On the contribution of direct intermacromolecular interactions to the viscosity of a suspension of hard spheres

George D. J. Phillies

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109
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The contribution of the contact interaction to the shear and bulk viscosities η and η_v of a suspension of hard spheres is evaluated by use of the Green–Kubo integral forms. To lowest (second) order in the volume fraction ϕ, $\eta = \eta_0(1 + 13.44\phi^2)$ and $\eta_v = \eta_{v0}(1 + 4.32\eta_0\phi^2)$. Since [J. Chem. Phys. **67**, 4690 (1977)] direct interactions contribute to the drag coefficient f in first order in the density, a sphere suspension whose dissipative properties include a substantial contribution from direct intermacromolecular interactions is predicted not to show Debye-type behavior, i.e., for such a system f/η will not be independent of concentration.

In a previous paper,[1] the fluctuation–dissipation relation

$$\delta f \hat{v} = \frac{-\beta}{v_0} \left\langle \int_0^\infty dt\, \mathbf{F}(0)\mathbf{F}(t)\cdot\mathbf{v}(t)dt \right\rangle \tag{1}$$

was used to calculate the contribution δf of direct intermacromolecular interactions to the Stokes-law drag coefficient f of a single probe macromolecule. Here $\mathbf{F}(t)$ is the fluctuating force on the probe due to direct interactions between the macromolecules, $\mathbf{v}(t) = v_0\hat{v}$ is the velocity of the probe, $\beta = (K_B T)^{-1}$, and the brackets indicate an ensemble average. $\mathbf{F}(t)$ is determined by concentration fluctuations around the probe. For a suspension of hard spheres, the first order contribution of direct interactions to f was found to be

$$f = f_0\left(1 + \tfrac{8}{3}\varnothing\right) \tag{2}$$

f_0 and $\varnothing$ being the zero-concentration drag coefficient and the volume fraction of the spheres, respectively.

In this note, the same approximations are used to evaluate the contribution of the hard sphere interaction to the shear and bulk viscosities η and η_v of a hard sphere suspension. The viscosities are obtained from the Green–Kubo forms[2]

$$\eta = \frac{\beta}{V} \int_0^\infty dt\, \langle \sigma_{xy}(0)\sigma_{xy}(t) \rangle\,, \tag{3a}$$

$$\eta_v = \frac{\beta}{V} \int_0^\infty dt\, \langle \sigma_{xx}(0)\sigma_{yy}(t) \rangle\,, \tag{3b}$$

where

$$\sigma_{ab}(t) = \sum_{i=1}^{N} \left\{ p_{ia}(t)p_{ib}(t)m_i^{-1} + r_{ia}(t)F_{Tib}(t) \right\} - \langle \sigma_{ab} \rangle \tag{4}$$

The subscripts a, b refer to the cartesian axes x, y, z; $p_{ia}(t)$, $r_{ia}(t)$, and $F_{Tia}(t)$ are the ath component of the momentum, position, and total applied force for particle i at time t. The force $\mathbf{F}_{Ti}(t)$ is composed of a part $\mathbf{F}_s(t)$ due to the solvent and a part $\mathbf{F}_i(t)$ due to direct intermacromolecular interactions, the latter being[1]

$$\mathbf{F}_i(t) = \frac{iK_B T}{(2\pi)^3} \sum_k \mathbf{k}a_k(t)h^{(2)}(\mathbf{k})\, e^{i\mathbf{k}\cdot\mathbf{r}_i(t)}\,, \tag{5}$$

where $a_k(t)$ is the kth spatial fourier component of the concentration at time t, $h^{(2)}(\mathbf{k}) = \int dr(g^{(2)}(\mathbf{r}) - 1)\exp(i\mathbf{k}\cdot\mathbf{r})$,

and $g^{(2)}(r)$ is the two-body equilibrium radial distribution function. For diffusing macromolecules, whether interacting or not,[3]

$$\langle a_k(0)a_{-k}(t) \rangle = \langle |a_k(0)|^2 \rangle\, e^{-D_m k^2 t}\,, \tag{6}$$

where D_m is the mutual diffusion coefficient.

