Long-time behavior of the shear-stress autocorrelation function in two-dimensional colloidal fluids

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Brownian dynamics simulations of two-dimensional Yukawa particles have been performed over a range of fluid densities in order to study the long-time behavior of the stress autocorrelation function in simple models for colloidal liquids. The system size and the trajectory length dependence of the shear stress autocorrelation function have been investigated in detail for simulation trajectories of length in excess of $1600\sigma^2/D_0$. The results indicate that the decay of the shear-stress autocorrelation function has a fractional exponential form and is not algebraic in time, certainly up to times $\sim\sigma^2/D_0$ at which time the correlation function has decayed statistically to zero. [S1063-651X(97)02605-6]

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I. INTRODUCTION

Green-Kubo theory has been widely used to compute transport coefficients in computer simulations. The integrand in the Green-Kubo formula is a time correlation function, whose long-time decay is generally held to be nonexponential. This behavior was initially observed by molecular-dynamics MD simulation studies of the velocity autocorrelation function of hard-sphere and disk fluids [1]. These simulations revealed that the velocity autocorrelation function decays algebraically as $t^{-d/2}$, where d is the dimensionality of the system. More extensive simulations of hard-core and other molecular fluids confirmed the existence of this so-called long-time tail behavior [2].

This algebraic decay has also been predicted by kinetic [3] and hydrodynamic mode-coupling theory (MCT) [4]. The velocity autocorrelation function determines self-diffusion (the simplest transport coefficient) and is a one-particle quantity. Mode-coupling and kinetic theories lead one to expect that the decay of the shear-stress autocorrelation function (which determines the shear viscosity) should have the same algebraic form as in the case of the velocity autocorrelation function [5]. It should be noted, however, that kinetic theory only predicts this algebraic decay for the kinetic part of the stress correlation function, whereas the interaction part is far more important at liquidlike densities. The long-time behavior of the the stress autocorrelation function has been computed by MD many times (e.g., [6–8]). These studies showed that the long-time decay of both the kinetic *and* interaction parts appeared to have an algebraic decay consistent with MCT and kinetic theories, although the amplitude of the total correlation function was found to be orders of magnitude greater than predicted by these theories. The viscosity being a collective quantity is less tractable than self-diffusion and the evidence for algebraic decay itself at liquid densities has now been questioned [9–12].

Despite many years of study the issue of the slow decay of the transport time correlation functions is far from being solved satisfactorily. An outstanding problem, caused by the long-time tails, is the divergence of two-dimensional transport coefficients. Very recently, this problem has been reinvestigated independently by Hoover and Posch [13] and Gravina, Ciccotti and Holian [14]. Their extensive equilibrium and nonequilibrium MD calculations of the shear problem in two-dimensional (2D) simple fluids have shown no evidence for a divergence of the shear viscosity with system size and cast doubt on the generality of the divergence argument. The results strongly suggest that viscosity is a meaningful material property in two dimensions. The authors point out the relative importance of fluctuations and surface effects in two dimensions, which both contribute terms of order $N^{-1/2}$ to N-body intensive terms. This fact is not build into the expressions for the transport coefficients, which could be the reason of the long-standing view that 2D transport coefficients diverge.

There is also evidence of a slow decay in the time correlation functions of colloidal suspensions. Experiments carried out on colloidal liquids confirmed the slow decay of the velocity autocorrelation function in 3D colloidal suspensions, but the evidence of its algebraic form was rather equivocal [15–17]. Only recently with the method of diffusive wave spectroscopy has it been possible to measure with sufficient accuracy the decay of the velocity autocorrelation function of a colloidal particle on the fast-time scale of momentum relaxation and confirmed unequivocally its algebraic form $t^{-3/2}$ [18]. This ''short-time'' dynamics is an area of extensive theoretical [19] and numerical investigation [20].

