

Interpretation of the complex viscosity of dense hard-sphere dispersions

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The complex viscosity of dense hard-sphere dispersions has been determined recently over a large frequency range. If conceived as a homogeneous system with continuously distributed elasticity and viscosity, the complex viscosity can be described theoretically with a constant relaxation strength and relaxation times $\tau_p = \tau_1/p^2$, with p the relaxation number. This is consistent with the empirical analysis of the data. The distributed elasticity can be interpreted microscopically as due to statistical springs acting between the spheres. The springs are modeled as Fraenkel springs to take into account the excluded-volume effect. The relaxation strength has been calculated quantitatively. The resulting deduced relaxation strengths are in fair agreement with the experimentally observed ones. The given interpretation is compared with literature theory.

The macroscopic stress tensor for a dispersion of hard spheres, of which the complex viscosity has been determined recently,¹ contains contributions of the continuous phase, of the stresslet which is calculated as an integral over the sphere's surfaces and a direct force contribution of type $\langle \mathbf{x}_i \mathbf{F}_i \rangle$ which is the volume average of the dyad of \mathbf{F}_i and \mathbf{x}_i where \mathbf{F}_i is the force acting on a sphere at position \mathbf{x}_i . The forces to be considered for hard spheres are the fluctuating force leading to Brownian motion and the hard spheres interactions.

Batchelor² considered a dilute dispersion in which pairs of spheres can be discerned. For this system he calculated two limiting viscosities: for pure hydrodynamic interactions only and for hydrodynamic interactions plus Brownian motion. In a harmonically oscillating shear flow these limits are found in the real part of the complex viscosity at high (η'_∞) and at low (η'_0) frequencies, respectively. Such a change in η' is pertaining to the occurrence of a shear modulus $G' = \omega\eta''$ which is zero at low frequencies and G'_∞ at high frequencies. Implicitly this elasticity is also given in Batchelor's theory and turned out to be proportional to a^{-3} with a the radius of the spheres. Thus one can calculate an average relaxation time defined as $\tau_a = (\eta'_0 - \eta'_\infty)/G'_\infty$ which is proportional to a^3 . Batchelor's formalism has been used by Russel and Gast³ to include the interactions between the spheres. Their average relaxation time is on the same order as derivable from Batchelor's theory. It decreases with increasing volume fraction. So far a few theoretical

aspects.

On the experimental side an excellent hard-sphere model system came available⁴ while sensitive apparatus for the determination of the complex viscosity^{5,6} has been developed. In a preparatory study⁷ it has been demonstrated that the predicted linear viscoelastic effects exist indeed. Recently the results of an extensive study of hard-sphere dispersions with radii of 28, 46, and 76 nm and volume fractions ϕ between 0.42 and 0.60 have been reported.¹ Compared to theory,^{2,3} the experimental viscoelastic effects are larger in magnitude, the experimental longest relaxation time is longer than the mentioned average relaxation time (by a factor of 5 or more), and it increases with volume fraction while theoretically it decreases. In addition, there is no prediction of the frequency dependence of η^* . These discrepancies are unsatisfactory and in this paper an attempt is made to understand them.

Careful study¹ of the experimental data led to a consistent description of all complex viscosity η^* data with

$$\eta^* - \eta'_\infty = G_1 \tau_1 \sum_{p=1}^M \frac{1}{p^2 + i\omega\tau_1} \quad (1)$$

In (1) the relaxation times $\tau_p = \tau_1/p^2$ with p an integer. The number of relaxation times involved is M . If M and ω are large,

$$\eta^* - \eta'_\infty = 1.11 G_1 \tau_1^{1/2} \omega^{-1/2} (1-i) .$$

This frequency decay is, apart from the mere existence of

elasticity for a hard-sphere dispersion, one of the most striking characteristics of the experimental viscoelastic behavior of this system to understand. The parameters of each sample are η'_∞ , G_1 , and τ_1 , the first depending on ϕ only and the latter two on a and ϕ (see Table I). The temperature was the same for all samples: 25°C. In this manner all data could be plotted on to one master curve.