It is convenient to assume that the direct and solvent-based forces $\mathbf{F}_i(t)$ and $\mathbf{F}_{si}(t)$ are uncorrelated. In this case, cross-terms between $\mathbf{F}_{si}(t)$ and $\mathbf{F}_i$ vanish; the contribution of direct interactions to the viscosities then arises from terms of σ_{ab} which depend solely on $\mathbf{F}_i$. Since $\mathbf{F}_{si}$ and $\mathbf{F}_i$ have greatly different correlation times, this assumption is not unreasonable; however, it clearly cannot be exact. The momentum p_i is determined by the forces acting on particle i at all previous times; for time intervals comparable with the (long) correlation time of $\mathbf{F}_i$, $\langle p_i(t)\mathbf{F}_i(t+\tau) \rangle$ and $\langle p_i(t)p_i(t+\tau) \rangle$ are therefore nonvanishing. For simplicity, possible corrections due to hydrodynamic interactions between the particles are ignored.

Substitution of Eq. (4) into Eqs. (3a) or (3b) gives rise to four terms; in a liquid, the term proportional to $\langle F_i F_j \rangle$ ought to be expected to dominate. For the shear viscosity, this term is

$$(I) = \frac{-K_B T}{(2\pi)^6 V} \left\langle \int_0^\infty dt \sum_{i,j=1}^{} r_{ix}(0)r_{jx}(t) \sum_{k,q} a_k(0)a_q(t) \right.$$
$$\left. \times k_y q_y h^{(2)}(\mathbf{k})h^{(2)}(\mathbf{q}) \exp[i(\mathbf{k}\cdot\mathbf{r}_i(0) + \mathbf{q}\cdot\mathbf{r}_j(t))] \right\rangle. \tag{7}$$

Integration by parts and the substitution $\Delta r_{ij}(t) = r_j(t) - r_i(0)$ yields

$$(I) = \frac{K_B T}{(2\pi)^6 V} < \int dt \sum_{\substack{ij \\ kq}} \exp[i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}_i(0) + i\mathbf{q}\cdot\Delta r_{ij}(t)]k_y q_y$$
$$\times \frac{\partial}{\partial k_x}\frac{\partial}{\partial q_x}[a_k(0)a_q(t)h^{(2)}(\mathbf{k})h^{(2)}(\mathbf{q})] \tag{8}$$

The difficulty with further simplification of Eq. (8) is that $\Delta r_{ij}(t)$ depends on both $r_i(0)$ and on the $a_q(t)$. This is readily seen for the self $(i = j)$ term. Ignoring inertial effects,

$$\Delta r_{ii}(t) = \int_0^t d\tau (\mathbf{v}_{Br}(\tau) + \mathbf{F}_i(\tau)/f)\,, \tag{9}$$

$\mathbf{v}_{Br}(\tau)$ being the Brownian (solvent-induced) component of particle i's velocity and f being its drag coefficient. $\mathbf{F}_i(\tau)$ is given by Eq. (5). On expanding the exponential in $\mathbf{q} \cdot \Delta \mathbf{r}_{ij}(t)$ of Eq. (8), the average over the $a_k(t)$ is

$$\left\langle \left\{ 1 + i\mathbf{q} \cdot \left(\int d\tau (\mathbf{v}_{Br}(\tau) + \frac{iK_BT}{(2\pi)^3} \sum_{\mathbf{p}} \mathbf{p} h^{(2)}(\mathbf{p})e^{i\mathbf{p}\cdot\mathbf{r}_i(\tau)} \right. \right. \right.$$
$$\left. \left. \left. \times a_{\mathbf{p}}(\tau) \right) + \cdots \right\} \frac{\partial}{\partial k_x} \frac{\partial}{\partial q_x} [a_k(0)a_q(t)h^{(2)}(k)h^{(2)}(q)] \right\rangle \quad (10)$$

the second term of which depends on $\mathbf{r}_i(0)$ through the exponential. The terms in $\langle \mathbf{v}_{Br}a_k a_q \rangle$ vanish because the random force $\mathbf{F}_{si}(t)$ due to the solvent is not correlated with the concentration fluctuations $a_k(t)$. The random phase approximation

$$\langle a_k(0)a_p(\tau)a_q(t) \rangle = 0 \quad (11)$$

eliminates all other terms in Eq. (10) except for the very first. In this approximation, the average over initial particle positions $\mathbf{r}_i(0)$ yields $(2\pi)^3\delta(\mathbf{k}+\mathbf{q})$, so that the self term is