On the time scale of the particle position relaxation, however, the investigations of the long-time form of the transport correlation functions are less well developed for colloidal than for simple liquids. The microscopic dynamics of colloidal or Brownian particles is driven by the Langevin equations, which are substantially different from the Newtonian particle dynamics that are used in MD [21]. Theoretical investigations (based on the weak-coupling and mode-mode-coupling approximations) of strongly overdamped Brownian particle fluids without hydrodynamic interactions predict a $t^{-3/2}$ decay of the time-dependent self-diffusion coefficient

and assert that the shear stress relaxation function (the potential part) decays asymptotically with time as $t^{-7/2}$ [22]. This form of decay is considered to be universal (i.e., does not depend on the thermodynamic state and interparticle interaction). This result has been used as the main assumption in various phenomenological descriptions of the dynamic viscosity of model colloidal suspensions [23–25].

To date there have been very few accurate calculations dealing with the long-time behavior of the stress correlation functions in the model colloidal liquids or liquids of interacting Brownian particles. One reason for this is that such studies require extremely long trajectories for relatively large systems, which make the calculations hardly tractable.

We present results of extensive Brownian dynamics (BD) simulations of the model 2D colloidal suspension. The main aim is to investigate the long-time behavior of the shear-stress autocorrelation function of an interacting Brownian particle liquid.

II. MODEL AND SIMULATION METHOD

We consider a system of N interacting particles suspended in an incompressible fluid of viscosity η_0. The interaction between two particles is modeled by a Yukawa pair potential of the form

$$u(r) = U_0 \exp[-\lambda(r-1)]/r, \tag{1}$$

where r is the distance between the particles, U_0 sets the energy scale, and λ is the screening parameter characterizing the steepness and range of the potential. The Yukawa potential, being the electrostatic part of the Derjaguin-Landau-Verwey-Overbeek potential, is considered to give a good description of the interaction of a dilute charge-stabilized colloidal suspensions [22].

The time evolution of the Brownian particles is determined by the position Langevin equations. When many-body hydrodynamic interactions are neglected the position update algorithm for the particles is [26,27]

$$\mathbf{r}_i(t+\Delta t) = \mathbf{r}_i(t) + \frac{D_0}{k_B T}\mathbf{F}_i \Delta t + \delta\mathbf{r}_i. \tag{2}$$

$\delta\mathbf{r}$ is the random displacement sampled from a Gaussian distribution of zero mean and variance $\langle \delta r^2 \rangle = 2D_0 \Delta t$. $D_0 = k_B T/3\pi\sigma\eta_0$ is the self-diffusion coefficient at infinite dilution. It was set to unity as the calculated quantities are independent of its value. $\mathbf{F}_i$ is the net force, derived from the potential in Eq. (1) acting on particle i. All quantities reported here are in dimensionless units, using σ, σ^2/D_0, and U_0/σ as the characteristic values for length, time, and forces, respectively (σ is a measure of the particle diameter.) Energy is in U_0, temperature is in U_0/k_B, and k_B is the Boltzmann constant.

Our primary aim is to calculate the stress autocorrelation function

$$C_S(t) = \langle \Delta P(t)\Delta P(0)\rangle, \tag{3}$$

where ΔP in two dimensions can represent either P_{xy} or $(P_{xx}-P_{yy})/2$, in our simulations both forms have been calculated and used to reduce the statistical noise. The time
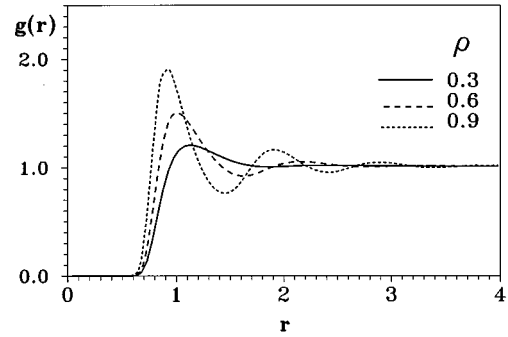

