New Theory of Transport
in Dilute Suspensions and Pure Fluids
II. Intrinsic Shear and Bulk Viscosities

Wokyung Sung
Department of Physics
State University of New York at Stony Brook
Long Island, New York 11794

and

G. Stell
Departments of Mechanical Engineering and Chemistry
State University of New York at Stony Brook
Long Island, New York 11794

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We calculate the intrinsic shear and bulk viscosities of a hard-sphere solute in a hard-sphere solvent by using the ideas, developed in the preceding paper, of an effective collision radius and effective reduced mass of a solute-solvent collision, which differ from the bare radius and reduced mass because of the presence of the surrounding solvent treated as a continuum. We combine these ideas with the development of an extended hydrodynamic theory. Our final result incorporates both the Enskog theory and the extended hydrodynamic description of the solvent, so as to include both molecular collisional effects and hydrodynamic collective effects. Our synthesis of the two descriptions yields intrinsic viscosities that are analytically simple and manifest the correct hydrodynamic results in the limit $\sigma_{11}/\sigma_{22} \to 0$ with solvent density fixed, as well as a reasonable approach to the Enskog results when $\sigma_{11}/\sigma_{22} \geq 1$. Here $\sigma_{11}$ and $\sigma_{22}$ are the diameters of the solvent and solute particles, respectively.
1. INTRODUCTION

A well-known and long-standing problem in hydrodynamics is calculation of the effective viscosity of a suspension. Since the pioneering work of Einstein on the intrinsic shear viscosity of a dilute suspension\(^1\) many workers have dealt with generalizations of his treatment to include such features as higher concentration of suspended solute particle, their nonspherical shapes, etc.\(^2\) However, all these hydrodynamic considerations are based on the assumption that the solute consists of macroparticles large enough to permit the treatment of the solvent as a continuum. To our knowledge, however, no work has been fully successful in generalizing the hydrodynamic result to the case of a solute particle of arbitrary dimension and mass in a way that yields the correct hydrodynamic result in the limit of large solute particle.

Here, we present a microscopic theory of shear and bulk viscosities of dilute suspension by utilizing the idea and results of the preceding paper.\(^3\) In I, we derived the generalized boundary condition (B.C.) and the effective contact distance \(\sigma\) and reduced mass \(\mu\) for solute-solvent collisions, which (along with the use of hydrodynamics for \(r \geq \sigma\)) effectively describe the microscopic translational motion of the solute particle. This description was found to yield a sensible translational diffusivity, for the molecular solute, and yields as well the exact hydrodynamic limit. Our notations and definitions will be identical to those of paper I.
Cited equations preceded by the letter I will refer to equations found in paper I.

Since our hard-sphere model for the molecular interaction does not allow the transfer of the angular momentum by collision, the hydrodynamic limit of the intrinsic shear viscosity is not $5/2$, the Einstein value that results from the usual stick B.C. Our result from (I-3-4) (I-3-12) will be unity for slip B.C. However, the intrinsic bulk viscosity obtained by us, apparently for the first time,

$$\langle \kappa \rangle_H \equiv \lim_{\xi_2 \to 0} \frac{\kappa_{\kappa} - \kappa}{\xi_2 \eta} = \frac{4}{3} + \frac{\kappa}{\eta},$$

is common to both boundary conditions.

Our presentation of this work is as follows: In sec. II we give a brief summary of our previous work on the shear and bulk viscosities based solely on Enskog theory. While Enskog theory yields reasonable approximations for a small solute particle, it is found to yield artificial divergences in $\{\eta\}$ and $\{\kappa\}$ that go like $\sigma_{22}/\sigma_{11}$ in the limit $\sigma_{22}/\sigma_{11} \to \infty$. In sec. III, we follow Batchelor's\textsuperscript{5} approach in defining the bulk stress, through which the effective viscosities are identified hydrodynamically. Utilizing the effective contact radius and generalized boundary condition of paper I, we obtain the intrinsic shear and bulk viscosities that yields the correct hydrodynamic limit. In sec. IV, we compare two theories of intrinsic viscosities: Enskog theory and the extended hydrodynamics of sec. III. Through a synthesis
of the two theories, the effective reduced masses appropriate to the intrinsic shear and bulk viscosities are introduced in sec. IV in such a way as to fully reflect the molecular nature of the solvent. The result incorporates all of the desired features of the Enskog theory for $\sigma_{22}/\sigma_{11} \leq 1$ and the hydrodynamic theory in the limit $\sigma_{22}/\sigma_{11} \to \infty$ (with $n_1$ fixed).
II. THE VISCOSITIES OF A BINARY MIXTURE: ENSKOG THEORY

In the kinetic-theory treatment, the suspension can be viewed as a binary mixture. The suspended (solute) particle is treated as a molecular entity in common with the solvent particle; each is described by a probability density function (DF).