$$I_s = \frac{-K_BT}{(2\pi)^3} \frac{N}{V} \int dt \langle e^{i\mathbf{k}\cdot\Delta\mathbf{r}(t)} \rangle$$
$$\times k_y^2 \left\langle \left[\frac{\partial}{\partial k_x} \frac{\partial}{\partial q_x} a_k(0)a_q(t) h^{(2)}(k)h^{(2)}(q) \right] \right\rangle_{q=-k}, \quad (12)$$

where the derivatives must be taken *before* setting $q = -k$. For hard spheres of radius R_0, in the low-concentration limit

$$h^{(2)}(k) = 32\pi R_0^3 \frac{\sin(2kR_0) - (2kR_0)\cos(2kR_0)}{(2kR_0)^3} \quad (13)$$

In the same limit, if $k = -q$,

$$\langle a_k(0)a_q(t) \rangle = \frac{N}{V} e^{-D_m k^2 t}, \quad (14a)$$

$$\langle e^{-i\mathbf{k}\cdot\Delta\mathbf{r}(t)} \rangle = e^{-D_m k^2 t} \quad (14b)$$

where $D_m = K_BT/6\pi\eta R_0$ is the diffusion coefficient of the particles to lowest (zeroth) order in the concentration. Corrections to D_m due to concentration effects contribute to I_s terms which are higher order in $\varnothing$ than those we wish to consider here.

On performing a series of elementary (albeit tedious) integrals, one obtains

$$I_s = \frac{336}{25} \eta\varnothing^2 \quad (15)$$

All contributions to η from direct interactions, other than those included in I_s, are now argued to be of order $\varnothing^3$ or greater. These terms, which involve the little-studied triple dynamic structure factor

$$S^{(3)}(k,q,t,t') = \langle a_k(0)a_q(t)a_{k-q}(t') \rangle, \quad (16)$$

will not be considered further. Specifically, the exponential in the distinct part of Eq. (10) may be rewritten

$$[\exp\{i(k+q)\cdot\mathbf{r}_i(0) + i\mathbf{q}\cdot[\mathbf{r}_j(0) - \mathbf{r}_i(0)] + i\mathbf{q}\cdot\Delta\mathbf{r}_{ij}(t)\}.$$

The factor $\exp[i\mathbf{q}\cdot\Delta\mathbf{r}_{ij}(0)]$ is, in the first approximation, the spatial fourier transform of the distinct part of the radial distribution function, which vanishes for noninteracting particles, and is thus of order at least N/V. The sum over i and the factor of $a_k(0)a_q(t)$ each give an

additional factor of N/V, so that the distinct part of Eq. (8) is like $(N/V)^3$.

Eqs. (3a), (3b) also contain terms

$$\text{(II)} = \frac{1}{V} \left\langle \sum_{i,j} \mathbf{p}_i(t)\mathbf{p}(t)\mathbf{r}_j(t')\mathbf{F}_j(t') \right\rangle m_i^{-1} \quad (16a)$$

$$\text{(III)} = \frac{1}{V} \left\langle \sum_{ij} \mathbf{p}_i(t)\mathbf{p}_i(t)\mathbf{p}_j(t')\mathbf{p}_j(t') \right\rangle m_i^{-1}m_j^{-1} \quad (16b)$$

By comparison with Eq. (9), $\mathbf{p}_i(t)$ contains a factor proportional to $m_i F_i(t)/\zeta$. (The contribution to $\mathbf{p}_i(t)$ from $\mathbf{v}_{Br}(t)$ has the very short correlation time (m_i/ζ) and may be neglected.) From Eq. (5), each factor of $\mathbf{F}_j(t)$ yields a factor $a_k(t)$. Eq. (16a) is thus proportional to $\langle a_k(t)a_q(t)a_p(t') \rangle$, which has been assumed to vanish. In Eq. (16b), the sum on i yields a first factor of N/V. The average over the forces is proportional to $\langle a_k(t)a_{k'}(t)a_q(t')a_q(t') \rangle$. Since $a_k(t)$ is a Gaussian random variable, this term includes both factors eliminated by the random phase approximation and factors $\langle |a_k(t)|^2 \rangle \langle |a_q(t)|^2 \rangle$, which are like $(N/V)^2$. The leading terms of Eq. (16b) are therefore also of order $(N/V)^3$. Eq. (15) is therefore a complete expression to order $\varnothing^2$ for the contribution of the hard-sphere interaction to η.