The understanding of theory which calculates $\eta'_\infty(\phi)$ (only hydrodynamic interactions) is growing⁸⁻¹⁰ but not specific for linear viscoelasticity and will not be pursued in this paper. It turned out that G_1 and τ_1 are at a certain volume fraction proportional to a^{-3} and a^3 , respectively, as predicted in Refs. 2 and 3 by G'_∞ and τ_a , though one may wonder how they are related. A few experimental trends have to be explained since they differ from available theory: the ϕ dependence of τ_1 and G_1 and a possible sequence of τ_p in accordance with $\tau_p = \tau_1/p^2$. To deal with these questions a shift in point of view can be advantageous.

The linear viscoelastic behavior of a system which can be considered as continuous at a certain length scale and which possesses continuously distributed parameters of elastic and viscous nature has been treated by Gross and Fuoss.¹¹ In a previous paper we have already applied this concept on single molecules in dilute polymer solutions.¹² Here we consider the whole system since no discrete elements with viscoelastic properties exist in hard-sphere dispersions.

Consider a fluid with a thickness L along the z axis. Boundary effects in the x and y directions are neglected. The fluid is assumed to be continuous but can be thought to be built up as an elastic medium with shear modulus G_0 [$\sigma(z,t) = G_0 \partial \xi / \partial z$, with $\sigma(z,t)$ and $\xi(z,t)$ the local stress and displacement, respectively, in the y direction] which "feels" in each point a friction force proportional to the local velocity of the elastic medium. The local equation of motion is given by (inertia neglected)

$$G_0 \frac{\partial^2 \xi}{\partial z^2} = f \frac{\partial \xi}{\partial t} \quad (2)$$

(where f is a friction coefficient per unit length with the dimension of viscosity per unit surface) and can be written as a diffusion equation

$$\frac{\partial^2 \xi}{\partial z^2} = k^2 \frac{\partial \xi}{\partial t} \quad \text{with } k^2 = \frac{f}{G_0} \quad (3)$$

At rest, gravity neglected, the situation with no external surface forces at $z=0$ and $Z=L$ gives for the boundary conditions

$$\frac{\partial \xi}{\partial z}(0,t) = \frac{\partial \xi}{\partial z}(L,t) = 0 \quad (4)$$

The solution of (3) is

$$\xi(z,t) = \sum_p [A_p(t) \cos b_p z + B_p(t) \sin c_p z] \quad (5)$$

because the sine and the cosine functions constitute a complete set of orthogonal functions. In (5) $A_p(t)$ and $B_p(t)$ are time-dependent functions and b_p and c_p are constants. Substitution of boundary conditions (4) leads to

$$\xi(z,t) = \sum_p A_p(t) \cos \left[\frac{p\pi}{L} z \right] \quad (6)$$

In a thought experiment each p th deformation can be applied at $t=t_0$ and then be released. The time dependence of $A_p(t)$ is then given by a differential equation with as solution a decay with a relaxation time given by

$$\tau_p = \frac{2fL^2}{G_1} \frac{1}{\pi^2 p^2} \quad (7)$$

In a harmonic shear experiment, the external applied flow field can excite all these normal modes of motions as follows from η^* of such a system. In order to find the complex viscosity of the fluid, a harmonic shear experiment with gap loading is considered. Then $\xi(0,t)=0$ and $\sigma(L,t) = \sigma_0 \exp i\omega t$, while the gap loading implies that the

TABLE I. Experimental parameters τ_1 , G_1 , and η'_∞ [Eq. (1)] of the complex viscosity of hard-sphere dispersions.

	ϕ	$\frac{\eta'_0}{\eta_s}$ ^a	$\frac{\eta'_\infty}{n_s}$ ^a	$\frac{G_1}{nk_B T} \left[1 - \frac{\phi}{\phi_m} \right]^{2/3}$ ^b	$\frac{\tau_1 G_1 \pi^2}{6(\eta'_0 - \eta'_\infty)}$
$a = 28$ nm	0.46	12.9	5.12	2.3	1.04
	0.58	162	10.0	1.9	1.17
	0.60	467±26	16.8	1.5	1.46±0.10
$a = 46$ nm	0.42	9.2	4.26	1.9	0.80
	0.44	12.3	4.98	2.5	0.98
	0.48	18.5	6.34	3.2	0.89
	0.52	35	7.45	2.5	0.91
	0.54	54	9.9	3.1	0.95
	0.57	142	11.4	1.7	0.98
$a = 76$ nm	0.46	14.1	5.75	1.5	0.93
	0.47	17.6	6.77	1.6	0.99
	0.51	28.4	7.43	2.8	1.04

^a $\eta_s = 0.9$ mPas, error 2–3 %.