Enskog theory gives an expression for $p_M$, the pressure (stress) tensor in the binary mixture with trace concentration of component 2 (solute), in terms of probability DF’S $f_1(r,V,t)$:

$$p^M = \frac{p^M}{2} + \frac{p^{12}}{2} + \frac{p^{21}}{2}$$  \hspace{1cm} (2-1)

$$p^{11} = \int m_1(V_1 - u)(V_1 - u)f_1(r,V_1,t)dV_1$$

$$+ \frac{m_1}{2} \sigma_{11} \gamma_{11} \int dV_1 dV_2 \sigma(\gamma_{11})^2 \sigma \gamma(\gamma_{11})$$

$$\times f_1^0 f_1^0 \left[ 1 + \phi_1(r,V_1,t) + \phi_1(r,V_1,t) \right]$$

$$+ \frac{1}{2} \sigma_{11} \gamma \ell n f_1^0 / f_1^0 \right]$$

$$p^{12} = \mu_1 \sigma_{12} \gamma_{12} \int dV_2 dV_1 \sigma(\gamma_{12})^2 \sigma \gamma(\gamma_{12})$$

$$\times f_1^0 f_2^0 \left[ 1 + \phi_1(r,V_1,t) + \phi_2(r,V_2,t) \right]$$

$$+ \frac{1}{2} \sigma_{12} \gamma \ell n f_1^0 / f_2^0 \right].$$

The quantities appearing here and in the rest of the equations of this paper are all defined in I, to which we refer the reader. By using the Standard Chapman-Enskog method, 6,7 we find

$$p^M = p^M - 2n^M_d - 3k^M \Delta I$$  \hspace{1cm} (2-2)

$$p^{11} = p^{11} - 2n^{11} d - 3k^{11} \Delta I$$  \hspace{1cm} (2-3)

$$p^{12} = p^{12} - 2n^{12} d - 3k^{12} \Delta I$$  \hspace{1cm} (2-4)
where the shear and bulk viscosities of the mixture, by using the lowest Sonine polynomial approximation, was calculated through the first order $\xi_2$, the volume fraction of the solute.\(^4\)

Here

\[
\eta^M = \eta^1 + \eta^{12} = (\eta)_0 + \xi_2(\eta)_1
\]

\[
(\eta)_0 = \left\{ \frac{1}{Y_{11}} \left[ 1 + \frac{8}{5}\xi_1 Y_{11}^0 \right]^2 + \frac{768}{25\pi}\xi_2 Y_{11}^0 \right\} \eta^B
\]

\[
(\eta)_1 = \left\{ \frac{1}{Y_{11}} \left[ 1 + \frac{8}{5}\xi_1 Y_{11}^0 \right] \left( \frac{2}{5} (1+q) \right)^3 \left[ 1 + \frac{\mu_{12}}{m_1} \right] Y_{11}^{12} - \frac{Y_{11}^0}{Y_{11}^{11}} + \frac{8}{5}\xi_1 Y_{11}^{11,2} \right\} \eta^B
\]

\[
+ \left\{ \frac{768}{25\pi}\xi_2 Y_{11}^0 \right\} \left( \frac{1}{Y_{11}^{11}} \left[ 1 + \frac{8}{5}\xi_1 Y_{11}^0 \right] \left( \frac{2}{3} \right)^3 \left[ 1 + \frac{\mu_{12}}{m_1} \right] Y_{11}^{12} - \frac{5}{12} \right\}
\]

\[
+ \frac{96}{25\pi}\left( \frac{2\mu_{12}}{m_1} \right) \left( \frac{1+q}{1+q} \right)^4 \xi_1 Y_{11}^{12}
\]

\[
+ \frac{2}{5} \left( \frac{\mu_{12}}{m_1} - 1 \right) \left( 1+q \right)^3 \xi_1 Y_{11}^{12}
\]

\[
+ \xi_1^{-1} \left[ \frac{1}{Y_{11}^{11}} \left( \frac{2}{5} \right)^3 \left[ 1 + \frac{8}{5}\xi_1 Y_{11}^0 \right] \left( \frac{2}{3} \right)^3 \left[ 1 + \frac{\mu_{12}}{m_1} \right] Y_{11}^{12} - \frac{5}{12} \right]
\]

\[
+ 4 \left[ \left( 1+q \right)^2 \left[ \frac{2\mu_{12}}{m_1} \right] \left( \frac{1}{1+q} \right) \right] \left( \frac{2}{3} \right)^3 \left[ 1 + \frac{\mu_{12}}{m_1} \right] \xi_1 Y_{11}^{12}
\]

\[
\kappa^M = \kappa^1 + \kappa^{12} = (\kappa)_0 + \xi_2(\kappa)_1
\]

\[
(\kappa)_0 = \frac{256}{5\pi} \xi_2 Y_{11}^0 \eta^B
\]

\[
(\kappa)_1 = \left\{ \frac{256}{5\pi} \xi_2 Y_{11}^0 \right\} \left[ \frac{32}{5\pi} \left( \frac{2\mu_{12}}{m_1} \right) \right] q^{-1} (1+q)^4 \xi_1 Y_{11}^{12}
\]

\[
+ \frac{4\sqrt{2}}{5} \frac{\mu_{12}}{m_1} \left[ pq(1+q)^2 \right] \left[ \frac{3}{12} \left( \frac{1}{Y_{11}^{11}} \right)^{-1} \left( \frac{3}{12} \right)^3 \frac{\mu_{12}}{m_1} \right] \xi_1 Y_{11}^{12}
\]

where
\[ p = \frac{m_1}{m_2}, \quad q = \frac{\sigma_{11}}{\sigma_{22}} \]

\[ \gamma_{ij}^{0} = \gamma_{ij} \mid \xi_2 = 0, \quad \gamma_{ij,k}^{0} = \frac{\partial}{\partial \xi_k} \gamma_{ij} \mid \xi_2 = 0. \]

