NEW THEORY OF TRANSPORT IN DILUTE SUSPENSIONS AND PURE FLUIDS

I. TRANSLATIONAL DIFFUSION

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ABSTRACT

We develop a new theory of transport for dilute suspensions
and solutions in which the dynamics of the solute-solvent (i.e.,
tagged particle-fluid particle) collision is treated on a level of
the Enskog approximation, appropriately modified by the presence of
the solvent sea, which is described hydrodynamically. The treatment
of the solvent as a continuum gives rise to an effective solute-
solvent collision radius as well as an effective reduced mass. In
this paper, we consider translational diffusion of the solute particle
of arbitrary size and mass. We derive an analytically simple expres-
sion for the coefficient of diffusion, which yields the correct
hydrodynamic limit (Stokes-Einstein law). Our expression for self-
diffusion (diffusion of a tagged particle in a fluid of identical
particles) is in excellent agreement with molecular-dynamical results,
showing both an increase over the Enskog value at low fluid density
as well as a quite precipitous drop at liquid densities (the caging
effect). The caging effect in our theory follows directly from an
effective solute-solvent collision radius that is greater than the
bare radius.

I. INTRODUCTION

In the study of the transport processes in a suspension of particles, there are two approaches which represent opposite extremes. These are the Enskog kinetic theory and the hydrodynamic description, which, respectively, neglect the collective dynamic effects and the molecular-collisional details. The status of the solvent is entirely different in the two approaches: in the kinetic theory the solvent particles are considered as a component of a molecular binary mixture while hydrodynamics treats the solvent as a continuum.

It was Einstein[1] who first gave a hydrodynamic description for the dilute suspension in his theory of Brownian motion. The size of the solute particle is assumed to be sufficiently large to permit the treatment of the solvent as a homogeneous continuum. Among others, his formulae for the diffusion (Stokes-Einstein relation) and the intrinsic shear viscosity are of interest to us here.

Enskog theory represents the best currently available microscopic theory capable of yielding analytic expressions for the transport coefficients of hard-sphere dense fluid. When applied to a test particle of diameter σ_{22} in a fluid of particles of diameter σ_{11}, however, this theory is found to yield translational diffusivity of a drastically different limiting behavior in the limit $\sigma_{22}/\sigma_{11} \to \infty$ from that of hydrodynamics (which one expects to recover for finite solvent density n_1 fixed). The former yields a diffusivity that depends linearly on σ_{22}^{-2}, the latter on σ_{22}^{-1}. This is due to the assumption of the "velocity

chaos" in the Enskog theory, i.e., an absence of velocity correlation between two particles about to collide. This assumption breaks down badly for collision between the large solute and small solvent particles at high solvent density. To develop an improved microscopic theory in a way that yields the correct hydrodynamic behavior in the limit $\sigma_{22}/\sigma_{11} \to \infty$, one might follow one of the several approaches. A self-consistent kinetic theory (renormalized kinetic theory) represents one such approach, but the results[2,3,4] obtained from it as yet suggest that this approach is likely to yield the correct limiting behavior only when brought to a high enough level of approximation to be too complicated to be analytically manageable for arbitrary σ_{22}/σ_{11}. An alternative approach has recently been suggested by Hynes and his co-workers,[6,7] who have introduced the idea of describing only the the binary interaction of the test particle with a colliding solvent particle on a detailed molecular level, treating the effect of all collisions among solvent particles in a hydrodynamical way. Technically, the treatment matches the collision dynamics to the hydrodynamics by using the conservation of momentum. Conceptually, the treatment is closely analogous to the Bethe[8] or quasichemical approximation for spin systems, in which only the interaction between a central spin and its immediate neighbors is treated in microscopic detail, with the effect of all the more distant neighbors upon the central spin being treated only through a mean field.

In its original version, the treatment of Hynes, et al.[6] has a shortcoming: Though it yields a correct hydrodynamic limit when

$\sigma_{22}/\sigma_{11} \to \infty$ (n_1 fixed) for the translational diffusion, it fails to describe adequately the diffusivity of a small solute particle. Here, we discover through more detailed analysis of collisional dynamics that the idea of approximating the solvent as a continuum can be optimized by introducing a renormalized or modified contact distance and reduced mass of the solute and solvent particle. Our modification improves the result of [6] for the translational diffusion in a significant way, yielding excellent agreement with the result of molecular dynamics for self-diffusion at high solvent density.

Throughout this work, we shall confine ourselves to the smooth-sphere model which does not allow the exchange of the angular momentum by collision. Thus, the corresponding hydrodynamic limit of the translational diffusion will be what one usually obtains for the hydro-dynamics of slip boundary condition. We also assume the uniformity of temperature without loss of generality.

Our presentation of this work is as follows: In Sec. II, the force per unit area acting on the solute particle by the solvent molecule is evaluated from the revised Enskog theory by using the Chapman-Enskog solution method. In Sec. III, we will discuss the matching of two dynamics, and match the force considered in Sec. II to the hydrodynamic one at the surface of contact, $r = \sigma$, around the solute particle, which yields the "generalized boundary condition". The matching of two dynamics in the level of thermodynamics necessitates an introduction of an effective solvent-solute collision diameter.

This will prove to be an important ingredient in the subsequent developments. In Sec. IV, we discuss the (microscopic) hydrodynamic disturbances around the solute particle due to the generalized boundary condition which includes the collisional detail. In Sec. V, we apply the results of the foregoing sections to evaluate translational diffusion. Here the effective reduced mass for the binary collision is introduced to make the theory fit to Enskog theory in the low-density limit.

II. THE AVERAGE FORCE ACTING ON A PARTICLE THROUGH MOLECULAR COLLISION: REVISED ENSKOG THEORY

We begin with the kinetic equations for the probability distribution functions (DFs) for a binary mixture of the hard-sphere molecules:

$$\left(\frac{\partial}{\partial t} + \underset{\sim}{V}_i \cdot \nabla_{\underset{\sim}{R}}\right) f_i(\underset{\sim}{R}, \underset{\sim}{V}_i, t) = \sum_{j=1,2} J_{ij}$$

$$J_{ij} \equiv \sigma_{ij}^2 \int d\underset{\sim}{V}_j d\underset{\sim}{\sigma} (\underset{\sim}{\sigma} \cdot \underset{\sim}{V}_{ji}) \Theta(\underset{\sim}{\sigma} \cdot \underset{\sim}{V}_{ji})$$

$$[F_{ij}(\underset{\sim}{R}, \underset{\sim}{V}_i'; \underset{\sim}{R} + \sigma_{ij}\underset{\sim}{\sigma}, \underset{\sim}{V}_j'; t)$$

$$- F_{ij}(\underset{\sim}{R}, \underset{\sim}{V}_i; \underset{\sim}{R} - \sigma_{ij}\underset{\sim}{\sigma}, \underset{\sim}{V}_j; t)] \qquad (2.1)$$

Here f_i, F_{ij} are one and two particle DFs respectively with i,j (= 1,2) being the species indices, σ_{ij} is the contact distance between the centers of i and j, $\underset{\sim}{V}_{ji} = \underset{\sim}{V}_j - \underset{\sim}{V}_i$, the primes on the velocities denotes the post-collisional value, $\underset{\sim}{\sigma}$ unit vector along the apse line, the Heaviside step function $\Theta(\underset{\sim}{\sigma} \cdot \underset{\sim}{V}_{ji})$ imposes the condition of the collision.

Our interest here is the force transferred to the solute particle 2 in the solvent-solute collision. Multiplying $m_2\underset{\sim}{V}_2$ the equation (2.1) (with i = 2) and integrating with respect to $\underset{\sim}{V}_2$ yields the equation for the average velocity of the particle 2, $\overline{\underset{\sim}{V}}_2$, enabling us to identify

$$n_2\underset{\sim}{F}^{21} = \int m_2\underset{\sim}{V}_2 J(f_2 f_1) d\underset{\sim}{V}_2 \qquad (2.2)$$

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as the force per unit volume of the species 2, n_2 being its number density. Here, $\underset{\sim}{F}^{12}$, an average force, is an appropriate one to consider for a single particle on the molecular level.

$$\underset{\sim}{F}^{21} = - \frac{\sigma_{21}^2}{n_2} \int d\underset{\sim}{\sigma}\, d\underset{\sim}{V}_1\, d\underset{\sim}{V}_2\, m_2 \underset{\sim}{V}_2 (\underset{\sim}{\sigma} \cdot \underset{\sim}{V}_{12}) \Theta(\underset{\sim}{\sigma} \cdot \underset{\sim}{V}_{12})$$

$$[F_{12}(\underset{\sim}{R} + \sigma_{12}\underset{\sim}{\sigma}, \underset{\sim}{V}_1'; \underset{\sim}{R}\ \underset{\sim}{V}_2'; t)$$

$$- F_{12}(\underset{\sim}{R} - \sigma_{12}\underset{\sim}{\sigma}, \underset{\sim}{V}_1; \underset{\sim}{R}\ \underset{\sim}{V}_2; t)] \tag{2.3}$$

This can be put as

$$\underset{\sim}{F}^{21} = - \frac{\sigma_{21}^2}{n_2} \int d\underset{\sim}{\sigma}\, d\underset{\sim}{V}_1\, d\underset{\sim}{V}_2 (\underset{\sim}{\sigma} \cdot \underset{\sim}{V}_{12}) \Theta(\underset{\sim}{\sigma} \cdot \underset{\sim}{V}_{12}) (m_2 \underset{\sim}{V}_2' - m_2 \underset{\sim}{V}_2)$$

$$F_{12}(\underset{\sim}{R} - \sigma_{12}\underset{\sim}{\sigma}, \underset{\sim}{V}_1; \underset{\sim}{R}\ \underset{\sim}{V}_2; t) \tag{2.4}$$

by noting that $d\underset{\sim}{V}_1'\, d\underset{\sim}{V}_2' = d\underset{\sim}{V}_1\, d\underset{\sim}{V}_2$, $\underset{\sim}{\sigma} \cdot \underset{\sim}{V}_{12} = -\underset{\sim}{\sigma} \cdot \underset{\sim}{V}_{12}'$ in the first term of the integral in (2.3).