^b $n = \phi / (\frac{4}{3} \pi a^3)$, $\phi_m = 0.63$ (random closest packing).

wavelength of the shear wave is much larger than L and $\sigma(L, t) = \eta^* \xi(L, t)/L$. Gross and Fuoss¹¹ have solved this problem and find as a solution for η^* expression (1), with $G_1 = 2G_0$ and τ_p given by (7).

It can easily be demonstrated that (1) implies that $\eta' - \eta'_\infty$ and η'' decay with $\omega^{-1/2}$ at high frequencies. Thus a medium with continuous distributed elasticity and viscosity shows the experimentally observed $\omega^{-1/2}$ behavior. The next step is an attempt to interpret G_0 and f in terms of microscopic parameters of the hard-sphere dispersion.

If hard spheres are dispersed in a Newtonian fluid, no microstructural source of elasticity exists. The spheres "feel" each other with an infinite potential when they collide and a zero potential when they are separated. In all situations there is also hydrodynamical interaction. If the hard spheres are contained in a vessel at temperature $T=0$ they can be piled up to closest packing. At finite temperature, however, expansion takes place by Brownian motion until the spheres are dispersed (gravity neglected) in the vessel and have some average distance to each other as if some interaction potential keeps them at those positions. This obviously is a superficial view, since at a larger time scale each individual particle moves over large distances. The occurrence of elasticity can only be of entropic nature. It pertains to the positions of all spheres, but apparently, relevant relative positions are the distances between centers of mass minus the excluded volume distance at closest packing: the excess excluded volume distance. The source of elasticity can be imagined as a network of entropic springs connecting the "surfaces" of the spheres.

The source of friction is clear: the spheres move with friction under influence of the external flow field through the suspending fluid continuously feeling the influence of the presence of other spheres through fluid dynamical interactions. Their friction coefficient can be considered as constant in the frequency range of the experiments in Ref. 1, since inertia effects and the influence of nonsteadiness of the viscous fluid occur at much higher frequencies (see, e.g., Ref. 13).

Assuming N spheres in a vessel the average free energy available for the entropic springs is $(N-1)\frac{3}{2}k_B T$. Each particle is entropically connected with all other spheres, thus $\frac{1}{2}N(N-1)$ springs are present. In polymer rheology entropic springs are often approximated as linear springs¹³ and we follow this line to estimate the shear modulus G_0 due to the entropic springs. Let the force \mathbf{F} between two spheres whose centers of mass are separated by $R\mathbf{e}_R$ be proportional to the excess excluded volume distance (the Fraenkel spring¹⁴),

$$\mathbf{F} = H(R - R_0)\mathbf{e}_R, \quad (8)$$

with H the spring constant. The distance R_0 represents the influence of the excluded volume.¹⁴

On the average the free energy available for a spring is $\frac{3}{2}(N-1)k_B T / [\frac{1}{2}N(N-1)]$. Thus the energy stored per spring is, on the average,

$$\frac{1}{2}H(R - R_0)^2 = 3k_B T / N. \quad (9)$$

For the calculation of G_0 (see also Ref. 12) a spring is

thought to be elongated with a strain ϵ . The deformation energy in a harmonically oscillating strain, where the linear term in ϵ averages out to zero, is

$$\begin{aligned} \frac{1}{2}HR^2\epsilon^2 &= \frac{1}{2}H(R - R_0)^2 \left(\frac{R}{R - R_0} \right)^2 \epsilon^2 \\ &= \frac{3k_B T}{N} \left(\frac{R}{R - R_0} \right)^2 \epsilon^2. \end{aligned} \quad (10)$$