FIG. 1. Radial distribution functions of the 2D Yukawa fluid at three different densities studied in the work for $T=3$.

integral of this function is important as, through the Green-Kubo expression, it gives the shear viscosity

$$\eta_S = \frac{V}{k_B T}\int_0^\infty C_S(t)dt. \tag{4}$$

In our calculations the screening parameter was $\lambda=8$ and the interaction was truncated for $r>2.5$ because of the rapidly decaying nature of the pair potential. As the potential is strongly repulsive a sufficiently small time step had to be used. [A problem with the algorithm in Eq. (2) and in general with BD simulations is that, unlike the MD algorithm, there is no conserved quantity that can be used to check the stability of the time-stepping algorithm.] The procedure to determine an optimum value of Δt was to perform preliminary calculations with different values of Δt and then to choose one such that, for shorter-time steps, all properties are statistically indistinguishable. In addition to this we also have carried out canonical MD and Monte Carlo (MC) simulations to establish the correct structural and thermodynamic values for the system (static properties of a given system calculated by MC, MD, and BD methods have to be the same). The actual BD time step was optimized on the basis of these data and its value in the simulations was $\Delta t = 2\times10^{-5}$.

III. RESULTS AND DISCUSSION

Simulations have been performed at nine state points (ϱ,T) comprising three densities and three temperatures, which are representative of dilute, intermediate, and dense fluid states. The radial pair correlation functions $g(r)$, shown in Fig. 1 for one temperature, confirm the presence of these three regions. In our calculations four different sizes of the system were used: $N=289,625,1600,3600$. The statistical error of the calculated data, at each state point, was estimated by calculating the mean-square deviation of the averages from n equal subruns (the number of subruns in the simulation varied from 6 to 10 depending on the total simulation time).

The resulting normalized shear-stress autocorrelation functions (SSAFs) are slightly density- and temperature-dependent monotonically decaying functions. An example of the function is shown in Fig. 2. The inset clearly shows that for $t>0.3$ the function is statistical zero with fluctuation amplitudes less than 0.005. The contribution of this region to
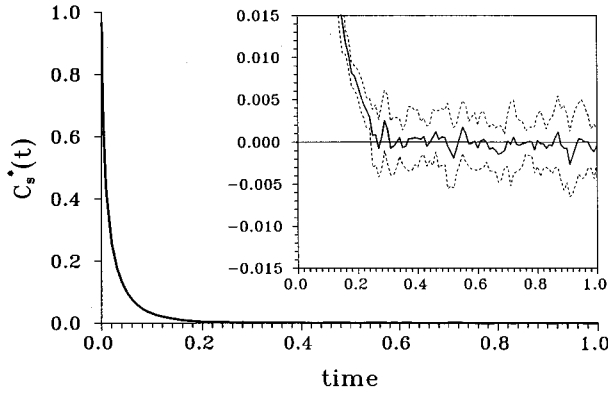
FIG. 2. Normalized shear-stress autocorrelation function for a 2D Yukawa fluid at $\varrho=0.3$ and $T=3$ using $N=1600$ and $t_{max}=1600$. The inset magnifies the long-time region. The dashed lines represent the bounds of the uncertainty of the simulation data (solid line).

the integral (4), at all state points studied, is negligible (less than 0.2%).

The long-time region of the time correlation function is an especially sensitive region of the numerical computation and is subject to a number of possible sources of uncertainty that have to be assessed. We have made a careful study of an $N=625$ system using different computers (Cray J916, SGI Power Challenge, IBM SP2, Hewlett-Packard workstations) to confirm that the influences of the random number generator and the finite number of digits in the floating point number are negligible. Similarly, we showed that the use of different time steps $\Delta t/2$ and $\Delta t/4$ and several potential cutoffs $r_c=2.8,3.0$ did not change our results.