$\underset{\sim}{F}_\sigma$, the force per unit _area_ on the surface of $r = \sigma_{12}$ around the particle 2 is defined through the relation

$$\underset{\sim}{F}^{21} = \int \underset{\sim}{F}_\sigma \sigma_{12}^2 d\underset{\sim}{\sigma} \tag{2.5}$$

Then,

$$\underset{\sim}{F}_\sigma = - \frac{2\mu_{12}}{n_2} \underset{\sim}{\sigma} \int d\underset{\sim}{V}_1\, d\underset{\sim}{V}_2 (\underset{\sim}{\sigma} \cdot \underset{\sim}{V}_{12})^2 \Theta(\underset{\sim}{\sigma} \cdot \underset{\sim}{V}_{12})$$

$$F_{12}(\underset{\sim}{R} - \sigma_{12}\underset{\sim}{\sigma}, \underset{\sim}{V}_1; \underset{\sim}{R}, \underset{\sim}{V}_2; t) \tag{2.6}$$

where the substitution $m_2(\underset{\sim}{V}_2' - \underset{\sim}{V}_2) = 2\mu_{12}(\underset{\sim}{V}_{12} \cdot \underset{\sim}{\sigma})\underset{\sim}{\sigma}$ [with μ_{12} being

the reduced mass $\mu_{12} = (m_1 m_2)/(m_1 + m_2)]$ has been made.

In the Enskog theory, this is reduced to[9,10]

$$\underset{\sim}{F}_\sigma = - \frac{2\mu_{12}}{n_2} g_{12}(\sigma_{12})\underset{\sim}{\sigma} \int d\underset{\sim}{V}_1 d\underset{\sim}{V}_2 \Theta(\underset{\sim}{\sigma}\cdot\underset{\sim}{V}_{12})(\underset{\sim}{\sigma}\cdot\underset{\sim}{V}_{12})^2$$

$$f_1(\underset{\sim}{R} - \sigma_{12}\underset{\sim}{\sigma},\underset{\sim}{V}_1,t)f_2(\underset{\sim}{R},\underset{\sim}{V}_2,t) \qquad (2.7)$$

according to the approximation

$$F_{12}(\underset{\sim}{R} - \sigma_{12}\underset{\sim}{\sigma},\underset{\sim}{V}_1;\underset{\sim}{R},\underset{\sim}{V}_2;t) = g_{12}(\sigma_{12})f_1(\underset{\sim}{R} - \sigma_{12}\underset{\sim}{\sigma},\underset{\sim}{V}_1 t)f_2(\underset{\sim}{R},\underset{\sim}{V}_2,t)$$

$$(2.8)$$

Here $g_{12}(\sigma_{12})$ is the nonuniform equilibrium pair DF at contact that depends functionally on the number density field $n_i(\underset{\sim}{r},t)$. This dependence represents the difference that distinguishes the revised Enskog theory (RET)[10] from the standard Enskog theory (SET)[9,12] which replaces $g_{12}(\sigma_{12})$ by $Y_{12}(\sigma_{12})$, the equilibrium pair DF evaluated as a function of the local densities at $\underset{\sim}{r} = \underset{\sim}{R} - \frac{1}{2}\sigma_{12}\underset{\sim}{\sigma}$. The RET overcomes a number of inadequacies and difficulties that SET has, especially when applied to the mixture.[13] With regard to our final result for the usual binary diffusivity defined[9] directly in terms of the diffusing force (2.14), however, we shall not see any difference between the two theories.

To evaluate (2.7), we follow the Chapman-Enskog procedure of normal solution,[9] which establishes the direct connection with the hydrodynamics. The C-E expansion[14] through 1st order is

$$f_i(\underset{\sim}{r}_i, \underset{\sim}{V}_i, t) = f_i^{\,o}(\underset{\sim}{r}_i, \underset{\sim}{V}_i, t)[1 + \Phi_i(\underset{\sim}{r}_i, \underset{\sim}{V}_i, t)]$$

$$\overset{\circ}{\Phi}_i = -A_i(C_i)\underset{\sim}{C}_i \cdot \nabla \ell nT(\underset{\sim}{r}_i, t) - B_i(C_i)\overset{o}{\underset{\sim}{C}}\,\underset{\sim}{C} : \nabla^o \underset{\sim}{u}(\underset{\sim}{r}_i, t)$$

$$+ H_i(C_i)\underset{\sim}{\nabla} \cdot \underset{\sim}{u}(\underset{\sim}{r}_i, t) - D_i(C_i)\underset{\sim}{C}_i \cdot \underset{\sim}{d}_i \qquad (2.9)$$

Here, the hydrodynamic or thermodynamic variables are given as follows:

the number density:

$$n = \int d\underset{\sim}{V}_1 f_1 + \int d\underset{\sim}{V}_2 f_2 = n_1 + n_2 \qquad (2.10)$$

the mass density:

$$\rho = \int d\underset{\sim}{V}_1 m_1 f_1 + \int d\underset{\sim}{V}_2 m_2 f_2 = n_1 m_1 + n_2 m_2 \qquad (2.11)$$

the hydrodynamic velocity:

$$\underset{\sim}{u} = \frac{1}{\rho}\left[\int d\underset{\sim}{V}_1 m_1 \underset{\sim}{V}_1 f_1 + \int d\underset{\sim}{V}_2 m_2 \underset{\sim}{V}_2 f_2\right] \qquad (2.12)$$

the temperature:

$$\frac{3}{2} nkT = \int d\underset{\sim}{V}_1 \frac{1}{2} m_1 V_1^2 d\underset{\sim}{V}_1 + \int d\underset{\sim}{V}_2 \frac{1}{2} m_2 V_2^2 d\underset{\sim}{V}_2 \qquad (2.13)$$

the diffusion driving force:

$$\underset{\sim}{d}_i = \frac{n_i}{n}\left\{\frac{1}{kT}(\nabla\mu_i)_T - \frac{m_i}{\rho kT}\nabla P + \nabla \ell nT\right.$$

$$\left. \times \left[1 + \frac{4\pi}{3}\sum_j \sigma_{ij}^{\,3} Y_{ij} n_j \frac{m_j}{M_{ij}}\right]\right\} \qquad (2.14)$$

where μ_i is the chemical potential, P pressure, $M_{ij} = m_i + m_j$.

$$f_i^{\,o} = n_i \left(\frac{m_i}{2\pi kT}\right)^{3/2} \exp\left[-\frac{m_i}{2kT} C_i^2\right] \qquad (2.15)$$

is the local equilibrium DF, $C_i = \underset{\sim}{V}_i - \underset{\sim}{u}$ being the peculiar velocity.

The circle carried by a 2nd-order tensor refers to its symmetric traceless part:

$$\underset{\sim}{C_i} {}^{\circ} \underset{\sim}{C_i} \equiv \left[\underset{\sim}{C_i}\underset{\sim}{C_i} - \frac{1}{3} C_i^2 \underset{\approx}{I} \right] \tag{2.16}$$

$$\nabla^{\circ}\underset{\sim}{u} \equiv \frac{1}{2} \left[\underset{\sim\sim}{\nabla u} + (\underset{\sim\sim}{\nabla u})^+ - \frac{2}{3} \underset{\sim}{\nabla} \cdot \underset{\sim\approx}{u I} \right] \tag{2.17}$$

We shall limit ourselves to the case $\nabla T = 0$ throughout this work.

With the hydrodynamic variables n_i and $\underset{\sim}{u}$ expanded up to the first-order gradient around $\underset{\sim}{r_2} = \underset{\sim}{R}$, the center of the particle 2, we have

$$\underset{\sim}{F_\sigma} = - \frac{2\mu_{12}}{n_2} g_{12}\underset{\sim}{\sigma} \int d\underset{\sim}{V_1} d\underset{\sim}{V_2} \Theta(\underset{\sim}{\sigma} \cdot \underset{\sim}{V_{12}})(\underset{\sim}{\sigma}\cdot\underset{\sim}{V_{12}})^2$$
$$f_1^{\circ}f_2^{\circ}[(1 - \sigma_{12}\underset{\sim}{\sigma}\cdot\nabla f_1^{\circ}/f_2^{\circ})$$
$$+ (\Phi_1(\underset{\sim}{R},\underset{\sim}{V_1},t) + \Phi_2(\underset{\sim}{R},\underset{\sim}{V_2},t))] \tag{2.18}$$

The integration is done in the center-of-mass frame where $\underset{\sim}{g} = \underset{\sim}{V_2} - \underset{\sim}{V_1} = \underset{\sim}{C_2} - \underset{\sim}{C_1}$, $\underset{\sim}{G} = m_1\underset{\sim}{C_1} + m_2\underset{\sim}{C_2}/m_1 + m_2$, giving the first part pertaining to the local equilibrium as

$$\underset{\sim}{F_\sigma}{}^0 = - \frac{2\mu_{12}}{n_2} g_{12}\underset{\sim}{\sigma} \int d\underset{\sim}{C_1} d\underset{\sim}{C_2} \Theta(\underset{\sim}{\sigma}\cdot\underset{\sim}{g})(\underset{\sim}{\sigma}\cdot\underset{\sim}{g})^2 f_1^{\circ}f_2^{\circ}$$
$$\left\{ 1 - \sigma_{12}\underset{\sim}{\sigma} \cdot \left[\nabla_R \ell n n_1 + \frac{m_1\underset{\sim}{C_1}}{kT}\cdot\nabla_R\underset{\sim}{u} \right] \right\}$$
$$= -g_{12}\underset{\sim}{\sigma}\left[-n_1 kT + kT\underset{\sim}{\sigma}\cdot\nabla_R n_i + 2n_1\left(\frac{2kT\mu_{12}}{\pi}\right)^{1/2} \sigma_{12}\underset{\sim\sim}{\sigma\sigma}:\nabla_R\underset{\sim}{u} \right] \tag{2.19}$$

The part of deviation from local equilibrium is

$$\underset{\sim}{F}_\sigma^{\ 1} = \underset{\sim}{F}_\sigma(\underset{\sim}{\nabla}\underset{\sim}{u}) + \underset{\sim}{F}_\sigma(\underset{\sim}{d})$$

$$\underset{\sim}{F}_\sigma(\underset{\sim}{\nabla}\underset{\sim}{u}) = \frac{2\mu_{12}}{n_2}\, g_{12}\underset{\sim}{\sigma} \int d\underset{\sim}{C}_1 d\underset{\sim}{C}_2 \Theta(\underset{\sim}{\sigma}\cdot\underset{\sim}{g})(\underset{\sim}{\sigma}\cdot\underset{\sim}{g})^2 f_1^{\ o} f_2^{\ o}$$

$$\left\{ -[B_1(C_1)\underset{\sim}{C}_1^{\ o}\underset{\sim}{C}_1 + B_2(C_2)\underset{\sim}{C}_2^{\ o}\underset{\sim}{C}_2]:\underset{\sim}{\nabla}^o\underset{\sim}{u} \right.$$

$$\left. + [H_1(C_1) + H_2(C_2)]\underset{\sim}{\nabla}\cdot\underset{\sim}{u} \right\} \qquad (2.20)$$

$$\underset{\sim}{F}_\sigma(\underset{\sim}{d}) = \frac{2\mu_{12}}{n_2}\, g_{12}\underset{\sim}{\sigma} \int d\underset{\sim}{C}_1 d\underset{\sim}{C}_2 \Theta(\underset{\sim}{\sigma}\cdot\underset{\sim}{g})(\underset{\sim}{\sigma}\cdot\underset{\sim}{g})^2 f_1^{\ o} f_2^{\ o}$$

$$(-D_1\underset{\sim}{C}_1\cdot\underset{\sim}{d}_1 - D_2\underset{\sim}{C}_2\cdot\underset{\sim}{d}_2) \qquad (2.21)$$

