PHYSICAL REVIEW E **76**, 062502 (2007)

Simplified self-consistent theory of colloid dynamics

R. Juárez-Maldonado,[1] M. A. Chávez-Rojo,[2] P. E. Ramírez-González,[1] L. Yeomans-Reyna,[3] and M. Medina-Noyola[1]
[1]*Instituto de Física "Manuel Sandoval Vallarta," Universidad Autónoma de San Luis Potosí,*
Álvaro Obregón 64, 78000 San Luis Potosí, SLP, Mexico
[2]*Facultad de Ciencias Químicas, Universidad Autónoma de Chihuahua, Venustiano Carranza S/N, 31000 Chihuahua, Chih., Mexico*
[3]*Departamento de Física, Universidad de Sonora, Boulevard Luis, Encinas y Rosales, 83000, Hermosillo, Sonora, Mexico*
(Received 28 September 2007; published 19 December 2007)

One of the main elements of the self-consistent generalized Langevin equation (SCGLE) theory of colloid dynamics [Phys. Rev. E **62**, 3382 (2000); **72**, 031107 (2005)] is the introduction of exact short-time moment conditions in its formulation. The need to previously calculate these exact short-time properties constitutes a practical barrier for its application. In this Brief Report, we report that a simplified version of this theory, in which this short-time information is eliminated, leads to the same results in the intermediate and long-time regimes. Deviations are only observed at short times, and are not qualitatively or quantitatively important. This is illustrated by comparing the two versions of the theory for representative model systems.

DOI: 10.1103/PhysRevE.76.062502 PACS number(s): 64.70.Pf, 47.57.J−, 61.20.Gy

In recent work a new first-principles theory of dynamic arrest has been proposed [1,2]. This consists essentially of the application of the self-consistent generalized Langevin equation (SCGLE) theory of colloid dynamics [3–6] to the description of the singular behavior characteristic of dynamic arrest phenomena in specific colloidal systems and conditions. The SCGLE theory was originally devised to describe tracer and collective diffusion properties of colloidal dispersions in the short- and intermediate-times regimes [7,8]. Its self-consistent character, however, introduces a nonlinear dynamic feedback, leading to the prediction of dynamic arrest in these systems, similar to that exhibited by the mode coupling theory (MCT) of the ideal glass transition [9]. The resulting theory of dynamic arrest in colloidal dispersions was applied in recent work to describe the glass transition in three monodisperse experimental model colloidal systems with specific (hard-sphere, screened electrostatic, and depletion) interparticle effective forces [1,2]. The results indicate that the SCGLE theory of dynamic arrest has the same or better level of quantitative predictive power as conventional MCT, but is built on a completely independent conceptual basis, thus providing an alternative approach to the description of dynamic arrest phenomena.

There is, however, a possible practical disadvantage of the SCGLE with respect to the MCT, and it refers to the fact that the MCT only requires the static structure factor of the system as an external input, whereas the SCGLE theory requires this information plus other additional static properties involved in the exact short-time conditions that the theory has built-in [5]. As it happens, however, the long-time asymptotic solutions of the relaxation equations that constitute the SCGLE theory are independent of such exact short-time properties [2]. The questions then arise of whether a simplified version of the SCGLE theory, in which this short-time information is eliminated, could be proposed, and to what extent such a simpler theory will still provide a reliable representation of the dynamics of the colloidal system not only in the asymptotic long-time regime, but also at earlier stages. In what follows we demonstrate that there is a simple manner to build this simplified version of the SCGLE theory, and that it is virtually as accurate as the full version, even in the short- and intermediate-time regimes. This finding will greatly simplify the application of the SCGLE theory of dynamic arrest.