An important source of uncertainty is the number of time steps or the total time length of the simulation t_{max}. As one can see in Fig. 3, the time convergence of the SSAF to the form presented in Fig. 2 is rather sluggish. A simulation for as long as $t_{max}=1000$ is necessary to obtain reliable information about the SSAF at $t\approx0.2$ and a stable value of its integral (and hence shear viscosity). This time is almost two orders of magnitude longer than usually one needs in BD calculations (e.g., for thermodynamic quantities and the self-diffusion coefficient). A further extension of the simulation time does not lead to any significant reduction of the statistical noise for times longer than 0.25. Consequently, the data presented in the figures are shown only up to $t\approx0.25$ [or $\ln(t)=-1.4$].

The size of the system does influence the SSAF, but seems to be less critical than t_{max}. In Fig. 4 the SSAF at $\varrho=0.6$, $T=3$ is shown on a log-log scale. The number dependence of the SSAF is clearly visible for $\ln(t)<-2.6$. The general trend seems to be independent of system size, although all the data taken from the small system $N=289$ differ in a quite systematic way from the data of the large systems $N=1600$ and 3600. The SSAFs of the large systems are mutually consistent. From Fig. 4 it is also clear that the size $N=625$ may not be sufficient to obtain quantitative information about the long-time behavior of the SSAF. The data obtained from the calculations are summarized in Table I.

On the basis of the above analyses it is reasonable to
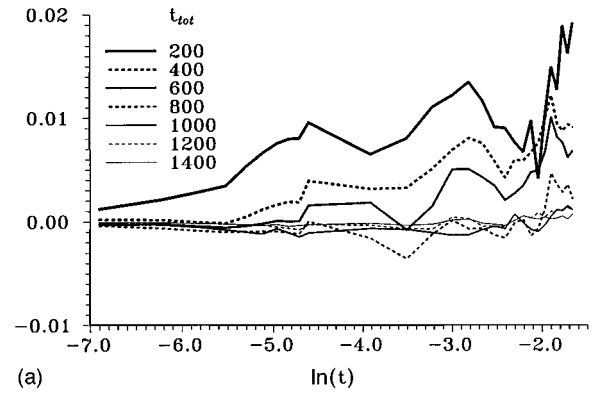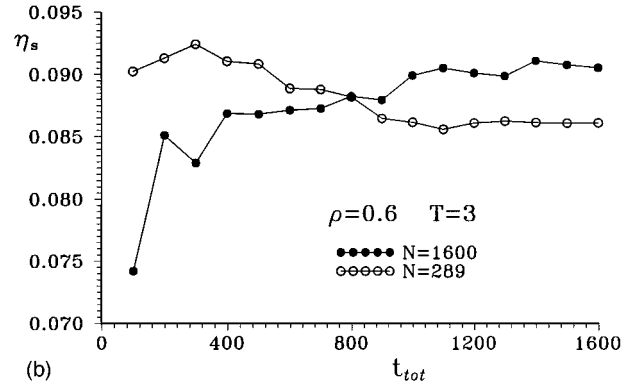
FIG. 3. (a) Deviations of the SSAF from its final form in Fig. 2 as a function of accumulated simulation time t_{tot}. (b) Integral from Eq. (4) after various lengths of simulation t_{tot} have been accumulated.