Because $\underset{\sim}{C}_i^{\ o}\underset{\sim}{C}_i$, a traceless tensor, vanishes upon integration, in (2.20), only the term involving $\underset{\sim}{\nabla}\cdot\underset{\sim}{u}$ survives. Substitution of the lowest-order Sonine polynomial approximation for H_i,[15]

$$H_i = h_1^{(i)}\, S_{1/2}^{(i)}\left[\frac{m_i}{2kT}\, C_i^2\right]$$

$$= h_1^{(i)}\left[\frac{3}{2} - \frac{m_i}{2kT}\, C_i^{\ 2}\right], \qquad (2.22)$$

yields

$$\underset{\sim}{F}_\sigma(\underset{\sim}{\nabla}\underset{\sim}{u}) = \frac{1}{2}\, n_1 kT g_{12}\underset{\sim}{\sigma}(\mu_2 h_1^{(1)} + \mu_1 h_1^{(2)})\underset{\sim}{\nabla}\cdot\underset{\sim}{u}$$

$$= n_1 kT g_{12}\left(1 - \frac{m_2}{m_1}\frac{n_2}{n_1}\right)h\sigma_{12}\underset{\sim}{\sigma}(\underset{\sim}{\nabla}\cdot\underset{\sim}{u}) \qquad (2.23)$$

where

$$h = \frac{m_1}{M_{12}}\, h_1^{(2)} = \frac{1}{12}\left\{\left(\frac{m_1}{M_{12}}\right)^2 - \frac{Y_{11}}{2Y_{12}}\frac{m_1}{M_{12}}\left(\frac{\sigma_{11}}{\sigma_{12}}\right)^3\right\}\frac{\pi M_{12}}{(2\pi kT\mu_{12})^{1/2}}$$

$$+ O(n_2) \, .$$

Here Y_{ij} is the equilibrium pair DF at contact, evaluated as a function of the local density at $\underset{\sim}{R}$. Since $m_2 n_2 \ll m_1 n_1$, we find

$$\underset{\sim}{F}_\sigma(\nabla \underset{\sim}{u}) = \frac{n_1 g_{12}}{24} (2\pi\mu_{12}kT)^{1/2}\left\{ \left(\frac{m_1}{m_2}\right)^2 - \frac{Y_{11}}{2Y_{12}}\frac{m_1}{\mu_{12}}\left(\frac{\sigma_{11}}{\sigma_{12}}\right)^3 \right.$$

$$\left. \times \sigma_{12}'\underset{\sim}{\sigma}(\underset{\sim}{\nabla}\cdot\underset{\sim}{u}) \right\} . \tag{2.24}$$

$\underset{\sim}{F}_\sigma(\underset{\sim}{d})$, the force driven by diffusion is calculated by employing the lowest-order Sonine approximation for D_i,[9] i.e.,

$$D_i = d_0^{\,i}S_{3/2}^{(0)} = \text{constant.} \tag{2.25}$$

We find

$$\underset{\sim}{F}_\sigma^{\,d} = \frac{2}{n_2}\frac{\mu_{12}}{M_{12}} g_{12}n_1 n_2\underset{\sim\sim}{\sigma\sigma}\cdot(m_2 D_1\underset{\sim}{d}_1 - m_1 D_2\underset{\sim}{d}_2) , \tag{2.26}$$

where $\underset{\sim}{d}_1$, $\underset{\sim}{d}_2$ are identified by writing the mass flux

$$n_i m_i \overline{\underset{\sim}{C}}_i = \underset{\sim}{J}_M^{\,i} = \int d\underset{\sim}{C}_i m_i \underset{\sim}{C}_i f_i$$

$$= \int d\underset{\sim}{C}_i m_i \underset{\sim}{C}_i f_i^{\,o}\Phi_i$$

$$= -n_i kTD_i \underset{\sim}{d}_i , \tag{2.27}$$

Then,

$$\underset{\sim}{F}_\sigma^{\,d} = 2g_{12}n_1\left(\frac{2kT\mu_{12}}{\pi}\right)^{1/2}(\overline{\underset{\sim}{C}}_1 - \overline{\underset{\sim}{C}}_2)\cdot\underset{\sim\sim}{\sigma\sigma} . \tag{2.28}$$

Summing up the contributions to $\underset{\sim}{F}_\sigma$, we get

$$\underset{\sim}{F}_{\sigma} = \underset{\sim}{F}_{\sigma}{}^{0} + \underset{\sim}{F}_{\sigma}\underset{\sim}{u} + \underset{\sim}{F}_{\sigma}{}^{d}$$

$$= g_{12}\underset{\sim}{\sigma}\left[n_1 kT - kT\sigma_{12}\underset{\sim}{\sigma}\cdot\nabla_R n_1 \right.$$

$$- 2\left(\frac{2\mu_{12}kT}{\pi}\right)^{1/2} n_1 \left\{ \sigma_{12}\underset{\sim}{\sigma}\underset{\sim}{\sigma}:\nabla_R\underset{\sim}{u} \right.$$

$$\left. \left. + \underset{\sim}{\sigma}\cdot(\overline{\underset{\sim}{C}}_2 - \overline{\underset{\sim}{C}}_1) - \lambda\sigma_{12}\nabla_R\cdot\underset{\sim}{u} \right\} \right]_R \qquad (2.29)$$

where

$$\lambda = \frac{\pi}{48} \left\{ \left(\frac{m_1}{m_2}\right)^2 - \frac{1}{2}\frac{m_1}{\mu_{12}}\frac{Y_{11}}{Y_{12}}\left(\frac{\sigma_{11}}{\sigma_{12}}\right)^3 \right\} . \qquad (2.30)$$

Here n_i, C_i, $\underset{\sim}{u}$ and the gradients are evaluated at $\underset{\sim}{r} = \underset{\sim}{R}$, i.e., at the center of the particle 2.

It is desireable, however, to express quantities of interest at the center of the particle of species to which the indices refer. Noting that

$$(\overline{\underset{\sim}{C}}_2 - \overline{\underset{\sim}{C}}_1)_R = \overline{\underset{\sim}{V}}_2 - \overline{\underset{\sim}{V}}_1 + \sigma_{12}\underset{\sim}{\sigma}\cdot\nabla_R\underset{\sim}{u}$$

$$n_1(\underset{\sim}{R}) = n_1 - \sigma_{12}\underset{\sim}{\sigma}\cdot\nabla_R n_1$$

we finally get, up through 1st order in gradients

$$\underset{\sim}{F}_{\sigma} = \underset{\sim}{\sigma}g_{12}\left[n_1 kT - 2\left(\frac{2\mu_{12}kT}{\pi}\right)^{1/2} n_1 \left\{ (\overline{\underset{\sim}{V}}_2 - \overline{\underset{\sim}{V}}_1)\cdot\underset{\sim}{\sigma} - \lambda\sigma_{12}\nabla\cdot\underset{\sim}{u} \right\} \right] \qquad (2.31)$$

where n_i, $\overline{\underset{\sim}{V}}_i$ are evaluated at the position of the particles at contact. Equation (2.31) can be written as

$$\underset{\sim}{F}_{\sigma} = \underset{\sim}{\sigma}\left[g_{12}n_1 kT - \frac{3\zeta_E(\sigma_{12})}{4\pi\sigma_{12}{}^2} \left\{ \underset{\sim}{\sigma}\cdot(\overline{\underset{\sim}{V}}_2 - \overline{\underset{\sim}{V}}_1) - \lambda\sigma_{12}\nabla\cdot\underset{\sim}{u} \right\} \right] \qquad (2.32)$$

where $\zeta_E(\sigma_{12})$ is the friction coefficient given by

$$\zeta_E(\sigma_{12}) = \frac{kT}{D_E(\sigma_{12})} = \frac{8}{3}(2\pi kT\mu_{12})^{1/2}n_1\sigma_{12}{}^2g_{12}(\sigma_{12}) \; . \qquad (2.33)$$

Here, $D_E(\sigma_{12})$ is the coefficient of binary diffusion evaluated[9] in the first-order Sonine polynomial approximation (2.25). This approximation is found to be exact in the limit $m_2/m_1 \to \infty$, the "quasi-Lorentz" limit.[16,21] Inclusion of the higher-order Sonine polynomial yields a significant correction[9,21] (13.2% larger) in the Lorentz limit, i.e., $m_2/m_1 \to 0$, but only a negligible correction[9] (1.9%) in the case $m_1 = m_2$, $\sigma_{11} = \sigma_{22}$. Since we shall confine ourselves to the mixture in which

$$0 < \frac{m_1}{m_2} \lesssim 1, \quad 0 < \frac{\sigma_{11}}{\sigma_{22}} \lesssim 1 \; , \qquad (2.34)$$

(2.33) is regarded as sufficient to serve our purpose.

What we have derived here is the result of C-E solution procedure with the local-equilibrium distribution as the lowest order. But our interest in the subsequent sections will be in the system that deviates infinitesimally from absolute equilibrium. Then (2.32) will be formally unchanged except that $g_{12}(\sigma_{12})$, the nonuniform equilibrium DF (and hence local equilibrium DF) is replaced by $Y_{12}(\sigma_{12})$, the absolute equilibrium DF. The first term in (2.3) is the contribution from absolute equilibrium and the velocities $\overline{V}_1$, $\overline{V}_2$, u then are to be understood as the deviation from their equilibrium values, which vanishes.