Let us summarize the four distinct fundamental elements of the full self-consistent generalized Langevin equation theory of colloid dynamics. The first consists of general and exact memory-function expressions for the intermediate scattering function $F(k,t)$ and its self-component $F_S(k,t)$, derived with the generalized Langevin equation (GLE) formalism [10], which in Laplace space read [3]

$$F(k,z) = \frac{S(k)}{z + \dfrac{k^2 D_0 S^{-1}(k)}{1 + C(k,z)}}, \tag{1}$$

$$F_S(k,z) = \frac{1}{z + \dfrac{k^2 D_0}{1 + C_S(k,z)}}, \tag{2}$$

where D_0 is the free-diffusion coefficient, $S(k)$ is the static structure factor of the system, and $C(k,z)$ and $C_S(k,z)$ are the corresponding memory functions.

The second element is an approximate relationship between collective and self-dynamics. In the original proposal of the SCGLE theory [3], two possibilities, referred to as the additive and the multiplicative Vineyard-like approximations, were considered. The first approximates the difference $[C(k,t) - C_S(k,t)]$, and the second the ratio $[C(k,t)/C_S(k,t)]$, of the memory functions, by their exact short-time limits, using the fact that the exact short-time expressions for these memory functions, denoted by $C^{\mathrm{SEXP}}(k,t)$ and $C_S^{\mathrm{SEXP}}(k,t)$, are known in terms of equilibrium structural properties [5,11]. The multiplicative approximation was devised to describe more accurately the very early relaxation of $F(k,t)$ [6], but the additive approximation was found to provide a more accurate prediction of dynamic arrest phenomena [2]. In this paper, for "full SCGLE theory" we refer to the theory that involves the *additive* Vineyard-like approximation,

$$C(k,t) = C_S(k,t) + [C^{\mathrm{SEXP}}(k,t) - C_S^{\mathrm{SEXP}}(k,t)]. \qquad (3)$$

The third ingredient consists of the independent approximate determination of $F_S(k,t)$ [or $C_S(k,t)$]. One intuitively expects that these k-dependent self-diffusion properties should be simply related to the properties that describe the Brownian motion of individual particles, just like in the Gaussian approximation [7], which expresses $F_S(k,t)$ in terms of the mean-squared displacement (MSD) $\overline{(\Delta x(t))^2}$ as $F_S(k,t) = \exp[-k^2\overline{(\Delta x(t))^2}/2]$. We introduce an analogous approximate connection, but at the level of their respective memory functions. The memory function of $\overline{(\Delta x(t))^2}$ is the so-called time-dependent friction function $\Delta\zeta(t)$. This function, normalized by the solvent friction ζ_0, is the *exact* long wavelength limit of $C_S(k,t)$, i.e., $\lim_{k\to 0} C_S(k,t) = \Delta\zeta^*(t) \equiv \Delta\zeta(t)/\zeta_0$. Thus, we interpolate $C_S(k,t)$ between its two limits, namely,

$$C_S(k,t) = C_S^{\mathrm{SEXP}}(k,t) + [\Delta\zeta^*(t) - C_S^{\mathrm{SEXP}}(k,t)]\lambda(k), \qquad (4)$$

where

$$\lambda(k) \equiv [1 + (k/k_c)^2]^{-1} \qquad (5)$$

is a phenomenological interpolating function, with k_c being the position of the first minimum that follows the main peak of $S(k)$ [5].

The fourth ingredient of our theory is another exact result, also derived within the GLE approach [10], this time for $\Delta\zeta^*(t)$. This exact result may, upon a well-defined simplifying approximation, be converted into the following approximate but general expression [2]:

$$\Delta\zeta^*(t) = \frac{D_0}{3(2\pi)^3 n}\int d\mathbf{k}\left[\frac{k[S(k)-1]}{S(k)}\right]^2 F(k,t)F_S(k,t). \qquad (6)$$

Equations (1)–(6) constitute the full SCGLE theory of colloid dynamics. Besides the unknown dynamic properties, it involves the equilibrium properties $S(k)$, $C^{\mathrm{SEXP}}(k,t)$, and $C_S^{\mathrm{SEXP}}(k,t)$, determined by the methods of equilibrium statistical thermodynamics. We should also point out that Eqs. (1) and (2) are exact results, and that Eq. (6) derives from another exact result. Hence it should not be a surprise that the same results are used by other theories; in fact, the same equations are employed in MCT. The difference lies, of course, in the manner we relate and use them. In this sense, the distinctive elements of the SCGLE theory are the Vineyard-like approximation in Eq. (3) and the interpolating approximation in Eq. (4).