For the pressure contributions, we find

\[ p^M = p_{11}^{11} + p_{12}^{12} = (P)_0 + \xi_2 (P)_1 \quad \text{(2-7)} \]

\[ (P)_0 = n_1 kT \left( 1 + 4\xi_1 \gamma_{11}^{0} \right) \]

\[ (P)_1 = n_1 kT \left\{ 4\xi_1 \gamma_{11}^{0} + (1+q) \gamma_{12}^{0} \right\}. \]

The viscosities and pressure in the pure solvent are found from the expression of \( p_{11} \) in which \( \xi_1 \) is replaced by \( \xi_1^0 \), the volume fraction of the pure solvent

\[ \eta_{10} = \left\{ \frac{1}{\gamma_{11}^{0} (\xi_1^0)} \left( 1 + \frac{8}{5} \xi_1 \gamma_{11}^{0} (\xi_1^0) \right)^2 + \frac{768}{25\pi} \xi_1^{0.2} \gamma_{11}^{0} (\xi_1^0) \right\} \eta^B \quad \text{(2-8)} \]

\[ \kappa_{10} = \frac{256}{5\pi} \xi_1^{0.2} \gamma_{11}^{0} (\xi_1^0) \eta^B \quad \text{(2-9)} \]

\[ p_{10} = n_1 kT \left( 1 + 4\xi_1^{0.0} \gamma_{11}^{0} (\xi_1^0) \right). \quad \text{(2-10)} \]

Here \( \xi_1^0 \) is generally different from \( \xi_1 \) as exemplified as below.

To compare the viscosities of the mixture and those of the pure solvent, each measurement of the viscosities should be made under common thermodynamic condition. Keeping the pressure and temperature of the mixture unchanged from that of the pure solvent, we have, from (2-7) and (2-10)

\[ p_{10} = p^M \quad \text{(2-11)} \]

or

\[ n_1 kT \left( 1 + 4\xi_1^{0.0} \gamma_{11}^{0} (\xi_1) \right) = n_1 kT \left( 1 + 4\xi_1 \gamma_{11}^{0} (\xi_1) \right) + \xi_2 \left( 4\xi_1 \gamma_{11}^{0} + (1+q) \gamma_{12}^{0} \right). \]
As was shown previously, this equality demands the change of the solvent density after the mixing, given by

$$\xi_1 = \xi_1^0 (1 - M \xi_2) \quad (2-12)$$

where

$$M(\xi_1^0, q) \equiv -\{\xi_1\} = \frac{1}{\xi_1^0} \frac{q^3 + (1+q)^3 \xi_1^0 \xi_2^0 Y_{10}^0 (\xi_1^0, q) + 4 \xi_1^0 \xi_2^0 Y_{11,2}^0 (\xi_1^0, q)}{1 + 8 \xi_1^0 \xi_2^0 Y_{11}^0 (\xi_1^0) + 4 \xi_1^0 \xi_2^0 Y_{11,1}^0 (\xi_1^0)}.$$ 

Physically, $M$ is the ratio of the overall volume increase to the total volume of the solute mixed. This difference between $\xi_1$ and $\xi_1^0$ results in a change in the viscosity $(n)_0$ (2-3) by

$$\xi_1^0 \Delta (n)_0 \equiv -M_1^0 \xi_1^0 \frac{\partial (n)_0}{\partial \xi_1^0} \bigg|_{\xi_1^1 = \xi_1^0} = -M_1^0 \xi_1^0 \frac{\partial n_1^0}{\partial \xi_1^0}.$$ 

We express the change of the viscosities by the nondimensional intrinsic quantities defined by

$$\{\eta\} \equiv \lim_{\xi_2 \to 0} \frac{\eta^M - \eta_{10}}{\xi_2^0 \eta_{10}} \quad (2-14)$$

$$\{\kappa\} \equiv \lim_{\xi_2 \to 0} \frac{\kappa^M - \kappa_{10}}{\xi_2^0 \kappa_{10}} \quad (2-15)$$

Substituting the relation (2-11), we finally arrive at

$$\{\eta\}_E = \{\Delta (n)_0 + (n)_1\}/\eta_{10} \quad (2-16)$$

$$\{\kappa\}_E = \{\Delta (\kappa)_0 + (\kappa)_1\}/\eta_{10} \quad (2-17)$$

The results are plotted vs. $q^{-1} = \sigma_{22}/\sigma_{11}$ in the case $m_1/m_2 = q^3$ for several densities of the solvent (Figure 1, 2, 3). For $Y_{ij}$, the expressions of MCSL adequately modified by us are used. (See the appendix of I.) It is observed that in the limit $q \to 0$ the results show artificial divergences that go like $q^{-1}$. These singular deviations from the conventional hydrodynamic results that are exact
in this limit appears to stem from the same cause as the failure of Enskog diffusivity in this limit—the assumption of velocity chaos, (i.e., the lack of the velocity correlation) which breaks down for collision between the large solute and small solvent particle at high solvent density. We shall discuss how to remedy this in sec. IV. However, Enskog theory does reflect an important exact molecular symmetry—the vanishing of the intrinsic viscosities at $q = 1, \rho = 1$, i.e. mixing of identical particles at fixed pressure and temperature does not change the viscosities. As the size of the solute particle becomes smaller ($q > 1$), the Enskog theory is expected to improve because of the larger possibility of uncorrelated solute-solvent collisions. The only approximation imbedded in the expressions (2-5), (2-6) is the lowest Sonine polynomial approximation which is expected to be good as long as the solute mass is not very much smaller than that of the solvent.
III. EXTENDED HYDRODYNAMIC THEORY OF VISCOSITIES OF THE DILUTE SUSPENSION

While the hydrodynamic viewpoint distinguishes the fluid from the solute particles through the boundary condition, it is often possible to regard the solute-fluid mixture as a homogeneous continuum and to ascribe to it certain effective properties (e.g. shear and bulk viscosities). This is possible when the dimension of the (solute) particles and the average separation between them are much smaller than the length scale describing the suspension as a whole. This situation is precisely analogous to the one which pertains to the Chapman-Enskog solution for the kinetic equation of binary mixture, in which the fluid mixture is considered as locally homogeneous in the hydrodynamic variables.