An essentially identical series of arguments allows evaluation of Eq. (3b) for the bulk viscosity, leading to the result

$$\eta_v = \eta_{v0} + \frac{108}{25}\eta_0\varnothing^2, \quad (17)$$

where η_{v0} is the bulk viscosity of the pure fluid and η_0 is the viscosity factor from the diffusion coefficient.

It is instructive to compare the results obtained here [Eqs. (15), (17)] with results from theoretical hydrodynamic calculations and from experiments on sphere suspensions. The concentration dependence of the viscosity may be expanded

$$\eta = \eta_0(1 + a_1\varnothing + a_2\varnothing^2 + a_3\varnothing^3 + \cdots). \quad (18)$$

Einstein[4] predicted $a_1 = 2.5$. For a_2, a variety of values have been calculated, including 9.15,[5] 12.6,[6] and 14.1.[7] Cheng and Schachman[8] report an experimental determination of a_1 and a_2 for a suspension of polystyrene latex finding good agreement with their data for $a_1 = 2.5$ and $a_2 = 14.1$. However, as Cheng and Schachman emphasized in their original paper, their measurements did not reach sufficiently high concentrations to determine a_3 with any accuracy, so there may be a substantial truncation error in the experimental determination of a_2. For a suspension of glass spheres, Manley and Mason[9] report $a_2 = 12.7$.

Calculated values for the hydrodynamic and contact contributions to a_2 are thus nearly the same size. Furthermore, if the hydrodynamic and direct forces are not correlated, their contributions to η_v are independent and additive, in which case one predicts $a_2 \sim 25$–27, which is somewhat larger than indicated by experiment. The discrepancy could be eliminated if the two forces were correlated, as would occur if the fluctuating hydrodynamic force on a particle were reduced by the presence of other, nearby particles.

In many systems, the Stokes' Law drag coefficient f depends linearly on the solution viscosity η, so that f/η is a constant. If one measures f indirectly, as by measuring the tracer diffusion coefficient $D_T = K_B T/f$, one continues to find

$$D_T \eta = \text{constant} \tag{19}$$

The calculation gives here indicates that Eq. (19) will not obtain in suspensions whose dissipative behavior includes a substantial concentration dependence due to direct interactions. From the previous calculation,[1] the contact interaction makes a first order contribution to f:

$$f = f_0 (1 + \tfrac{9}{4}\varnothing); \tag{20}$$

in contrast, the direct interactions contribute to η only in order $\varnothing^2$. f/η is therefore concentration dependent.

Detecting this effect in a hard sphere system may be somewhat difficult. Hydrodynamic interactions between the Brownian particles make a contribution to f as important as that of direct interactions; they also contribute to η in order $(N/V)^1$. However, it was first noted by Mazo[10] that, in a low-salt suspension of charged particles, electrostatic interactions can increase f far more effectively than the contact interaction does. An identical effect will obtain for the direct contribution to η. Since increasing the charge of a protein molecule has but a slight effect on its hydrodynamic interactions, the effects predicted above will probably be more prominent in a suspension of highly charged particles.

The results of this note appear to provide a qualitative explanation for the experimental results of Weissman and Ware,[11] who studied the ionic strength dependence of the mutual diffusion coefficient D_m and viscosity η of a solution of bovine serum albumin of average charge $\langle z \rangle = -20$. They found that f (as obtained from D_m) and the viscosity (as measured directly) both change with

decreasing ionic strength, but that f changes far more dramatically than η. In order to obtain quantitative agreement between the theory presented above and the experimental results of Weissman and Ware, it would at least be necessary to repeat the above calculations while using a form for $h^{(2)}(k)$ corresponding to a screened electrostatic interaction. This is not as easy as it might appear. Bovine serum albumin has a very large fixed electric dipole moment (~ 400 D),[12] which tends to dominate any electrostatic interaction calculation, greatly complicating the averaging procedure.

ACKNOWLEDGMENTS

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