assume that data for the large system should be sufficiently accurate to make some reliable statements about the possible analytical form of the SSAF decay. A stringent test for the possible analytic form of the $C_S(t)$ decay is to plot the $C_S(t)$ in a logarithmic form. For an exponential decay $\exp(-t/\tau)$, for example, we have that $\ln[C_S(t)]$ is linear with slope $-\tau^{-1}$. For a stretched exponential $C_S(t)=G_\infty\exp(-t/\kappa)^\beta$, $\ln\{-\ln[C_S(t)]\}$ has a slope of β and an intercept of $-\beta\ln(\kappa)$. An algebraic decay $C_S(t)=At^{-\alpha}$, when plotted as $\ln[C_S(t)]$ vs $\ln(t)$, has a slope of $-\alpha$. Therefore, a graphical presentation of these computed functions
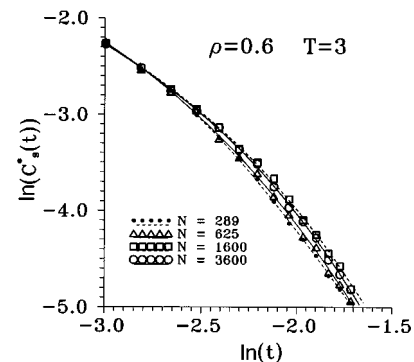

FIG. 4. Normalized shear-stress autocorrelation function in 2D Yukawa fluid at $\varrho=0.3$ and $T=3$ for different system sizes plotted in a log-log representation.

TABLE I. Shear modulus G_∞ and the Green-Kubo shear viscosities η_S for 2D Yukawa fluids at different reduced densities ϱ and temperatures T. N denotes the number of particles, t_{max} the maximum length of time in the trajectory, U the energy per particle, and P the pressure. β and κ are the stretched exponential parameters determined from a least-squares fit. The last row includes data taken from a simulation carried out with an inverse power r^{-18} fluid.

ϱ	T	N	t_{max}	G_∞	η_S	U	P	β	κ
0.3	4	289	1600	0.931(6)	0.0196(8)	0.524	0.659	0.529	0.0123
0.3	3	289	1600	0.799(4)	0.0180(7)	0.419	0.542	0.538	0.0129
0.3	3	625	1600	0.809(2)	0.0183(8)	0.422	0.545	0.559	0.0138
0.3	3	1600	1600	0.805(2)	0.0186(8)	0.421	0.544	0.553	0.0136
0.3	2	289	3200	0.643(3)	0.0148(6)	0.306	0.411	0.542	0.0136
0.3	2	625	1600	0.644(4)	0.0151(7)	0.307	0.413	0.542	0.0140
0.6	4	289	6400	5.22(3)	0.096(2)	1.541	3.801	0.591	0.0121
0.6	3	289	6400	4.62(3)	0.086(3)	1.280	3.243	0.599	0.0126
0.6	3	625	3200	4.62(5)	0.088(3)	1.282	3.247	0.597	0.0127
0.6	3	1600	1600	4.63(3)	0.090(3)	1.283	3.249	0.593	0.0129
0.6	3	3600	1600	4.63(3)	0.090(3)	1.283	3.249	0.594	0.0128
0.6	2	289	6400	3.92(2)	0.080(2)	0.991	2.604	0.585	0.0131
0.9	4	289	6400	16.66(4)	0.278(8)	3.548	12.745	0.668	0.0135
0.9	3	289	6400	15.29(7)	0.274(6)	3.081	11.322	0.618	0.0125
0.9	3	625	1600	15.33(8)	0.276(7)	3.083	11.329	0.621	0.0126
0.9	3	1600	1600	15.43(6)	0.280(7)	3.086	11.338	0.632	0.0128
0.9	3	289	6400	13.67(4)	0.272(5)	2.557	9.961	0.636	0.0136
0.6	3	625	3200	16.32(5)	0.185(6)	0.750	4.047	0.412	0.0035

should indicate clearly which of the analytic forms (if any) the data conform to.

In Fig. 5 we show a $\ln[C_S(t)]$ vs $\ln(t)$ plot for the long-time region at three densities. If the correlation functions were power-law analytic we would expect a linear curve. In fact, there is a continuous decrease in slope with increasing time. The best least-squares fit is provided by the third-order polynomial and at no point can a straight line justifiably be ascribed to the data points. Instead, the linear regression shown in Fig. 6 represents well the data points if they are plotted as $\ln\{-\ln[C_S(t)]\}$ vs $\ln(t)$. It is important to note that despite apparent similarities of the slopes (β) of the curves there is a detectable difference in the least-squares

"stretched" exponents for different densities (see Table I).