Einstein's original method of deriving the effective shear viscosity involves evaluation of the additional dissipation of energy due to the presence of the particles.\textsuperscript{1,10,11} As straightforward operationally as it is, this method is still controversial, since it involves a subtle nonconvergent integral. To bypass this difficulty, we follow Batchelor\textsuperscript{5} in deriving the linear constitutive relation between the bulk stress and the velocity gradients, through which the effective viscosities are identified. While yielding the identical result as Einstein's method, this will also provide a conceptional parallel to the kinetic-theory expression (2-2). A modification, however, will be made to incorporate
consideration of the bulk viscosity, which appears to have been neglected in conventional hydrodynamic treatments.

We can regard the suspension as statistically homogeneous over a sample volume \( V \) which is chosen to be small macroscopically and yet large enough to contain many particles. The ensemble average of the stress \( \frac{p}{g} \) is expressed as identical to the average over \( V \):

\[
\langle \frac{p}{g} \rangle = \frac{1}{V} \int_V \frac{p}{g} \, dV .
\]  

This can be written as

\[
\langle \frac{p}{g} \rangle = \frac{1}{V} \int_{V - \Sigma V_{\sigma}} \left( \frac{p}{g_2} - 2n_g - 3 \kappa \Delta I \right) \, dV + \frac{1}{V} \int_{\Sigma V_{\sigma}} \frac{p}{g} \, dV
\]  

(3-2)

where \( V_{\sigma} (= \frac{4}{3} \pi \sigma^3) \), \( A_{\sigma} \) are the volume and surface area generated by the effective contact distance (radius) \( \sigma = \frac{1}{2} (\sigma_{11} + \sigma_{22}) \) (I-3-14), the summation being over the solute particles inside \( V \). Substituting

\[
\int_{V_{\sigma}} \frac{p}{g} \, dV = \int_{A_{\sigma}} (P \cdot R) n \, dA
\]  

(3-3)

as a result of \( \nabla \cdot \frac{p}{g} = 0 \), and

\[
\langle \nabla \cdot u \rangle = \frac{1}{V} \int_V \nabla \cdot u \, dV
\]

\[
= \frac{1}{V} \int_{V - \Sigma V_{\sigma}} \nabla \cdot u \, dV + \frac{1}{V} \int_{\Sigma A_{\sigma}} u \cdot n \, dA
\]  

(3-4)

we get

\[
\langle \frac{p}{g} \rangle = \frac{1}{V} \int_{V - \Sigma V_{\sigma}} \left( (P - \eta_{\text{g}}) \, dV - \kappa \langle \Delta I \rangle + \langle \frac{p}{g} \rangle \right) \, dV
\]  

(3-5)

where \( \langle \frac{p}{g} \rangle \), the "particle stress" or "force dipole strength" is defined by
This is identified as the contribution to the bulk stress by the particles and is certainly the counterpart to $p_{12}^{12}$ (2-4). Let us decompose it into two parts:

$$<p^P>_o = \frac{1}{V} \sum \int_{A_o} \left[ (P \cdot r)_n + \eta(u_n + n u) - \frac{2}{3} u \cdot n \right] dA$$

$$+ \kappa u \cdot n I] dA \quad (3-6)$$

The surface integral involving the flow of the unperturbed solvent, converted into a volume integral, is calculated to be

$$<p^P>_o = \frac{1}{V} \sum \int_{A_o} \left[ P \cdot r_n + (p^0 \cdot r)_n + \eta(u^0_n + n u^0) - \frac{2}{3} u^0 \cdot n I \right]$$

$$+ \kappa u^0 \cdot n I] dA \quad (3-7)$$

$$<p^P>_r = \frac{1}{V} \int_{A_o} \left[ (P' \cdot r)_n + \eta(u' n + n u') - \frac{2}{3} u' \cdot n I \right]$$

$$+ \kappa u' \cdot n I] dA \quad (3-8)$$

The surface integral involving the flow of the unperturbed solvent, converted into a volume integral, is calculated to be

$$<p^P>_o = \frac{1}{V} \sum \int_{A_o} (P + p^0) \quad (3-9)$$

where the identity

$$\overline{(nn)}_{ij} = \frac{1}{A} \int n_i n_j dA = \frac{1}{3} \delta_{ij}$$

has been utilized.