Utilizing the relations (2.11) and (2.12) with the condition $n_1 m_1 \gg n_2 m_2$, we find $\underset{\sim}{u} \approx \overline{\underset{\sim}{V}}_1$. With changes of notation $\overline{\underset{\sim}{V}}_2 \equiv \underset{\sim}{U}$, $\underset{\sim}{n} \equiv -\underset{\sim}{\sigma}$, (2.32) is rewritten as

$$\underset{\sim}{F}_\sigma = \underset{\sim}{n}\left[-Y_{12}(\sigma_{12})n_1 kT - \frac{3\zeta_E(\sigma_{12})}{4\pi\sigma_{12}^{2}}\left\{\underset{\sim}{n}\cdot(\underset{\sim}{U}-\underset{\sim}{u}) + \lambda\sigma_{12}\nabla\cdot\underset{\sim}{u}\right\}\right]$$

(2.35)

wherein $\underset{\sim}{u}$ is now to be understood as the hydrodynamic velocity of the solvent at $r = \sigma_{12}$, not of the mixture (2.12). Equation (2.35) is now in a form that will enable us to make contact with the hydrodynamic considerations of later sections. This has two additional terms which were not considered in the original work of Hynes and his collaborators.[6] One is an equilibrium contribution, the other being the term that involves $\nabla\cdot\underset{\sim}{u}$.

III. MATCHING OF TWO DYNAMICS - GENERALIZED BOUNDARY CONDITION

The collisional force derived in the foregoing section follows from the assumption of uncorrelated precollisional velocities. This assumption is known to be rigorously correct only for short time and short distance. We shall now utilize this assumption in a context in which it can most appropriately be used, rather than to take it as the sole basis of a theory that attempts to predict kinetic behavior over all times and distances. We do this by using RET expressions only for the dynamics of collision between the solute and solvent particles, while treating the solvent as a continuum. Here, we essentially follow Hynes and his coworkers.[6,7] We depart from their treatment, however, by acknowledging that the dynamics of the solvent-solute collisions in the presence of the rest of the solvent particles, treated as a continuum, will not necessarily be best described by the "bare" solvent-solute parameters. Instead we seek to find the appropriate effective contact distance σ between the solute and solvent particle centers and the effective reduced mass μ, which will depart from their true values

$$\sigma_{12} = \frac{1}{2} (\sigma_{11} + \sigma_{22}) , \qquad (3.1)$$

$$\mu_{12} = m_1 m_2 / m_1 + m_2 \qquad (3.2)$$

as a result of the presence of the solvent sea, which we are treating

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hydrodynamically. What we are doing can be described by saying that we are introducing nonadditive solvent-solute collisional diameters and masses to accommodate our "mean field" (i.e., hydrodynamic) treatment of the solvent. These effective parameters compensate for our neglect of the detailed microscopic structure that exists around the solute particle. One aspect of this is the presence of a micro-scopic boundary layer about a solute particle extending over several mean free paths, inside which the hydrodyhamic description compatible to a Chapman-Enskog solution procedure breaks down. Another aspect is the short-range order of $Y_{12}(r)$, which oscillates over several σ_{11} at all but very low solvent densities. Only when σ_{11}/σ_{22} and ℓ/σ_{22} are both small, where ℓ = mean free path (as is the case for $\sigma_{22}/\sigma_{11} \to \infty$, fixed solvent density n_1, i.e., the hydrodynamic limit) can these two aspects be neglected; in our treatment they are incorporated into the σ and μ we use.

We use the conservation of momentum, as described below, to match the collisional dynamics and the hydrodynamics via the momentum flux across the surface of solute-solvent contact defined by $r = \sigma$. In considering such an approach, it is important to keep in mind that in practice the specific expressions that one obtains for σ, μ are inevitably dictated by the details of all the approximations one uses to describe the solvent-solute and solvent-solvent dynamics, as well as the thermodynamics. (In the limit $\sigma_{22}/\sigma_{11} \to \infty$, n_1 fixed, however, one expects to have $\mu = \mu_{12}$, $\sigma = \sigma_{12}$ independent of approximation, since hydrodynamics becomes exact in this case.) We make no claims as to finding the best possible prescriptions for σ and μ in the following treatment, but our procedure seems to us natural to use in the context of an Enskog-like description of the solvent-solute collision.

In spite of the different descriptions, we have a unifying law, the conservation of momentum. This dictates that the momentum flux in the two descriptions be matched at $r = \sigma$. For a steady state,

$$\underset{\sim}{n} \cdot \underset{\sim}{F}_\sigma = -(\underset{\sim}{n} \cdot \underset{\approx}{\pi} \cdot \underset{\sim}{n})_\sigma \tag{3.3}$$

$$0 = (\underset{\sim}{n} \times \underset{\approx}{\pi} \cdot \underset{\sim}{n})_\sigma \tag{3.4}$$

where $\underset{\approx}{\pi}$ is the hydrodynamic momentum tensor in the solvent fluid:

$$\underset{\approx}{\pi} = \rho \underset{\sim\sim}{uu} + P\underset{\approx}{I} - 2\eta\underset{\approx}{d} - 3\kappa\nabla\underset{\approx}{I} \tag{3.5}$$

$$\underset{\approx}{d} = \nabla^{o}\underset{\sim}{u} \equiv \frac{1}{2}[\nabla\underset{\sim}{u} + (\nabla\underset{\sim}{u})^{+} - \frac{2}{3}\nabla\cdot\underset{\sim}{u}\underset{\approx}{I}] \tag{3.6}$$

$$\Delta = \frac{1}{3}\nabla\cdot\underset{\sim}{u} \tag{3.7}$$

Here the pressure P is given via the exact virial theorem

$$P = n_1 kT\left(1 + \frac{2\pi}{3} n_1 \sigma_{11}^{3} Y_{11}\right) \tag{3.8}$$

where ξ_1 is the local volume fraction of the solvent: $\xi_1 = \frac{\pi}{6} n_1 \sigma_{11}^{3}$ and the shear and bulk viscosities of the solvent are expressed by

$$\eta = C_\eta \eta_E$$

$$\eta_E = \Lambda_\eta(\xi_1)\eta_B$$

$$\Lambda_\eta(\xi_1) = \frac{1}{Y_{11}}\left(1 + \frac{8}{5}\xi_1 Y_{11}\right)^2 + (1.016)^{-1} \times \frac{768}{25\pi}\xi_i^{2}Y_{11} \tag{3.9}$$

$$\kappa = C_\kappa \kappa_E$$

$$\kappa_E = \Lambda_\kappa(\xi_1)\eta_B$$

$$\Lambda_\kappa(\xi_1) = (1.016)^{-1} \times \frac{256}{5\pi}\xi_1^{2}Y_{11} \tag{3.10}$$

where $\eta_B = 1.016 \times \frac{5}{16}(m_1 kT)^{1/2}(1/\sigma_{11}^{2})$ is the shear viscosity from the Boltzmann theory and C_η, C_κ are the correction factors to the Enskog values η_E, κ_E, given by the molecular dynamics (MD).[17]

The relations (3.3), (3.4) are regarded as the boundary conditions: one is for the normal force and the velocity, the other for the tangential velocity (so-called slip B.C.). Substituting (2.35) and (3.5) into (3.3), we find

$$\left[-Y_{12}n_1kT - \frac{3\zeta_E}{4\pi\sigma^2}\, \underset{\sim}{n} \cdot (\underset{\sim}{U} - \underset{\sim}{u} + 3\lambda\sigma_{12}\Delta\underset{\sim}{n})\right]_\sigma$$

$$= [-P_e - \delta P + 2\eta \underset{\approx}{d} : \underset{\sim\sim}{nn} + 3\kappa\Delta]_\sigma \qquad (3.11)$$

where δP is the deviation from absolute equilibrium pressure. This condition has the proper hydrodynamic limit. Let us take a limit $\sigma_{12}/\sigma_{11} \to \infty$ with n_1 fixed; correspondingly $\zeta_E \to \infty$, $\lambda \to 0$. Since the RHS of (3.11), upon integration over the surface $4\pi\sigma_{12}{}^2$ ($\to \infty$) remains finite (being the hydrodynamic force) while LHS goes to infinity, we have

$$\underset{\sim}{n} \cdot (\underset{\sim}{U} - \underset{\sim}{u})_{\sigma_{22}/2} = 0 \; . \qquad (3.12)$$

This is the usual hydrodynamic B.C. based on the kinematic consideration that the fluid is impenetrable to the particle.

When the system relaxes into absolute equilibrium, Eq. (3.11) is reduced to

$$Y_{12}(\sigma)n_1kT = n_1kT(1 + 4\xi_1 Y_{11}) \; . \qquad (3.13)$$

This is indeed an exact relation in the limit in which the solvent can be exactly treated hydrodynamically (i.e., in the limit $\sigma_{11}/\sigma_{22} \to 0$, n_1 fixed, in which the solute particle becomes a macroparticle with a radius of curvature that is zero on the molecular scale).[18]

Development of our formalism matching hydrodynamics and collision dynamics via (3.3) and (3.11) dictates the use of (3.13) for arbitrary σ_{11}/σ_{22}. We shall use it as a means of finding σ, the effective

solvent-solute contact distance. We can equivalently speak of the effective radius $\sigma_{11}*/2$ of the solvent particle whenever it collides with a solute particle, defined by the relation

$$\sigma = \frac{1}{2} \, (\sigma_{11}* + \sigma_{22}) \, . \tag{3.14}$$

The $\sigma_{11}*$ is often more convenient to describe and visualize than σ itself, when we contemplate the limit $\sigma_{22} \to \infty$ for fixed σ_{11}, in which $\sigma \to \infty$ but $\sigma_{11}*$ remains finite. (As we shall see, $\sigma_{11}* \to \sigma_{11}$ for us in this limit.)

With our modified σ, we rewrite (3.11) for the deviation from equilibrium

$$- \frac{3\zeta_E(\sigma)}{4\pi\sigma^2} \, \underset{\sim}{n} \cdot [\underset{\sim}{U} - \underset{\sim}{u} + 3\lambda\sigma\underset{\sim}{n}\Delta]_\sigma$$

$$= [-\delta P + 2\eta\underset{\approx}{d}{:}\underset{\sim\sim}{nn} + 3\kappa\Delta]_\sigma \tag{3.15}$$

where

$$\zeta_E(\sigma) = \frac{8}{3} \, (2\pi\mu_{12}kT)^{1/2} \, n_1\sigma^2 Y_{12}(\sigma)$$

$$= \frac{8}{3} \, (2\pi\mu_{12}kT)^{1/2} \, n_1\sigma^2(1 + 4\xi_1 Y_{11}) \tag{3.16}$$

$$\lambda(\sigma) = \frac{\pi}{48} \left\{ \left(\frac{\mu_{12}}{m_2}\right)^2 - \frac{1}{2} \frac{\mu_{12}}{m_2} \frac{Y_{11}}{Y_{12}(\sigma)} \left(\frac{\sigma_{11}}{\sigma}\right)^3 \right\} \, . \tag{3.17}$$

Equation (3.15) is the key relation of this work. Its main difference from the assumption of Hynes and his colleagues is the introduction of the effective size σ, in addition to the term involving the velocity divergence, which has only slight numerical consequences in our calculations. As we shall find in Sec. V, σ is generally larger than

the "bare" σ_{12}, especially when the diameters of the solvent and solute particles are comparable. This accounts beautifully for the "caging effect" that leads to a drop in the self-diffusion coefficient D below its Enskog value D_E when $\sigma_{11} = \sigma_{22}$, $m_1 = m_2$ at higher density. In our theory the tagged (i.e., solute) particle collides with solvent particles with a larger effective collisional distance σ than the actual σ_{12}; at higher densities this tends to cage the tagged particle and substantially lowers the diffusivity from its Enskog value.