We have found additional indications of this lack of universality of the stretched exponent by performing BD calculations with a model colloidal inverse power fluid. As one can see in Fig. 7 (and also in the data given in Table I), the SSAF of the r^{-18} fluid follows a straight line whose slope is clearly different from that of the Yukawa fluid. Therefore, to summarize, our studies give strong evidence that the decay in $C_S(t)$ for $t > 0.05$ [or $\ln(t) < -3$] is very well represented by a stretched exponential.

IV. CONCLUSION

In this work the long-time behavior of the shear stress autocorrelation function in a model 2D colloidal fluid has been investigated. A fluid of repulsive Yukawa particles was
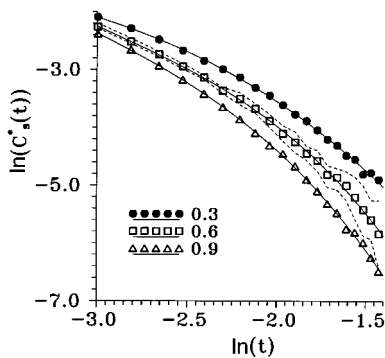
FIG. 5. Shear-stress autocorrelation function in the long-time region represented in logarithmic form at different densities for $N = 1600$. The bounds of the uncertainty in the $\varrho = 0.6$ data are shown as dashed lines. The continuous lines are third-order polynomial least-squares fits to the data points.
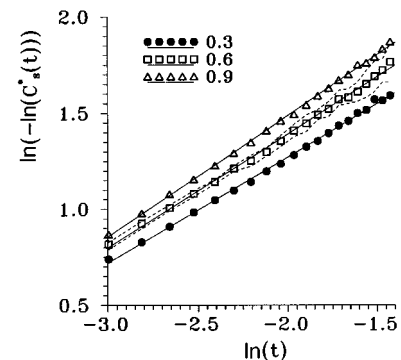
FIG. 6. Same data as in Fig. 5, but plotted as $\ln\{-\ln[C_S(t)]\}$ vs $\ln(t)$.
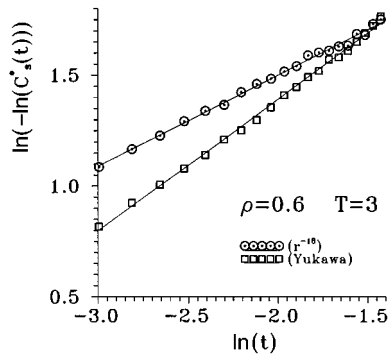
FIG. 7. Same quantities as for Fig. 6, except that the long-time region for the Yukawa and inverse power fluids are compared.

studied at several different state points using a hydrodynamics-free BD technique. We found that in order to study the long-time behavior of the SSAF relatively large systems were necessary (systems of $N > 600$ particles are required in the dense fluid region). We stress, however, that the statistical error depends mainly on the number of integration steps and trajectories for as long as $t = 1000$ should be used to get reliable information about the functional form of these functions. These conclusions are the same as have been found for the MD simulation of model simple fluid transport coefficients [28].

Using the $N = 1600$ systems and very long simulations, an attempt was made to establish the functional form of the time decay of the SSAF. On the basis of the performed analysis we can conclude that in the range of times and system sizes accessible to our BD simulations the form most consistent with the simulation data of the stress autocorrelation functions is not a power law but a stretched exponential. The lack of a universal value of the streched exponent can be viewed as an additional argument supporting this conclusion. If the exponents were the same it might suggest that at much longer times than could be considered here, the functions would converge to a common form more in line with algebraic decay.