In an extremely dilute suspension of effectively isolated particles the integral (3-8) may be evaluated from knowledge of the flow field due to one particle. Substituting (I-4-14), (4-15c), (I-4-21c), (I-4-21d) into (3-8) one finds after a lengthy but straightforward calculation
\[\langle p^p \rangle_E = \frac{1}{V} \sum \sigma_{ij} \eta \left[ d^0 \cdot \overline{nn} \left( -\frac{3Q}{\eta \sigma^3} + 10\varepsilon^{-5} \right) \right. \]
\[\left. + \frac{1}{15} \left( \frac{15Q}{\eta \sigma^3} - 25\varepsilon^{-5} \right) \right] \]
\[= \frac{V}{V} \sum d^0 \left( \frac{Q}{\sigma^3} \right) \]

(3-10)

where

\[\overline{nn} \cdot \overline{nn} = \frac{1}{15} \delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk} \]

has been used. The contribution of the flow field due to the infinitesimal compression (I-4-28), (I-4-37) can be found by retaining only the first order in \(\omega\)

\[\langle p^p \rangle_\phi = \frac{V}{V} \sum (4\eta+3\kappa)\Delta^0, \]

(3-11)

where \(\Delta^0\) should be understood as an inverse Fourier transform of \(\Delta_\omega\) (I-4-27). The Stokes flow (I-4-15b) is found to yield only vanishing contribution.

Summing up all the contributions, we obtain

\[\langle p^p \rangle = \frac{V}{V} \sum \left\{ \langle p^p \rangle^0 + 3 \left( \frac{Q}{\sigma^3} \right) d^0 + (4\eta+3\kappa) \phi_0 \Delta^0 \right\}. \]

(3-12)

By noting the identity

\[\frac{V}{V} \sum X = \xi \langle X \rangle \]

(3-13)

where \(\xi = N_2 V / V\), \(N_2\) being the total number of the solute particles inside \(V\), we obtain

\[\langle p^p \rangle = \xi \left[ \langle p^p \rangle^0 \right] + 3 \left( \frac{Q}{\sigma^3} \right) \phi_0 \langle \Delta^0 \rangle. \]

(3-14)

The total stress (3-5), then is
\[ \langle P \rangle = \langle P_e + P^0 \rangle \frac{I}{2} - 2\eta \langle d \rangle - 3\kappa \langle \Delta \rangle I \]
\[ + \xi (3Q/ \sigma^3) \langle d^0 \rangle + (3\kappa + 4\eta) \phi_0 \langle \Delta^0 \rangle \]. \quad (3-15)

From \( \langle d \rangle = \langle d^0 \rangle \), resulting from the spatial homogeneity inside \( V \) that requires \( \nabla <u'> = \nabla <u'> = 0 \), we finally find
\[ \langle P \rangle = \langle P_e + P^0 \rangle \frac{I}{2} - 2\eta \langle d \rangle \{1 - \xi (3Q/ 2\eta \sigma^3)\} \]
\[ - 3\kappa \langle \Delta \rangle I \{1 - \xi \{1 + \frac{4\eta}{3\kappa} \phi_0 \}\} \]
\[ = \langle P_e + P^0 \rangle \frac{I}{2} - 2\eta^* \langle d^0 \rangle - 3\kappa^* \langle \Delta^0 \rangle I \] \quad (3-16)

where \( \eta^* \), \( \kappa^* \) are to be identified as the effective viscosities.

Here we see that in this hydrodynamic formulation, the pressures of the suspension and the unperturbed solvent are automatically regarded as being equal:
\[ \langle P \rangle = \langle P_e + P^0 \rangle. \quad (3-17) \]

By utilizing the results (I-4-21c), (I-4-37) we find the effective viscosities to be
\[ \eta^* = \eta \{1 - (3Q/2\eta \sigma^3) \xi\} \]
\[ = \eta \left(1 + \frac{15H \cdot 40}{15H + 24} \xi \right) \quad (3-18) \]
\[ \kappa^* = \kappa \left\{1 - \left(1 - \frac{4\eta}{3\kappa} \phi_0 \right) \xi\right\} \]
\[ = \kappa \left\{1 - \xi \left(1 + \frac{4\eta}{3\kappa}\right) \left\{\frac{H(1 - 3\lambda) - \xi}{H + \frac{1}{3}}\right\}\right\} \]

where
\[ H \equiv H(\sigma) \equiv \frac{\xi_E(\sigma)}{\xi_H(\sigma)} = \frac{32 \Xi_{12}^2 m_1}{5\pi \left(\frac{2\mu_{12}}{m_1}\right)^{1/2}} \xi_1 q^{-1} (8q + 1)^{1/4} \lambda_{111} \frac{\lambda_{111} Y_{11}}{C_\eta^2 \eta} \]
\[ \lambda \equiv \frac{\pi}{48} \left\{\left(\frac{m_1}{m_2}\right)^2 - \frac{1}{2} \left(\frac{m_1}{\mu_{12}}\right) \frac{Y_{11}}{Y_{12}(\sigma)} \left(\frac{\sigma_{11}}{\sigma}\right)^3\right\}, \]
We find the intrinsic viscosities

\[
\{\eta\}_{h\sigma} \equiv \lim_{\xi_2 \to 0} \frac{\eta^*-\eta}{\xi_2 \eta} = \frac{15H-40}{15H+24(\sigma_{22})}\left(\frac{2\sigma}{\xi_2 + \xi_2^2}\right)^3
\]

\[
= \frac{15H-40}{15H+24(\beta q+1)^3}
\]

(3-20)

\[
\{\kappa\}_{h\sigma} \equiv \lim_{\xi_2 \to 0} \frac{\kappa^*-\kappa}{\xi_2 \eta} = \left(\frac{4}{3} + \frac{\kappa}{\eta}\right)H(1-3\lambda)-\frac{\kappa}{\eta}\left(\frac{2\sigma}{\xi_2 + \xi_2^2}\right)^3
\]

\[
= \left(\frac{4}{3} + \frac{\kappa}{\eta}\right)H(1-3\lambda)-\frac{\kappa}{\eta}(\beta q+1)^3
\]

(3-21)

wherein the subscripts \(h\sigma\) indicate our hydrodynamic results with generalized BC and the effective contact radius \(\sigma\).