The simplified version of the SCGLE theory is now suggested by the form that these distinctive equations [Eqs. (3) and (4)] attain for times longer than the relaxation time of the functions $C^{\mathrm{SEXP}}(k,t)$ and $C_S^{\mathrm{SEXP}}(k,t)$. Under those conditions, Eqs. (3) and (4) become, respectively,

$$C(k,t) = C_S(k,t) \qquad (7)$$

and

$$C_S(k,t) = [\Delta\zeta^*(t)]\lambda(k). \qquad (8)$$

It is not difficult to see that the original self-consistent set of equations [involving Eqs. (3) and (4)] shares the same long-time asymptotic stationary solutions as its simplified version. Such stationary solutions are given by [2]

$$\lim_{t\to\infty} F(k,t) = \frac{\lambda(k)S(k)}{\lambda(k)S(k) + k^2\gamma}S(k) \qquad (9)$$

and

$$\lim_{t\to\infty} F_S(k,t) = \frac{\lambda(k)}{\lambda(k) + k^2\gamma}, \qquad (10)$$

where γ is the solution of the following equation:

$$\frac{1}{\gamma} = \frac{1}{6\pi^2 n}\int_0^\infty dk\, k^4 \frac{[S(k)-1]^2\lambda^2(k)}{[\lambda(k)S(k) + k^2\gamma][\lambda(k) + k^2\gamma]}. \qquad (11)$$

The parameter γ is the long-time asymptotic value of the MSD, i.e., $\gamma \equiv \lim_{t\to\infty}\overline{(\Delta x(t))^2}$. In the arrested states, this parameter is finite, representing the localization of the particles, whereas in the ergodic states it diverges.

It is then natural to ask what the consequences would be of replacing Eqs. (3) and (4) of the full SCGLE set of equations by the simpler approximations in Eqs. (7) and (8) that no longer contain the functions $C^{\mathrm{SEXP}}(k,t)$ and $C_S^{\mathrm{SEXP}}(k,t)$. Our proposal of a simplified version of the SCGLE theory consists precisely of this replacement, so that the "simplified SCGLE theory" consists of the exact results in Eqs. (1) and (2) along with Eqs. (5) and (6), complemented by the closure approximations in Eqs. (7) and (8).

We have made a systematic comparison of the various dynamic properties involved in the SCGLE theory, including the intermediate scattering function $F(k,t)$, its self-component $F_S(k,t)$, and other tracer-diffusion properties such as the time-dependent friction function $\Delta\zeta^*(t)$, the mean-squared displacement or the time-dependent diffusion coefficient $D(t) \equiv \overline{(\Delta x(t))^2}/2t$. As expected, the scenario of dynamic arrest exhibited by this simpler theory is identical to that provided by the full SCGLE scheme. This is probably not surprising since, as indicated above, both sets of dynamic equations share the same long-time asymptotic behavior and the same asymptotic stationary solutions. What is surprising, however, is the degree of accuracy of the simplified theory in the short- and intermediate-time regimes. In our systematic comparison we considered systems with soft-sphere, hard-sphere, and repulsive Yukawa interactions, systems with attractive (Yukawa) interactions, systems in three and in two dimensions, and both monodisperse and bidisperse systems, in all cases with similar conclusions, that we illustrate with the following examples.

