertions in this paper regarding the Stokes-Boussinesq formula. Specifically, the claim that only its asymptotic value is valid for long times, whereas any corrections to this value omit equally important contributions from ignored transients. The transient behavior could be computed for the Stokes-Boussinesq formula and then compared with formula (57).

The modified mode-coupling approach presented here should be justified from a more microscopic point of view. This could involve the approach of nonlocal hydrodynamics[20] or kinetic theory. It would be of interest to pursue the generality of the observed interplay here between a spatial δ function and a temporal singularity. The removal of the phenomenological character of the theory presented here is also desirable.

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