In the limit \(q = \sigma_{22}/\sigma_{11} \to \infty\) with \(n_1\) fixed, i.e. \(H \to \infty\), \(2\sigma/\sigma_{22} \to 1\), \(\beta \to 0\), \(\lambda \to 0\), we obtain

\[
\{\eta\}_H = 1
\]

\[
\{\kappa\}_H = \frac{4}{3} + \frac{\kappa}{\eta}
\]

(3-22)

(3-23)

which is indeed the exact conventional hydrodynamic result with the slip BC. The bulk viscosity (3-23) still holds true for the stick BC which leads us to the Einstein value \(\{\eta\}_H = 5/2\) for the shear viscosity. The results (3-20) and (3-21) are shown (along with the Enskog results) in Figs. 1, 2, 3 in the case \(m_1/m_2 = q^3\), with use of the viscosities of pure fluid given by (I-3-9), (I-3-10).
IV. SYNTHESIS OF TWO THEORIES

The Enskog theory and the extended hydrodynamic theory represent two opposite extremes. The former describes well the short-time collision dynamics, the latter the long-time collective effect of the fluid; the regime best described by each theory is the one poorly described by the other.

This complimentarity of the two theories was well exemplified by the result of translational diffusivity in paper I. There the function $H(\sigma)$ or $H(\sigma, \omega)$ emerges as a criterion that determines the relative validity of the two theories: For large $H$, the hydrodynamic description is good and prevails over the kinetic (Enskog) theory. On the other hand, a smaller value of $H$ guarantees greater validity of the Enskog-theory description. This argument is an obvious one in light of the fact that $H \sim \sigma/t$, where $t$ is the mean free path of the solvent. We argue that this is also true for the shear and bulk viscosities, as shall be shown below.

In sec. II, we found the Enskog results for the viscosities diverge like $q^{-1}$ in the hydrodynamic limit $q \to 0$, as a symptom of the velocity-chaos assumption. A closer look at the term responsible for such divergence reveals that this term is proportional to $H(\sigma)$. For smaller value of $H(\sigma)$, this description would naturally be better. In contrast, in the extended hydrodynamic results of sec. III (based on the generalized boundary condition and the effective collision radius), it was found that the hydrodynamic limit is
achieved as $H$ goes to infinity. This is strong evidence that this extended hydrodynamic result improves with higher solvent density (i.e., higher $H$) as shown by the considerable overall similarity at higher $\xi_1^0$ between the Enskog and hydrodynamic result for small values of $q^{-1}$ (where the Enskog results are presumably at their best). The later results do not reflect the identity of all molecules at $q = 1 = p$, (i.e., $\{\eta\} = \{\kappa\} = 0$ at $q = 1 = p$) and deviation from this important symmetry condition is more serious at the lower densities. Such evidence leads us to conclude that the relative validity of hydrodynamic theory and Enskog theory is essentially determined by the size of $H$ in the case of the viscosities as well as diffusivity.

Here we describe a scheme to correct the two theories of the viscosities simultaneously in a way to synthesize the two disparate and defective theories into one more exact theory. This will be done in much the same manner that was described in the case of the translational diffusion in paper I. For correction to the Enskog results, we write $\{X\}$, the intrinsic quantity associated with $X$, as

$$\{X\} = \lim_{\xi_2 \rightarrow 0} \frac{X^M - X_{10}}{\xi_2 X_{10}} = \lim_{\xi_2 \rightarrow 0} \frac{M_M X_E^M - C_X X_{10E}}{\xi_2 C_X X_{10E}}$$

$$= \{X\}_E + \{C_X\}$$

where $C_X^M$, $C_X$ are the correction factors to the Enskog viscosities for the mixture and pure fluid, and
\[
\{C_X\} = \lim_{\xi_2 \to 0} \frac{C_X^M - C_X}{\xi_2 C_X}
\]

(4-2)

Our central problem is to determine \(\{C_X\}\). Since \(\{X\}_E\) has a term responsible for a divergence that is proportional to \(H\), in the limit \(q \to 0\) or \(H \to \infty\), the correction factor \(\{C_X\}\) should contain a term linear in \(H\) so that it cancels the divergence. In view of the condition \(\{C_X\} = 0\) at \(q = 1 = p\), we may write

\[
\{C_X\} = aH - a(1)H(1)
\]

(4-3)

where the argument 1 represents the point \(q = 1 = p\). This equation defines and introduces an unknown variable \(a\) which generally depends on \(p\) and \(q\) as well as \(\xi_1^0\). Since \(H\) vanishes as \(\xi_1^0 \to 0\), the Eqs. (4-1) and (4-3) naturally incorporates the Enskog result in the low density limit, as it should.