For the effective reduced mass μ, we shall follow a somewhat different rationale than for the effective radius σ. The μ appropriate to each transport process will be defined through the matching of the hydrodynamic and molecular-collisional expressions for the relevant transport coefficient.

IV. EXTENDED HYDRODYNAMICS OF THE FLOW AROUND A PARTICLE

Here we take a hydrodynamic viewpoint, considering the solute particle as an impurity that causes disturbance in the flow fields in the solvent continuum. In this description for $r \geq \sigma$, the interaction between the solvent and solute particle appears as the generalized boundary condition derived in the foregoing section, which the flow fields satisfy. This description, though fundamentally hydrodynamic, will use microscopic input in the form of Eqs. (3.8)-(3.10) and shall be referred to as the Extended hydrodynamics. We will here derive the flow fields around the solute particle under a general situation of the fluid that allows not only the consideration of the translational diffusivity, but also the extractions of the effective shear and bulk viscosities of the whole suspension, which will be the topics of our subsequent paper (II).[22]

The Navier-Stokes equations for the mass density $\rho(\underset{\sim}{r},t)$ and the velocity field $\underset{\sim}{u}(\underset{\sim}{r},t)$ of the solvent continuum is

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \underset{\sim}{u} = 0 \tag{4.1a}$$

$$\frac{\partial}{\partial t} \rho \underset{\sim}{u} + \nabla \cdot \underset{\approx}{\pi} = 0 \tag{4.1b}$$

where the momentum tensor $\underset{\approx}{\pi}$ is given by (3.5), with the molecular expressions for the pressure and viscosities (3.8), (3.9) and (3.10).

Considering a small deviation for the flow fields away from the equilibrium, the equations are linearized. We have

$$\frac{\partial \delta \rho}{\partial t} = -\rho_e \nabla \cdot \underset{\sim}{u} \tag{4.2a}$$

$$\rho_e \frac{\partial u}{\partial t} = -\nabla \delta P + \eta \nabla^2 \underset{\sim}{u} + (\frac{1}{3} \eta + \kappa)\nabla\nabla \cdot \underset{\sim}{u} \qquad (4.2b)$$

for the deviations

$$\delta\rho = \rho - \rho_e , \qquad \delta\underset{\sim}{u} = \underset{\sim}{u} - \underset{\sim}{u}_e = \underset{\sim}{u} .$$

Neglect of the nonlinear term $\underset{\sim}{u}\cdot\nabla\underset{\sim}{u}$ that follows from the linearization imposes the condition of the low Reynolds number flow, i.e.,

$$R \equiv \rho_e \sigma U/\eta \ll 1 . \qquad (4.3)$$

In steady state, which is of our ultimate concern here, the equations are considerably simplified:

$$\nabla \cdot \underset{\sim}{u} = 0 \qquad (4.4a)$$

$$\nabla \delta P - \eta \nabla^2 \underset{\sim}{u} = 0 . \qquad (4.4b)$$

We should note here the condition (4.4a) does not refer to an intrinsic property of fluid but is instead to be regarded as an approximate description of the dynamic situation we consider: In a steady slow flow (4.4a) is still relevant to a description of transport properties such as the diffusion and shear viscosity of a suspension even for a fluid whose thermodynamic compressibility is not low. However, for the bulk viscosity, which cannot be extracted without compression or expansion of the fluid, we should start with (4.2a,b).

To find the solution of (4.4a,b), we consider the unperturbed flow field $\underset{\sim}{u}^0$, P^0, which are the solutions of the equations when the solute particle is absent. They are expanded in Taylor series around $\underset{\sim}{R}$, the center of the particle:

$$\underset{\sim}{u}^0 = \underset{\sim R}{u}^0 + (\underset{\sim\sim}{\nabla u}^0)_R \cdot \underset{\sim}{r} + \frac{1}{2}(\underset{\sim\sim\sim}{\nabla\nabla u}^0)_R : \underset{\sim\sim}{rr} + \ldots \tag{4.5}$$

$$P^0 = P_R^0 + \nabla P^0 \cdot \underset{\sim}{r} + \frac{1}{2}(\underset{\sim\sim}{\nabla\nabla}P^0)_R : \underset{\sim\sim}{rr} + \ldots \tag{4.6}$$

where the subscript R denotes the evaluation at $\underset{\sim}{R}$. For the present purpose of evaluating the transport coefficients, it suffices to have

$$\underset{\sim}{u}^0 = \underset{\sim R}{u}^0 + (\underset{\sim\sim}{\nabla u}^0)_R \cdot \underset{\sim}{r} \tag{4.7}$$

$$P^0 = P_R^0 \tag{4.8}$$

as a solution of (4.4a,b), the higher-order terms being neglected by considering only the situation that the flow fields vary slowly over the size of the particle. This is very similar to the approximation imbedded in the first order Chapman-Enskog expansion in kinetic theory.

Decomposing the tensor $(\underset{\sim}{\nabla u}^0)_R$ into three irreducible components, we have

$$(\underset{\sim}{\nabla u}^0)_R = \underset{\approx}{d}^0 + \underset{\approx}{\omega}^0 + \Delta^0 \underset{\approx}{I} \tag{4.9}$$

where

$$\underset{\approx}{d}^0 \equiv \frac{1}{2} [\underset{\sim\sim}{\nabla u}^0 + (\underset{\sim\sim}{\nabla u}^0)^+ - \frac{2}{3} \underset{\sim}{\nabla} \cdot \underset{\sim}{u}^0 \underset{\approx}{I}]_R$$

$$\underset{\approx}{\omega}^0 \equiv \frac{1}{2} [\underset{\sim\sim}{\nabla u}^0 - (\underset{\sim\sim}{\nabla u}^0)^+]_R$$

$$\Delta^0 \equiv \frac{1}{3} (\underset{\sim}{\nabla} \cdot \underset{\sim}{u}^0)_R$$

The boundary conditions of the foregoing section (3.3) or (3.15) and (3.4) are rewritten by noting that $\delta u = u = u^0 + u'$, $\delta P = P^0 + P'$ where the primed quantities are the perturbed flow fields, and from (4.7), (4.8),

$$\frac{3\zeta_E}{4\pi\sigma^2} [\underset{\sim}{n} \cdot \underset{\sim}{V} + \underset{\sim}{n} \cdot \underset{\sim}{u}' + \sigma \underset{\sim\sim}{nn} : \underset{\approx}{d}^0 + \sigma\Delta(1-3\lambda) - 3\lambda\sigma\Delta']_\sigma$$

$$= [-P^0 - P' + 2\eta(\underset{\approx}{d}^0 + \underset{\approx}{d}') : \underset{\sim\sim}{nn} + 3\kappa(\Delta^0 + \Delta')]_\sigma \qquad (4.10)$$

$$[\underset{\sim}{n} \times \underset{\sim}{n} \cdot (\underset{\approx}{\pi}^0 + \underset{\approx}{\pi}')]_\sigma = 0 \qquad (4.11)$$

where

$$\underset{\sim}{V} \equiv \underset{\sim R}{u}^0 - \underset{\sim}{U}$$

In the reference frame of a particle that is moving with the velocity $\underset{\sim}{U}$, (4.7) is rewritten as

$$\underset{\sim}{u}^0 = \underset{\sim}{V} + (\underset{\approx}{d}^0 + \underset{\approx}{\omega}^0 + \Delta^0\underset{\approx}{I})\underset{\sim}{r} . \qquad (4.12)$$

We observe that the perturbed flow $\underset{\sim}{u}'$, P' now should be expressed linearly in terms of the parameters of the unperturbed flow, by virtue of the linearity in the governing equations (4.4a,b) and the boundary conditions (4.10), (4.11).

Taking a divergence of (4.4b), we find

$$\nabla^2 P' = 0 . \tag{4.13}$$

The solution is the harmonic function that tend to vanish at infinity:

$$P' = (MP^0 + D\underset{\sim}{V} \cdot \underset{\sim}{\nabla} + Q\underset{\approx}{d}{}^0 : \underset{\sim\sim}{\nabla\nabla}) \frac{1}{r} . \tag{4.14}$$

We observe here the constants M, D, Q represent respectively the strength of the monopole, dipole, quadrupole disturbances in the pressure, caused by the presence of the particle.

The perturbed velocity is expressed as

$$\underset{\sim}{u}' = \underset{\sim\psi}{u}' + \underset{\sim S}{u}' + \underset{\sim E}{u}' \tag{4.15}$$

$$\underset{\sim\psi}{u}' = \psi(r)P^0\underset{\sim}{r} \tag{4.15a}$$

$$\underset{\sim S}{u}' = S_1(r)\underset{\sim}{V} + S_2(r)(\underset{\sim}{V}\cdot\underset{\sim}{r})\underset{\sim}{r} \tag{4.15b}$$

$$\underset{\sim E}{u}' = E_1(r)\underset{\approx}{d}{}^0\cdot\underset{\sim}{r} + E_2(r)(\underset{\approx}{d}{}^0:\underset{\sim\sim}{rr})\underset{\sim}{r} , \tag{4.15c}$$

which represents the only linear combination of relevant parameters to form a polar vector. Here $\underset{\sim S}{u}'$ and $\underset{\sim E}{u}'$ are the generalized "Stokes flow" due to particle translation and "Einstein flow" due to pure straining, respectively.