Thus, in Fig. 1 we plot the intermediate scattering function $F(k,t)$ as a function of time, evaluated at the position $k_{\max}$ of the first maximum of the static structure factor of a soft-sphere system. The pair potential, in units of the thermal energy $k_BT = \beta^{-1}$, is given by $\beta u(r) = 1/(r/\sigma)^{2\nu} - 2/(r/\sigma)^{\nu} + 1$ for $0 < r < \sigma$, and it vanishes for $r > \sigma$. The system in Fig. 1 corresponds to $\nu = 18$ and to the volume fractions $\phi \equiv \pi n\sigma^3/6 = 0.515$, 0.60, 0.612, and 0.613. The static structure factor was calculated using the prescription of Verlet and Weis [12]. The results correspond to the simplified version, and to the full version, of the

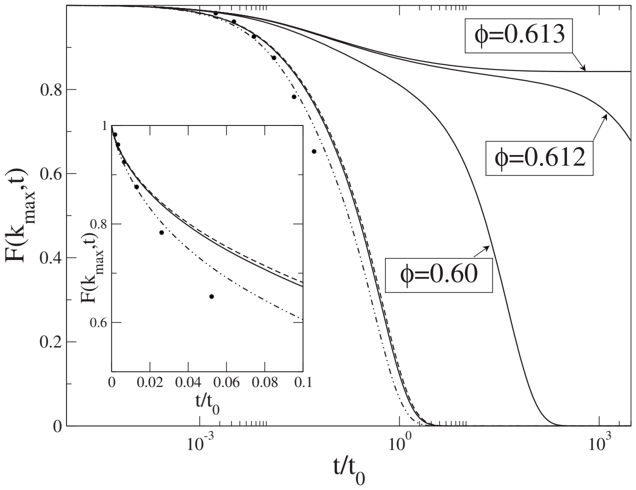

FIG. 1. $F(k,t)$ as a function of time (in units of $t_0 \equiv \sigma^2/D_0$) at the position $k_{\max}$ of the first maximum of $S(k)$ of a soft-sphere system with $\nu=18$ and volume fractions $\phi=0.515$, 0.60, 0.612, and 0.613. For $\phi=0.515$ we show Brownian dynamics data (solid circles) and the results of the simplified (solid line) and the full (dashed line) versions of the SCGLE theory, and of the SCGLE theory with the multiplicative approximation (dot-dashed line); the inset is a closeup of the short-time relaxation of $F(k,t)$. For the other volume fractions we only show the indistinguishable results (solid curves) of the simplified and the full SCGLE theory.

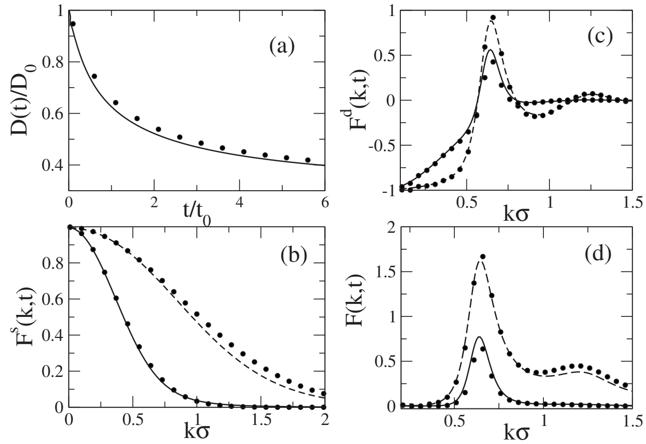

FIG. 2. (a) Time-dependent diffusion coefficient $D(t)$ and intermediate scattering functions, (b) $F^s(k,t)$, (c) $F^d(k,t)$, and (d) $F(k,t)$, of a repulsive Yukawa system with $z=0.15$, $K=500$, and $\phi=4.4\times10^{-4}$. Results of the simplified SCGLE theory for the intermediate scattering functions are shown for times $t=t_0$ (dashed curves) and $t=10t_0$ (solid lines). The solid circles are Brownian dynamics data of Ref. [14]. The full SCGLE theory is not shown since it completely coincides with the BD data.