On the other hand, correction to the hydrodynamic result (3-20), (3-21) is to be obtained by introducing \(\mu\), the effective reduced mass that will include the molecular nature of the solute and solvent. Replacing \(\mu_{12}\) in \(H\) by \(\mu\), the equations (3.20) and (3.21) take the form

\[
\{X\}_{H\sigma_{\mu}} = \{X\}_H(\beta q + 1)^3 \frac{aH-A}{aH+B}
\]

(4-4)

if \(\lambda\) is neglected in (3.21), where \(\alpha = (\mu/\mu_{12})^{3/2}\), and \(\{X\}_H = 1\), \(A = 8/3\), \(B = 8/5\) for shear viscosity and \(\{X\}_H = 4/3 + \kappa/\eta\), \(A = \kappa/\eta\), \(B = 4/3\) for bulk viscosity. We neglect \(\lambda\) on the basis of its direct computation, which suggests that contribution to (3-21) is small. The numerical consequences of this approximation are absorbed into
the value of \( \alpha \), which we must now determine. From (4-1), (4-3), (4-4) we have a relation

\[
\{X\} = \{X\}_E + b\alpha H - b(1)\alpha(1)H(1) \\
= \{X\}_H(\beta q + 1)^3 \frac{\alpha H - A}{\alpha H + B},
\]

where the substitution \( \alpha = b\alpha \) has been made. Multiplying by \( E = H^{-1} \) for convenience, we have

\[
E\{X\}_E + \gamma - \gamma(1)H(1)E = \{X\}_H(\beta q + 1)^3 \frac{\alpha - AE}{\alpha + BE} E
\]

where \( \gamma = b\alpha \). To determine \( \alpha \) and \( \gamma \), we can follow exactly the same procedure that we described in the preceding paper (I). However, in the case of intrinsic viscosities, we have one more condition represented by (1-5-23), i.e. \( \{X\} = 0 \) at \( q = 1 = p \).

The simplest nontrivial approximation is obtained by making an ad hoc assumption that \( b \) is independent of \( p \) and \( q \) and that the dependence of \( \{C_X\} \) on \( q \) and \( p \) is only given through \( H(\sigma, \mu) = \alpha H \) (4-5) the only factor that emerges in our binary dynamics in the bath of solvent continuum. Utilizing an important observation that \( \mu \rightarrow \mu_{12} \), i.e., \( \alpha \rightarrow 1 \) in the limit \( q \rightarrow 0 \), and the fact that \( \{X\} \rightarrow \{X\}_H \) in this limit, we get from (4-5), (2-5), (2-6), the following conditions for the shear and bulk viscosities, respectively,

\[
0 = \frac{96}{25\pi} \left( \frac{2\mu_{12}}{m_1} \right)^{1/2} q^{-1} (\xi_{1}^{0}, 0)_{\xi_1}^{0} (\xi_{12}^{0}, q=0) + b \frac{32}{5\pi} \left( \frac{2\mu_{12}}{m_1} \right)^{1/2} \\
\times \xi_{1}^{0} q^{-1} \frac{(1+4\xi_{112}^{0})}{C_{\eta}^{A} \eta^{10} / \eta_{B}}.
\]
0 = \frac{32}{5\pi} \left( \frac{2\mu_{12}}{m_1} \right)^{\frac{3}{2}} q^{-1} \xi_1^0 \tilde{\xi}_1^0 (\xi_1^0, q=0) + b \frac{32}{5\pi} \left( \frac{2\mu_{12}}{m_1} \right)^{\frac{3}{2}}

\times \xi_1^0 q^{-1} \left( \frac{1+4\xi_1^0\gamma_{111}^0}{C_{\eta}} \right) \frac{\eta^{10}}{\eta^B},

which must be satisfied we get rid of the q^{-1} divergence as q \to 0.

We find by noting \gamma_{12}^0 (\xi_1^0, q=0) = 1+4\xi_1^0\gamma_{111}^0 (I-3-13), \eta^{10}/\eta^B = \Lambda_\eta (I-3-9),

that

\begin{align}
\text{for the shear and bulk viscosities, respectively. In addition, the} \\
\text{condition \{X\} = 0 at q = 1 = p requires that} \\
\alpha(1)H(1) = A, \\
\text{which enables us to rewrite (4-5) as a quadratic equation for } \alpha H - A \\
\{X\}_E + b(\alpha H - A) = \{X\}_H (\beta q+1)^3 \frac{\alpha H - A}{\alpha H + B}.
\end{align}

The root of the above equation that satisfies the condition (4-11) is

\begin{align}
\alpha H - A = (2b)^{-1} & \left[ - \{X\}_E - b(A+B) + \{X\}_H (\beta q+1)^3 \\
& - \{ [\{X\}_E + b(A+B) - \{X\}_H (\beta q+1)^3]^2 \\
& - 4b(A+B) \{X\}_E \right]^{\frac{1}{2}}
\end{align}

We find \{C_X\} and \alpha:

\begin{align}
\{C_X\} = \frac{1}{2} & \left[ - \{X\}_E - b(A+B) + \{X\}_H (\beta q+1)^3 \\
& - \{ [\{X\}_E + b(A+B) - \{X\}_H (\beta q+1)^3]^2 \\
& - 4b(A+B) \{X\}_E \right]^{\frac{1}{2}}
\end{align}
\[ \alpha = H^{-1} \{ A + (2b)^{-1} \left[ -\{X\}_E - b(A+B) + \{X\}_H(\beta q+1)^3 \right. \\
\left. - \left[ (\{X\}_E + b(A+B) - \{X\}_H(\beta q+1)^3 \right]^{1/2} - 4b(A+B)\{X\}_E^{1/2} \right] \}, \tag{4-15} \]

and our final result is

\[ \{X\} = \{X\}_E + \{C_X\} = \{X\}_H(\beta q+1)^3 \frac{\alpha H - A}{\alpha H + B} \]

\[ = \{X\}_E - \frac{1}{2} \left( \{X\}_E + b(A+B) - \{X\}_H(\beta q+1)^3 \right) \\
+ \left[ (\{X\}_E + b(A+B) - \{X\}_H(\beta q+1)^3 \right]^{1/2} - 4b(A+B)\{X\}_E^{1/2} \right]. \tag{4-16} \]