Molecular-dynamics simulations carried out by Ladd, Alley, and Alder [11] also gave strong evidence for nonalgebraic decay in time of the shear-stress autocorrelation function for dense hard-sphere fluids (stretched exponential in three dimensions, but exponential in two dimensions). The authors suggest that the reason for nonalgebraic decay is that this relaxation is structural rather than hydrodynamic in origin. It is possible that the same mechanism, i.e., a slow structural relaxation, is responsible also for the stretched exponential decay of the SSAF in Brownian fluids, although more work to confirm this is required.

[1] B. J. Alder and T. E. Wainwright, Phys. Rev. Lett. **18**, 988 (1967); Phys. Rev. A **1**, 18 (1970).

[2] J. J. Erpenbeck and W. W. Wood, Phys. Rev. A **26**, 1648 (1982); **32**, 412 (1985).

[3] J. R. Dorfman and E. G. D. Cohen, Phys. Rev. Lett. **25**, 1257 (1970).

[4] M. H. Ernst, E. H. Hauge, and J. M. J. van Leeuwen, Phys. Rev. Lett. **25**, 1254 (1970). See also *Statistical Mechanics, Part B: Time-Dependent Processes*, Vol. 6 of *Modern Theoretical Chemistry*, edited by B. J. Berne (Plenum, New York, 1977), Chaps. 4–6.

[5] Y. Pomeau and P. Résibois, Phys. Rep. **19**, 63 (1975).

[6] D. J. Evans, J. Stat. Phys. **22**, 81 (1980).

[7] W. W. Wood and J. J. Erpenbeck, J. Stat. Phys. **24**, 455 (1981).

[8] G. P. Morriss and D. J. Evans, Phys. Rev. A **32**, 2425 (1985).

[9] B. J. Alder, *Molecular-Dynamics Simulation of Statistical-Mechanical Systems*, edited by G. Ciccotti and W. G. Hoover (North-Holland, Amsterdam, 1986).

[10] H. Stassen and W. E. Steele, J. Chem. Phys. **102**, 932 (1995).

[11] A. J. C. Ladd, W. E. Alley, and B. J. Alder, J. Stat. Phys. **48**, 1147 (1987).

[12] M. Ferrario, G. Ciccotti, B. L. Holian, and J. P. Ryckaert, Phys. Rev. A **44**, 6936 (1991).

[13] W. G. Hoover and H. A. Posch, Phys. Rev. E **51**, 273 (1995).

[14] D. Gravina, G. Ciccotti, and B. L. Holian, Phys. Rev. E **52**, 6123 (1995).

[15] Y. W. Kim and J. E. Matta, Phys. Rev. Lett. **31**, 208 (1973).

[16] A. Bouiller, J. P. Boon, and P. Deguent, J. Phys. (Paris) **39**, 159 (1978).

[17] P. D. Fedele and Y. W. Kim, Phys. Rev. Lett. **44**, 691 (1980).

[18] J. X. Zhu, D. J. Durian, J. Müler, D. A. Weitz, and D. J. Pine, Phys. Rev. Lett. **68**, 2559 (1992).

[19] B. Cichocki and B. U. Felderhof, Phys. Rev. E **51**, 5549 (1995).

[20] C. P. Lowe and D. Frenkel, Phys. Rev. E **54**, 2704 (1996).

[21] H. Löwen, J. P. Hansen, and J. N. Roux, Phys. Rev. A **44**, 1169 (1991).

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

[23] B. Cichocki and B. U. Felderhof, Phys. Rev. A **46**, 7723 (1992).

[24] B. Cichocki and B. U. Felderhof, Physica A **198**, 423 (1993).

[25] B. Cichocki and B. U. Felderhof, J. Chem. Phys. **101**, 7850 (1994).

[26] D. L. Ermak and J. A. McCamon, J. Chem. Phys. **69**, 1352 (1978).

[27] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987).

[28] D. Levesque and L. Verlet, Mol. Phys. **61**, 143 (1987).