SCGLE theory. The very first feature to notice is the virtual coincidence of the results of these two approximations; in fact, only for $\phi=0.515$ the difference is appreciable. For the other volume fractions the results are not distinguishable in the scale of the figure, and this includes the vicinity of the glass transition which, as can be seen in the figure, is predicted to occur at $\phi_g=0.613$ for this soft-sphere system. For $\phi=0.515$ we also show the Brownian dynamics data and the results of the SCGLE theory within the *multiplicative* Vineyard-like approximation, both reported in Ref. [6], to recall the fact that the multiplicative approximation sometimes provides a slightly more accurate quantitative description of the initial relaxation of $F(k,t)$ (see the inset). In a longer time scale, as indicated in the main figure, the prediction of the overall relaxation provided by the SCGLE theory complemented with the additive and the multiplicative approximations is quite similar. Furthermore, as discussed in Ref. [2], the additive approximation provides a simpler and more accurate description of dynamic arrest, partly because these phenomena do not seem to depend strongly on the short-time behavior illustrated in the inset of Fig. 1. Thus, from now on, we shall omit further reference to the multiplicative approximation.

A similar situation is illustrated in Fig. 2, this time for a system of colloidal particles interacting through a hard-sphere potential of diameter σ plus an additional long-ranged repulsive Yukawa tail of the form $\beta u(r) = K\exp[-z(r/\sigma-1)]/(r/\sigma)$, with $z=0.15$ and $K=500$. For a volume fraction $\phi_1=4.4\times10^{-4}$, it corresponds to the conditions of Fig. 1 of Ref. [14]. In our present figure, however, we compare the full and the simplified SCGLE theory for the time-dependent diffusion coefficient $D(t)$ and for the intermediate scattering functions $F(k,t)$, $F^s(k,t)$, and $F^d(k,t)[\equiv F(k,t)-F^s(k,t)]$ in the short-time regime, where these differences are expected to be larger. Our present comparison indicates that the new simplified version of the SCGLE theory leads to essentially identical results, even in these time regimes.

Just like the MCT has been extended to mixtures [13], the SCGLE has also been extended to multicomponent colloidal systems [14,15]. Also in this case the simplified version of the SCGLE theory provides virtually the same description as

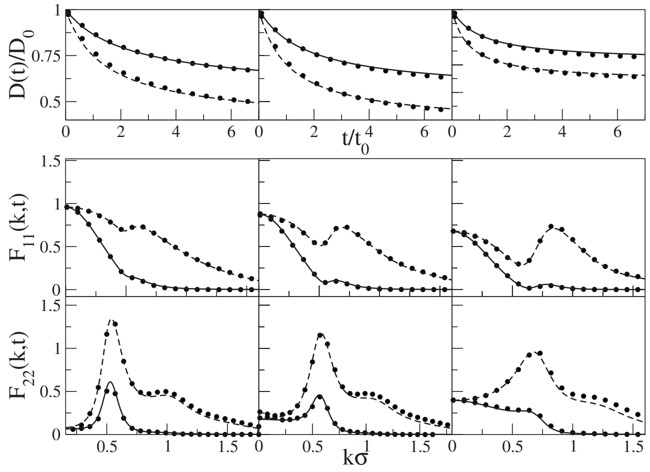

FIG. 3. Time-dependent diffusion coefficients as a function of time [$D_1(t)$, solid lines; $D_2(t)$, dashed lines] and total intermediate scattering functions $F_{\alpha\alpha}(k,t)$ ($\alpha=1,2$) of a repulsive Yukawa mixture with $z=0.15$, $K_1=100$, and $K_2=500$ for $t=t_0$ (dashed lines) and $t=10t_0$ (solid lines). The volume fraction of the more interacting species is kept fixed at $\phi_2=2.2\times10^{-4}$ and ϕ_1 takes the values $\phi_1=7.25\times10^{-5}$ (left column), 2.2×10^{-4} (center column), and 6.6×10^{-4} (right column). The $F_{\alpha\alpha}(k,t)$ of the full SCGLE theory, not shown, completely coincide with the BD data.