The factor $[R/(R - R_0)]^2$ can be estimated as follows. Consider n spheres with volume fraction ϕ per unit volume. If at this given volume fraction $\phi < \phi_m$ the spheres are not distributed over the unit volume but packed to the volume fraction ϕ_m at closest packing, the volume taken in by the n spheres plus the space in between is ϕ/ϕ_m . Thus the available free space between the dispersed spheres is $1 - (\phi/\phi_m)$. Then

$$\left(\frac{R - R_0}{R} \right)^2 = \left(1 - \frac{\phi}{\phi_m} \right)^{2/3}.$$

If the strain is part of an elongation field given by

$$\begin{pmatrix} -\frac{\bar{\epsilon}}{2} & 0 & 0 \\ 0 & -\frac{\bar{\epsilon}}{2} & 0 \\ 0 & 0 & \bar{\epsilon} \end{pmatrix}, \quad (11)$$

and the direction of the spring is arbitrary in this deformation field, then $\epsilon^2 = \frac{1}{2}\bar{\epsilon}^2$. The energy stored per unit volume is $\frac{3}{2}G_0\bar{\epsilon}^2$. The number of entropic springs attached to the n spheres in a unit volume is $\frac{1}{2}N(N-1) - \frac{1}{2}(N-n)(N-n-1)$. Dividing the contribution of springs pointing outwards by 2 and taking the limit $N \rightarrow \infty$, it follows that

$$G_1 = 2G_0 = nk_B T \left(1 - \frac{\phi}{\phi_m} \right)^{-2/3}. \quad (12)$$

Neglecting excluded volume effects ($\phi=0$) gives $G_1 = nk_B T$, which is consistent with the entropic shear elasticity for point particles at infinite frequency calculated by Zwanzig and Mountain.¹⁵ The proper choice of ϕ_m is related to the sampling of the position configuration space of the centers of mass of the spheres. Long-range order in the fluid below $\phi=0.60$ (as studied experimentally in Ref. 1) is highly improbable, as confirmed by our experiments.¹ Neglecting short-range order, as expressed in the pair correlation function, the first ansatz for ϕ_m is the value 0.63 corresponding to random closest packing. Using this value, G_1 in (12) can be compared with the experimental values (see Table I). There is fair agreement between these values but the excluded volume effects seem to be underestimated. This is easy to understand since the difference can be attributed to the fact that the pair correlation function of hard spheres deviates from 1 for spheres close to each other, which implies that less free space is available than assumed in the foregoing and inclusion of this effect would make G_1 larger.

The next logical step would be to calculate the relaxation time $\tau_1 = fL^2/G_0\pi^2$. From (1) it follows that

$$\eta'_0 - \eta'_\infty = G_1 \tau_1 \sum_{p=1}^{\infty} \frac{1}{p^2} = G_1 \tau_1 \frac{\pi^2}{6} = \frac{1}{3} fL^2.$$

This demonstrates that the calculation of fL^2 is equivalent to the calculation of $\eta'_0 - \eta'_\infty$, a well-known problem but not solved exactly for dense hard-sphere dispersions at the present state of art, and it is of no use to add another simple model.

In Table I the consistency of the experimentally deduced τ_1 , G_1 , and $\eta'_0 - \eta'_\infty$ values within the given analysis is shown by the column $\tau_1 G_1 \pi^2 / [6(\eta'_0 - \eta'_\infty)]$, which should be unity.

The interpretation of the feasibility of (1) for the description of the experimental complex viscosity as given in this paper implies that the relaxation properties

are due to collective modes of motion. The entropic source of elasticity approached as a network of linear springs predicts the relaxation strength, considering the simple approach, quite well, provided that the excluded volume effects are taken into account. The sophisticated theories of Batchelor² and Russel and Gast³ are difficult to interpret from the given point of view. The collective modes of motion of spheres have not been included. The pair approach in Ref. 3 takes into account the excluded volume effect to some extent by means of the proper radial distribution function but thus mixes up the two sphere motions in the several modes while averaging out the influence of the positions of all other spheres. One feels that the average relaxation time from Ref. 3 will be closer to the shorter relaxation times where the relative motion of two spheres is more important. Their average $\tau_a = (\eta'_0 - \eta'_\infty) / G'_\infty$ is a factor of 5 or more shorter than the experimental τ_1 , indeed.

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