Substituting (4.14) and (4.15) into (4.4) and collecting terms of the same tensorial character, which can be varied independently, we obtain two sets of equations:

$$3\psi(r) + \psi'(r)r = 0 \tag{4.16a}$$

$$S_1'(r)r^{-1} + S_2'(r)r + 4S_2(r) = 0 \tag{4.16b}$$

$$E_1'(r)r^{-1} + E_2'(r)r + 5E_2(r) = 0 \tag{4.16c}$$

$$M = 0 \tag{4.17a}$$

$$S_1'(r) - rS_2(r) - \frac{D}{\eta} r^{-2} = 0 \tag{4.17b}$$

$$2E_2(r) - E_1'(r)r^{-1} - \frac{3Q}{\eta} r^{-5} = 0 \tag{4.17c}$$

where the primes denote differentiation with respect to r. The solutions that vanish at $r = \infty$ are found to be

$$\psi(r) = \psi_\sigma \left(\frac{\sigma}{r} \right)^3 \tag{4.18a}$$

$$S_1(r) = sr^{-3} - \frac{1}{2} \frac{D}{\eta} r^{-1}$$
$$S_2(r) = -3sr^{-5} - \frac{1}{2} \frac{D}{\eta} r^{-3} \tag{4.18b}$$

$$E_1(r) = er^{-5}$$
$$E_2(r) = -\frac{5}{2} er^{-7} + \frac{3Q}{2\eta} r^{-5} \tag{4.18c}$$

The constants ψ_σ, s, e, D, Q are readily determined by the two B.C.s. From the slip B.C. (4.11), we find

$$[S_1' + S_2 r]_\sigma = 0 \tag{4.19a}$$

$$[r^2(E_1'r^{-1} + 2E_2) + 4]_\sigma = 0 \tag{4.19b}$$

The normal velocity B.C. (4.9), after lengthy, but straightforward calculations, yields

$$1 + 4\eta\ \psi_\sigma + \frac{3\zeta_E}{4\pi\sigma}\ \psi_\sigma = 0 \tag{4.20a}$$

$$\left[4\eta S_2 r - Dr^{-2} + \frac{3\zeta_E}{4\pi\sigma^2}(1 + S_1 + S_2 r^2)\right]_\sigma = 0 \tag{4.20b}$$

$$\left[-2\eta(1 + E_1 - 2E_2 r^2) + 3Qr^{-3} + \frac{3\zeta_E}{4\pi\sigma}(1 + E_1 + E_2 r^2)_\sigma\right] = 0 \tag{4.20c}$$

Then, we find

$$D = \eta\sigma\left(\frac{\zeta_E}{\zeta_E + \zeta_H}\right)\ ,\quad s = 0 \tag{4.21a,b}$$

$$Q = -\frac{2}{3}\eta\sigma^3\left(\frac{15\zeta_E - 40\zeta_H}{15\zeta_E + 24\zeta_H}\right) \tag{4.21c}$$

$$e = \sigma^5\left(\frac{16\zeta_H}{24\zeta_E + 15\zeta_H}\right) \tag{4.21d}$$

$$\psi_\sigma = -\frac{1}{\eta}\left(\frac{\zeta_H}{4\zeta_H + 3\zeta_E}\right) \tag{4.21e}$$

with

$$\zeta_H(\sigma) \equiv 4\pi\eta\sigma$$

$$\zeta_E(\sigma) = \frac{8}{3}(2\pi\mu_{12}kT)^{1/2}\ n_1\sigma^2 Y_{12}(\sigma)$$

$$= \frac{8}{3}(2\pi\mu_{12}kT)^{1/2}\ n_1\sigma^2(1 + 4\xi_1 Y_{11}) \tag{4.22}$$

The simple dependences of the various amplitudes on ζ_E, ζ_H are striking. In this way, our hydrodynamic description displays the microscopic collision dynamics. However, in the limit $\sigma_{22}/\sigma_{11} \to \infty$, i.e., $H \equiv \zeta_E/\zeta_H \to \infty$, we recover the results of the conventional hydrodynamics. The amplitude ψ_σ, a creation of our microscopic consideration, vanishes in this limit as it should, since it does not exist in the context of the conventional hydrodynamic boundary condition.

Let us return to (4.2a,b) to investigate the flow fields arising from an infinitesimal time-dependent compression or expansion. Taking Fourier transforms of the time-dependent fields, e.g.,

$$\underset{\sim}{u}(\underset{\sim}{r},t) = \int \underset{\sim\omega}{u}(\underset{\sim}{r},t) e^{-i\omega t}\, d\omega \qquad (4.23)$$

we have.

$$i\omega \delta \rho_\omega = \rho_e \nabla \cdot \underset{\sim\omega}{u} \qquad (4.24a)$$

$$-i\omega \rho_e \underset{\sim\omega}{u} = -\nabla \delta \tilde{P}_\omega + \eta \nabla^2 \underset{\sim\omega}{u} + \left(\tfrac{1}{3}\eta + \kappa\right) \nabla \nabla \cdot \underset{\sim\omega}{u} \qquad (4.24b)$$

By virtue of the relation

$$\nabla \delta P_\omega = \left(\frac{\partial P_e}{\partial \rho}\right)_T \nabla \delta \rho_\omega \qquad (4.25)$$

where $[(\partial P_e/\partial \rho)_T]^{1/2} = C$ is the velocity of sound in the solvent evaluated at equilibrium, we can close the equations: Substituting (4.24a) into (4.24b), we obtain

$$-i\omega \rho_e \underset{\sim\omega}{u} = -C^2 (\rho_e/i\omega) \nabla \nabla \cdot \underset{\sim\omega}{u} + \eta \nabla^2 \underset{\sim\omega}{u} + \left(\tfrac{1}{3}\eta + \kappa\right) \nabla \nabla \cdot \underset{\sim\omega}{u} \qquad (4.26)$$

From (4.24a) we also find for the unperturbed fields

$$\Delta_\omega^{\;0} = \tfrac{1}{3} i\omega P^0 / C^2 \rho_e \;. \qquad (4.27)$$

Let us seek the solution of the perturbed flow up to linear order in $\Delta_\omega^{\;0}$. The perturbed velocity can be put as

$$\underset{\sim}{u}'_\omega = \Delta_\omega^{\;0} \Phi(r) \underset{\sim}{r} \qquad (4.28)$$

Substitution of this term into (4.26) yields

$$\Phi'' + 4r^{-1}\Phi + k^2\Phi = 0 \tag{4.29}$$

where

$$k^2 \equiv \frac{\omega^2}{c^2} \delta \Big/ \left[1 - \frac{i\omega\eta}{\rho_e c^2} \delta\right]$$

$$\delta \equiv \left[1 - \frac{i\omega}{\rho_e c^2}\left(\frac{\eta}{3} + \kappa\right)\right]^{-1} \tag{4.30}$$

Assuming a solution of the type $\Phi = r^{-\gamma}J(r)$, we find for $\gamma = 3/2$

$$J'' + r^{-1}J' + \left[-\left(\frac{3}{2}\right)^2 r^{-2} + k^2\right]J = 0 \tag{4.31}$$

The solution of J satisfying the desired behavior at infinity is found to be a Bessel function $J_{-3/2}(kr)$. Thus

$$\Phi = \text{constant } r^{-3/2}J_{-3/2}(kr) \tag{4.32}$$

In a steady state limit, which is our ultimate concern,

$$\Phi \xrightarrow[\omega\to0]{} \Phi_\sigma(\sigma/r)^3 + O(\omega^2) \tag{4.33}$$

It is found that $\underset{\sim}{u}'_\omega$ in (4.28) naturally vanishes, in this limit. However, our trick is to retain Δ_ω^0 and the other terms up to the first order in ω, in order to extract the bulk viscosity. By expanding (4.32) in small k or ω and utilizing (4.27), (4.24), we find

$$\nabla\cdot\underset{\sim}{u}'_\omega = \Delta_\omega^0(3\Phi + \Phi'r) \sim O(\omega^3) \tag{4.34}$$

$$P'_\omega = \frac{c^2\rho_e}{i\omega} \Delta_\omega^0(3\Phi + \Phi'r) \sim O(\omega^2) , \tag{4.35}$$

which are negligible.

Substituting all these results into B.C. (4.10), we get

$$\frac{3\zeta_E}{4\pi\sigma^2} [\Phi_\sigma\sigma + \sigma(1-3\lambda)] = 3\kappa - 4\eta\Phi_\sigma \qquad (4.36)$$

$$\Phi_\sigma = -\frac{(1-3\lambda)\zeta_E - \kappa/\eta \ \zeta_H}{\zeta_E + 4/3 \ \zeta_H} \qquad (4.37)$$

V. TRANSLATIONAL DIFFUSION

To identify the friction coefficient in a translational motion of the particle, the hydrodynamic force acting on the surface $r = \sigma$ is to be calculated:

$$\underset{\sim}{F} = -\int_{A_\sigma} \underset{\sim}{n} \cdot \underset{\approx}{\pi} \cdot \underset{\sim\sim}{nn} dA \tag{5.1}$$

This is identical to $\underset{\sim}{F}^{12}$, the molecular collisional force of Sec. II, via the relation (3.3). From (2.35), (4.10) and (4.21a,b), we find

$$\underset{\sim}{F} = \frac{3\zeta_E(\sigma)}{4\pi\sigma^2} \int (\underset{\sim}{n}\cdot\underset{\sim}{V} + \underset{\sim}{n}\cdot\underset{\sim}{u}')\underset{\sim}{n} dA$$

$$= \zeta(\sigma)\underset{\sim}{V}$$

$$= -\zeta(\sigma)(\underset{\sim}{U} - \underset{\sim R}{u}^0) \tag{5.2}$$

where $\zeta(\sigma)$, the friction coefficient, is given by

$$\zeta^{-1}(\sigma) = \zeta_E^{-1}(\sigma) + \zeta_H^{-1}(\sigma) \tag{5.3}$$

This has the correct hydrodynamic behavior in the limit $q = \sigma_{11}/\sigma_{22} \to 0$; $H = \zeta_E/\zeta_H \to \infty$, $2\sigma_{22}/\sigma \to 1$, and (5.3) yields the exact Stoke's law,

$$\zeta(\sigma) \to \zeta_H(\sigma) = 4\pi\eta\sigma \to \zeta_S = 4\pi\eta\left(\frac{\sigma_{22}}{2}\right) . \tag{5.4}$$

In the low-density limit, $n_1 \to 0$,

$$\zeta(\sigma) \to \zeta_E(\sigma) \to \zeta_B(\sigma) \tag{5.5}$$

Thus, because $\sigma \neq \sigma_{12}$, this does not lead to the exact low-density (Boltzmann)

limit, $\zeta_B(\sigma_{12})$, except when $\sigma_{11}/\sigma_{22} \to 0$, since σ is generally different from the actual σ_{12} in our theory. As shall be discussed later, an effective reduced mass will be introduced to remedy this difficulty.