the full SCGLE scheme, but its practical application is far simpler. In Fig. 3 a comparison is presented for a binary Yukawa mixture, with pair potential $\beta u_{ij}(r) = \sqrt{K_i K_j} \exp[-z(r/\sigma - 1)]/(r/\sigma)$ $(1 \leq i, \ j \leq 2)$ in which a fraction x_1 of the particles (species 1) interact with a charge parameter $K_1 = 100$ and the other fraction x_2 (species 2) with $K_2 = 500$. The volume fraction of the more interacting species is kept fixed at $\phi_2 = 2.2 \times 10^{-4}$ and ϕ_1 takes the values 6.6×10^{-4} (right column), 2.2×10^{-4} (middle column), and 7.25×10^{-5} (left column), corresponding to $x_1 = 0.75$, $x_1 = 0.5$, and $x_1 = 0.25$. This figure corresponds to the same conditions as Fig. 3 of Ref. [15] and, as in our previous example, the simulated $S(k)$ was employed. It simply confirms the general conclusions of this Brief Report, namely that the simplified SCGLE theory provides a description of the relaxation of concentration fluctuations in colloidal suspensions qualitatively and quantitatively virtually identical to the full SCGLE theory. Its practical implementation, however, is much simpler than either the full SCGLE or the MCT schemes. This has simplified the application of the SCGLE theory to the discussion of dynamic arrest in colloidal mixtures [16] and in colloidal fluids adsorbed in model porous media [17] that we report in separate papers.

This work was supported by the Consejo Nacional de Ciencia y Tecnología (CONACYT, México), through Grants Nos. SEP-2004-C01-47611 and No. SEP-2006-C01-60064, and by FAI-UASLP.

[1] P. Ramírez-González, R. Juárez-Maldonado, L. Yeomans-Reyna, M. A. Chávez-Rojo, M. Chávez-Páez, A. Vizcarra-Rendón, and M. Medina-Noyola, Rev. Mex. Fis. **53**, 327 (2007); eprint arXiv:0712.2071v1.

[2] L. Yeomans-Reyna, M. A. Chávez-Rojo, P. E. Ramírez-González, R. Juárez-Maldonado, M. Chávez-Páez, and M. Medina-Noyola, Phys. Rev. E **76**, 041504 (2007).

[3] L. Yeomans-Reyna and M. Medina-Noyola, Phys. Rev. E **62**, 3382 (2000).

[4] L. Yeomans-Reyna, H. Acuña-Campa, and M. Medina-Noyola, Phys. Rev. E **62**, 3395 (2000).

[5] L. Yeomans-Reyna and M. Medina-Noyola, Phys. Rev. E **64**, 066114 (2001).

[6] L. Yeomans-Reyna, H. Acuña-Campa, F. Guevara-Rodríguez, and M. Medina-Noyola, Phys. Rev. E **67**, 021108 (2003).

[7] P. N. Pusey, in *Liquids, Freezing and the Glass Transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (Elsevier, Amsterdam, 1991).

[8] W. Hess and R. Klein, Adv. Phys. **32**, 173 (1983).

[9] W. Götze, in *Liquids, Freezing and Glass Transition*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Justin (North-Holland, Amsterdam, 1991).

[10] M. Medina-Noyola, Faraday Discuss. Chem. Soc. **83**, 21 (1987).

[11] J. L. Arauz-Lara and M. Medina-Noyola, Physica A **122**, 547 (1983).

[12] L. Verlet and J.-J. Weis, Phys. Rev. A **5**, 939 (1972).

[13] J. Bosse and J. S. Thakur, Phys. Rev. Lett. **59**, 998 (1987).

[14] M. A. Chávez-Rojo and M. Medina-Noyola, Physica A **366**, 55 (2006).

[15] M. A. Chávez-Rojo and M. Medina-Noyola, Phys. Rev. E **72**, 031107 (2005).

[16] R. Juárez-Maldonado and M. Medina-Noyola, eprint arXiv:0711.2021v1.

[17] R. Juárez-Maldonado, M. A. Chávez-Rojo, and M. Medina-Noyola, eprint arXiv:0712.2028v1.