In Figs. 4 and 5, we present the results of our theory (4-16) for the case \( \xi_1^0 = 0.4 \) and \( p = q^3 \). To emphasize the region of small value of \( q = \sigma_{11}/\sigma_{22} \) the trends are plotted against \( q \) instead of \( q^{-1} \), along with the results of the other theories that we have considered: Enskog theory and hydrodynamic theories based on the conventional BC and the generalized BC with and without modification of the parameters. Although the ad hoc assumption concerning our choice of \( b \) is hard to fully justify or test in the absence of MD results for mixtures, our results seem to yield an adequate description for the approach to the Enskog theory and to the hydrodynamic description around the points \( q = 1 \) and \( q = 0 \), respectively. Furthermore, our result supports the expectation that the Enskog theory is more likely to be exact for larger value of \( q \).

Noting that \( \{n\}_E \to -\infty \) as \( q \to -\infty \) for \( \delta > Q \) (where \( \delta \) was defined through \( p = q^\delta \)), (4-14) in this limit results in

\[ \{C_n\} \to 64/25, \tag{4-17} \]
which is negligible compared to $\{\eta\}_E$. Since the divergence of $\{\eta\}_E$, which is found to go as $q^3$ for $\delta > 0$ in the limit $q \rightarrow \infty$, does not lead to a singular behavior but to finite value in the change of the viscosity $\Delta \eta = \eta \{\eta\} \xi_2$ in light of the fact that $\xi_2 / \xi_1 = (n_2/n_1)q^{-3}$, $\{C\}_n$ itself gives a vanishingly small contribution. Thus, in the region $1 < q < \infty$, the correction to the Enskog value of $\{\eta\}$ approaches to asymptotically zero as $q$ become large. This is striking and encouraging because in deriving (4-14), (4-15), (4-16) no attempt has been made to match the two theories in the region $0 < q < \infty$. For bulk viscosity, our result shown in Fig. 5 also displays similar trends. However, the bulk viscosity exhibits different limiting behavior in the limit $q \rightarrow \infty$, i.e. it goes to positive infinity as $q^{1+\delta+3}$, and thus $\{C\}_\kappa$ does not approach a finite value. Therefore our choice of $b$ appears to be too simple to yield a fully accurate description of $\{C\}_\kappa$ and $\{\kappa\}$ over the full range of $q$. Nevertheless, it does give the desired feature of $\{\kappa\}$ for a wide ranged values of $q$ not too large as shown in Fig. 5. Furthermore, our finding that $\{C\}_\kappa$ is smaller than $\{C\}_\eta$ in the vicinity of $q = 1$ supports the MD result$^{12}$ for a pure fluid, which has shown that $C_\kappa$ is very close to unity.

Another interesting feature predicted by our results is the remarkable validity of $\{\eta\}_H$ and $\{\kappa\}_H$, the conventional hydrodynamic results over a large domain of $q$. For diffusivity this feature has already been observed in paper I,$^3$ and the unreasonable adequacy of
hydrodynamic results in general has been previously observed by many others. We find here that the resulting intrinsic shear and bulk viscosity are numerically approximated by the conventional hydrodynamics within error of 15% or so as long as $\sigma_{22}/\sigma_{11} > 1.5$. 
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REFERENCES

1. A. Einstein, Ann. Phys. 19, 289 (1906); 34, 591 (1911).


3. W. Sung, G. Stell

4. W. Sung, J. Karkheck, G. Stell


   Gases (Cambridge University, Cambridge 1952).

   Processes in Gases (North-Holland, Amsterdam 1972).

   (1974).


10. G. K. Batchelor, An Introduction to Fluid Dynamics (Cambridge
    University, Cambridge 1967).

11. J. Happel, H. Brenner, Low Reynolds Number Hydrodynamics with
    Special Applications to Particulate Media (Prentice Hall,
    Engelwood Cliffs, NJ, 1965)

FIGURE CAPTIONS

Figure 1. Intrinsic shear (A) and bulk viscosities (B) vs. \( \xi^{-1} = \sigma_{22}/\sigma_{11} \) at \( \xi^0 = 0.1 \) in the case \( (\sigma_{22}/\sigma_{11})^3 = m_2/m_1 \).

- \( \{x\}_E \): Enskog theory
- \( \{x\}_H \): Extended hydrodynamic theory (with the effective contact radius \( \sigma \))
- \( \{x\}_H \): Conventional hydrodynamic theory

Figure 2. As in Figure 1, except \( \xi^0 = 0.2 \).

Figure 3. As in Figure 1, except \( \xi^0 = 0.4 \).

Figure 4. Intrinsic shear viscosity vs. \( q = \sigma_{11}/\sigma_{22} \) at \( \xi^0 = 0.4 \), in the case \( (\sigma_{22}/\sigma_{11})^3 = m_2/m_1 \).

- \( \{\eta\} \): Our final result
- \( \{\eta\}_h \): Extended hydrodynamic theory without modification of parameters (HKW).
- \( \{\eta\}_h \): Extended hydrodynamic theory with the effective contact radius \( \sigma \)
- \( \{\eta\}_H \): Conventional hydrodynamic theory
- \( \{\eta\}_E \): Enskog theory

Figure 5. As in Figure 4, except for intrinsic bulk viscosity.
Figure 3

![Diagram](image)