For the diffusion coefficient, (5.3) with the Einstein relation

$$D = kT/\zeta \tag{5.6}$$

yields

$$D(\sigma) = D_E(\sigma) + D_H(\sigma) \tag{5.7}$$

where

$$D_E(\sigma) = kT/\zeta_E(\sigma) , \qquad D_H(\sigma) = kT/\zeta_H(\sigma)$$

respectively. This gives the limit $D(\sigma) \to D_S(\sigma)$, $D(\sigma) \to D_B(\sigma)$ corresponding to (5.4), (5.5).

The correction factor to the Enskog value is

$$C_D = \frac{D(\sigma)}{D_E(\sigma_{12})} = a[1 + H(\sigma)] \tag{5.8}$$

$$a \equiv \frac{\zeta_E(\sigma_{12})}{\zeta_E(\sigma)} = \frac{\sigma_{12}{}^2 Y_{12}(\sigma_{12})}{\sigma^2 Y_{12}(\sigma)} = \frac{(1+q)^2}{(1+\beta q)^2} \frac{Y_{12}(\sigma_{12})}{1 + 4\xi_1 Y_{11}}$$

$$H \equiv \frac{\zeta_E(\sigma)}{\zeta_H(\sigma)} = \frac{\frac{8}{3}(2\pi\mu_{12}kT)^{1/2} n_1 \sigma^2 Y_{12}(\sigma)}{4\pi\eta\sigma}$$

$$= \frac{32}{5\pi}\left(\frac{2\mu_{12}}{m_1}\right)^{1/2} \xi_1 q^{-1}(\beta q + 1) \frac{1 + 4\xi_1 Y_{11}}{C_\eta \Lambda_\eta}$$

where $q = \sigma_{11}/\sigma_{22}$, $\beta = \sigma_{11}{}^*/\sigma_{11}$ and the relation (3.13), i.e.,

$Y_{12}(\sigma) = 1 + 4\xi_1 Y_{11}$, and (3.9) has been substituted. The value of β is to be evaluated from (3.13), (3.14) using our improved version of the Mansoori-Carnahan-Starling-Leland (MCSL) approximation[19] for Y_{ij} (see appendix):

$$1 + 4\xi_1 Y_{11}(\xi_1) = Y_{12}(\xi_1{}^*, q^*)$$

$$= Y_{12}^{MCSL}(\xi_1{}^*, q^*) \left[\frac{1 + 4\xi_1{}^* Y_{11}(\xi_1{}^*)}{Y_{12}^{MCSL}(q=0, \xi_1{}^*)} \right.$$

$$\left. + \left\{ 1 - \frac{1 + 4\xi_1{}^* Y_{11}(\xi_1{}^*)}{Y_{12}^{MCSL}(q=0, \xi_1{}^*)} \right\} q^* \right] \qquad (5.9)$$

where

$$q^* = \beta q, \qquad \xi_1{}^* = \beta^3 \xi_1 \; .$$

For the self-diffusion (when $q = 1$, $m_1 = m_2$, $Y_{12} = Y_{11}$) Eq. (5.8) is reduced to

$$C_D{}^S = \left(\frac{2}{\beta+1} \right) \left[\frac{Y_{11}}{1 + 4\xi_1 Y_{11}} \left(\frac{2}{\beta+1} \right) + \frac{64}{5\pi} \xi_1 Y_{11}/\Lambda_\eta C_\eta \right] \qquad (5.10)$$

The result is shown in Table 1 as result A in comparison with MD result of Alder, et al.[17] For C_η the MD result is used.

It is remarkable that the effective diameter that is obtained purely on thermodynamic grounds via (3.13), (5.9) shows a significant departure from the results of HKW[6] in which $C_D = 1 \ncong H(\sigma_{12}) \geq 1$. The increased size of the effective solvent-solute collision radius proves to yield an accurate description of the caging effect which lowers C_D below 1, as is shown by its excellent agreement with MD[17] at high

density.

However, in the low-density limit, our result A shows a nonnegligible deviation from the exact value of C_D, which is unity, as was mentioned in discussing the friction coefficient. This implies that our description cannot be extended with precision to low density without introducing an effective reduced mass μ as well as an effective collision radius.

Replacing μ_{12} by μ, in the expression of $\zeta_E(\sigma)$ (3.16) we find

$$\zeta_E(\sigma,\mu) = \frac{8}{3} n_1\sigma^2 Y_{12}(\sigma)(2\pi\mu kT)^{1/2}$$

$$= \left(\frac{\mu}{\mu_{12}}\right)^{1/2} \zeta_E(\sigma) \tag{5.11}$$

The friction coefficient and diffusion coefficient are now given by

$$\zeta^{-1}(\sigma,\mu) = \zeta_E^{-1}(\sigma,\mu) + \zeta_H^{-1}(\sigma,\mu)$$

$$= \left(\frac{\mu}{\mu_{12}}\right)^{-1/2} \zeta_E^{-1}(\sigma) + \zeta_H^{-1}(\sigma) \tag{5.12}$$

$$D(\sigma,\mu) = \left(\frac{\mu}{\mu_{12}}\right)^{1/2} D_E(\sigma) + D_H(\sigma) \tag{5.13}$$

Thus, the correction factor to the Enskog value is, from (5.8),

$$C_D = a\alpha^{-1}[1 + H(\sigma,\mu)] = a\alpha^{-1}[1 + \alpha H(\sigma)] \tag{5.14}$$

where

$$\alpha \equiv \left(\frac{\mu}{\mu_{12}}\right)^{1/2} \qquad H(\sigma,\mu) = \alpha H(\sigma) \ .$$

Demanding here that ζ, D approach their Enskog (Boltzmann) values in the low-density limit, i.e., $C_D = 1$, we find

$$\alpha = \alpha_B = a_B = \left(\frac{q+1}{q\beta_B + 1}\right)^2 , \qquad (5.15)$$

the subscript B denoting the low-density (Boltzmann) limit. Then

$$C_D = \frac{a}{a_B} [1 + a_B H(\sigma)]$$

$$= \left(\frac{\beta_B q + 1}{\beta q + 1}\right)^2 \frac{Y_{12}(\sigma_{12})}{1 + 4\xi_1 Y_{11}} + \frac{32}{5\pi} \left(\frac{2\mu_{12}}{m_1}\right)^{1/2} \frac{(1+q)^2}{q(1+\beta q)} \frac{\xi_1 Y_{12}(\sigma_{12})}{C_\eta \Lambda_\eta}$$

$$(5.16)$$

In self-diffusion where $q = \sigma_{11}/\sigma_{22} = 1$, $p = m_1/m_2 = 1$, we find

$$C_D^S = \left(\frac{\beta_B + 1}{\beta + 1}\right)^2 \frac{Y_{11}}{1 + 4\xi_1 Y_{11}} + \frac{128}{5\pi} (1 + \beta)^{-1} \frac{\xi_1 Y_{11}}{C_\eta \Lambda_\eta} \qquad (5.17)$$

This result is also shown in Fig. 1 as result B. This yields the correct low-density limit, although it is no better than result A (in which $\alpha = 1$) in describing the caging effect. We should acknowledge here the assumption that α is density independent has no obvious a priori justification, and the good agreement we obtain through the use of such simple approximations is remarkable. In fact this agreement with MD is better than any results[3,4] of the renormalized kinetic-theory treatments that involve the more rigorous and complicated analysis of dynamic correlation.

In the following, we present a very general approximation scheme for finding a better μ, which is applicable to all densities. We

start it by writing C_D as

$$C_D = 1 + cH(\sigma,\mu)$$

$$= 1 + bH(\sigma) \tag{5.18}$$

From (5.11), we then have the relation

$$\alpha^{-1}a[1 + \alpha H(\sigma)] = 1 + bH(\sigma) , \tag{5.19}$$

which exhibits that we are correcting the hydrodynamic theory through the LHS and the Enskog theory through the RHS simultaneously by determining the unknown parameters, α and b. In the low density limit, i.e., $H \to 0$, we recover (5.15) from (5.19). Equation (5.19) will be transformed to the more convenient form:

$$\gamma = G\alpha + F \tag{5.20}$$

where $\gamma = b\alpha$, and $F = H(\sigma)^{-1}a$ $G = a - H(\sigma)^{-1}$ are known variables.

To simplify the problem we confine ourselves to the case $p = q^\delta$ where $p = m_1/m_2$. With the assumption that α, γ are analytic functions of q, we may express them as Taylor series around the points $q = q_1$ and $q = q_2$.

$$\alpha = \alpha_{(N_\alpha)} = \sum_{k=0}^{N_\alpha} \frac{1}{k!} \alpha^{(k)}(q_1)(q-q_1)^k = \sum_{\ell=0}^{N_\alpha} \frac{1}{\ell!} \alpha^{(\ell)}(q_2)(q-q_2)^\ell \tag{5.21}$$

$$\gamma = \gamma_{(N_\gamma)} = \sum_{k=0}^{N_\gamma} \frac{1}{k!} \gamma^{(k)}(q_1)(q-q_1)^k = \sum_{\ell=0}^{N_\gamma} \frac{1}{\ell!} \gamma^{(\ell)}(q_2)(q-q_2)^\ell \tag{5.22}$$

Here the integers N_α, N_γ are to be taken large enough to guarantee good approximations for α and γ. Since $\alpha^{(k)}(q_1)$, $\alpha^{(\ell)}(q_2)$ $[\gamma^{(k)}(q_1)$,

$\gamma^{(\ell)}(q_2)$] depend on each other linearly, it suffices to determine $\alpha^{(k)}(q_1)$, $\gamma^{(k)}(q_1)$.

Suppose we have ν known conditions that enable us to relate the coefficients:

$$0 = f_n[\alpha(q_1), \alpha'(q_1), \alpha''(q_1) \ldots \alpha^{(N_\alpha)}(q_1);$$
$$\gamma(q_1), \gamma'(q_1), \gamma''(q_1) \ldots \gamma^{(N_\gamma)}(q_1)]$$

$$1 \leq n \leq \nu \qquad (5.23)$$

Taking derivatives $(\partial/\partial q)^n$ of (5.20) at $q = q_1$ successively starting from $n = 0$ to $n = N_1$, we obtain the relations

$$0 = P_n[\alpha(q_1), \alpha'(q_1) \ldots \alpha^{(n)}(q_1); \gamma(q_1), \gamma'(q_1) \ldots \gamma^{(n)}(q_1)]$$

$$0 \leq n \leq N_1 \qquad (5.24)$$

A similar procedure at $q = q_2$, yields

$$0 = R_n[\alpha(q_2), \alpha'(q_2) \ldots \alpha^{(n)}(q_2); \gamma(q_2), \gamma'(q_2) \ldots \gamma^{(n)}(q_2)]$$
$$= Q_n[\alpha(q_1), \alpha'(q_1) \ldots \alpha^{(N_\alpha)}(q_1); \gamma(q_1), \gamma'(q_1) \ldots \gamma^{(N_\gamma)}(q_1)]$$

$$0 \leq n \leq N_2 \qquad (5.25)$$

where a substitution of (5.21), (5.22) is made. The integers N_1, N_2 are arbitrary except for the constraint

$$N_1 + N_2 = N_\alpha + N_\gamma - \nu . \qquad (5.26)$$

If one is to predict C_D for q around $q = q_1$ with high precision, one might have to go to large N_1. The relations (5.23), (5.24) and (5.25) constitute $N_\alpha + N_\gamma + 2$ equations, whereby the unique solution of the $N_\alpha + N_\gamma + 2$ coefficients are determined. This procedure is tantamount to identifying the curves, LHS and RHS of (5.20) or (5.19), by matching their values, slopes, and curvatures, etc. at the points $q = q_1$ and $q = q_2$.

In practice, this matching procedure, although conceptually simple, may turn out to be extremely complicated for large N_α, N_γ. However, if one assumes that α, γ and the curves (5.20) vary weakly on q in the region of our interest, one may try small N_α, N_γ. This amounts to the assumption that the curve is smooth enough to allow it to be approximately defined by a small number of derivatives at $q = q_1$ and $q = q_2$. This is plausible since, in the relation (5.19), the relatively strong dependence on q is absorbed in $H(\sigma)$, presumably leaving the other parameters α, b or α, γ free of drastic change around $q = 0$. This is the significance of (5.19). The validity of this assumption can be tested through comparison of the two curves -- both sides of (5.20), -- gotten by substituting (5.21), (5.22). If the two curves are sufficiently close together over all regions of q of our interest, the small N_α, N_γ which we chose are accepted as appropriate. The ultimate criterion, however, is the result of MD.

Let us illustrate in a simple example, how the above scheme works out. Taking $q_1 = 1$, $q_2 = 0$, we approximate α, γ by

$$\alpha(q) = \alpha_2(q) = \alpha(1) + \alpha'(1)(q-1) + \frac{1}{2}\alpha''(2)(q-1)^2$$

$$\gamma(q) = \gamma_2(q) = \gamma(1) + \gamma'(1)(q-1) + \frac{1}{2}\gamma''(2)(q-1)^2 \qquad (5.27)$$

We can utilize the fact that $\alpha(0) = 1$, on the grounds that the hydro-dynamic theory is correct in the limit $q \to 0$, without choosing the effective parameters σ, μ. From (5.27)

$$\alpha(0) = \alpha(1) - \alpha'(1) + \frac{1}{2}\alpha''(2) = 1 \ . \qquad (5.28)$$

Evaluations of the value, slope and curvature of (5.20) at $q = 1$ give us the equations

$$G(1)\alpha(1) - \gamma(1) + F(1) = 0 \qquad (5.29)$$

$$G'(1)\alpha(1) + G(1)\alpha'(1) - \gamma'(1) + F'(1) = 0 \qquad (5.30)$$

$$G''(1)\alpha(1) + 2G'(1)\alpha'(1) + G(1)\alpha''(1) - \gamma''(1) + F''(1) = 0$$

$$(5.31)$$

A similar procedure for the value and slope at $q = 0$ yields

$$G(0)\alpha(0) - \gamma(0) + F(0) = 0 \qquad (5.32)$$

$$G'(0)\alpha(0) + G(0)\alpha'(0) - \gamma'(0) + F(0) = 0 \ , \qquad (5.33)$$

which, by noting $F(0) = 0$, $G(0) = a(0) = 1$, are reduced to

$$\alpha(0) - \gamma(0) = 0 \qquad (5.34)$$

$$\alpha'(0) + G'(0) - \gamma'(0) = 0 \qquad (5.35)$$

Substituting (5.24), the above are written as

$$\alpha(1) - \alpha'(1) + \frac{1}{2}\alpha''(1) - \gamma(1) + \gamma'(2) - \frac{1}{2}\gamma''(1) = 0 \quad (5.36)$$

$$\alpha'(1) - \alpha''(1) - \gamma'(1) + \gamma''(1) + a'(0) = 0 \quad (5.37)$$

Now the six linear equations (5.28), (5.29), (5.30), (5.31), (5.36), (5.37) enable us to solve $\alpha(1)$, $\alpha'(1)$, $\alpha''(1)$, $\gamma(2)$, $\gamma'(2)$, $\gamma''(2)$, i.e., the approximate $\alpha(q)$, $\gamma(q)$ and C_D via (5.19). This approximation is presumably best around $q = 1$, where three conditions (5.29), (5.30), (5.31) are given.

It is straightforward to generalize this procedure to include the dependence on the mass ratio, p. One can also extend this scheme to the Lorentz limit in which $p \to \infty$, $q \to \infty$. Though Y_{ij}^{MCSL} has not been shown to be valid for large q, α and γ can compensate for its approximate nature.

We now go back to the binary case to assess the deviation of ζ from the hydrodynamic limiting value, i.e., the Stokes law $\zeta_S = 2\pi\eta\sigma_{22}$. Considering the effective mass given by (5.15), we have

$$\zeta/\zeta_S = \left(\frac{2\sigma}{\sigma_{22}}\right)[1 + H^{-1}(\sigma,\mu)]$$

$$= (1 + \beta q)\left[1 + \frac{5\pi}{32}\left(\frac{m_1}{2\mu_{12}}\right)^{1/2}\xi_1^{-1}q(\beta q + 1)\right.$$

$$\left. \times \frac{C_\eta \Lambda_\eta}{1 + 4\xi_1 Y_{11}}\left(\frac{\beta_B q + 1}{q + 1}\right)^2\right]^{-1} \quad (5.38)$$

The numerical results are presented in Figs. 2, 3 for the solvent volume fractions $\xi_1 = 0.4$, 0.1 respectively. We also for convenience

restrict ourselves to the cases $p = m_1/m_2 = q^\delta$ (δ = 0, 3, 5). Strikingly enough, in the case of the high solvent density (ξ_1 = 0.4), we observe only small deviations of ζ from the Stokes value ζ_S for various cases of q, even for the case q = 1. This remarkable feature, together with the hydrodynamic structure in the velocity field around the diffusing particle was discovered by Alder, et al. through their MD studies[17] (self-diffusion). This stimulated some workers[20] to attempt at describing this phenomena on purely hydrodynamic grounds. In spite of the moderate successes in this route, we follow Hynes and his coworkers in regarding this coincidence ($\zeta/\zeta_S \sim 1$) as fortuitous and not fundamental, since, for small and light solute particle the microscopic collisional contribution plays a significant role in determining the diffusivity. The insensitivity of ζ or D_{12} to the solute mass in approaching the hydrodynamic limit is manifested through the way the results for the various cases δ = 0, 3, 5 tend to converge toward an asymptotic value.

VI. SUMMARY AND CONCLUDING REMARKS

Here, we have argued that the original idea of Hynes, et al. should be modified so as to more fully accommodate the approximate nature of the continuum description for the solvent. For this, we have introduced σ, μ the effective (or renormalized) contact distance and reduced mass of the solvent and solute particles, and presented a scheme for finding the effective parameters through a synthesis of the Enskog theory and hydrodynamics. The σ and μ are found to deviate significantly from their true values, i.e., σ_{12}, μ_{12}, in the regime where the hydrodynamic description is bound to fail, i.e., for the low-solvent density and small solute particle. When applied to self-diffusion, these yield results in an excellent agreement with MD results. We believe this scheme may be capable of giving a good description even for the Lorentzian gas regime. Finally our results show how the hydrodynamic Stokes-Einstein result for D_{12} happens to be a good numerical approximation at high solvent density for all regions of q of interest to us.

In the following paper, we shall study the intrinsic shear and bulk viscosity, by utilizing the results developed in Sec. IV.

APPENDIX

1) MCSL expressions for Y_{ij}

$$Y_{11} = (1 - \xi)^{-3}\left\{1 - \xi + \frac{1}{2}(\xi_1 + q\xi_2)\right\}\left\{1 - \xi + (\xi_1 + q\xi_2)\right\}$$

$$Y_{12} = (1 - \xi)^{-3}\left\{1 - \xi + 2(1 + q)^{-1}(\xi_1 + q\xi_2)\right\}$$
$$\times \left\{1 - \xi + (1 + q)^{-1}(\xi_1 + q\xi_2)\right\}$$

$$Y_{22} = (1 - \xi)^{-3}\left\{1 - \xi + \frac{1}{2} q^{-1}(\xi_1 + q\xi_2)\right\}$$
$$\times \left\{1 - \xi + q^{-1}(\xi_1 + q\xi_2)\right\}$$

where

$$\xi = \xi_1 + \xi_2$$

$$\xi_i = \frac{\pi}{6} n_i \sigma_{ii}^{3}$$

$$q = \sigma_{11}/\sigma_{22}$$

In the case of trace concentration of the species 2, which is of concern to us here, the above are reduced to

$$Y_{11} = (1 - \xi_1)^{-3}(1 - \frac{1}{2} \xi_1)$$

$$Y_{12} = (1 - \xi_1)^{-3}[1 - \xi_1 + 2(1 + q)^{-1}\xi_1][1 - \xi_1 + (1 + q)^{-1}\xi_1]$$

$$Y_{22} = (1 - \xi_1)^{-3}(1 - \xi_1 + \frac{1}{2} q^{-1}\xi_1)(1 - \xi_1 + q^{-1}\xi_1)$$

2) The validity of MCSL Y_{ij} for $0 < q \leq 1$

At $q = 1$, Y_{ij} is reduced to the Carnahan-Starling (CS) Y_{11} of one-component fluid, which yields the exact equation of state.

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$P/n_1kT = 1 + 4\xi_1 Y_{11}$. But, for the binary mixture of disparate size, the validity of Y_{ij} has not been tested extensively. Our relation (3.13), i.e., $Y_{12} = 1 + 4\xi_1 Y_{11}$ in the limit $q \to 0$ now can serve as the criterion. As is shown in Table 2, MCSL is even good at $q = 0$, far better than the Percus-Yevick (PY) Y_{ij}. For large values of q, however, no exact criterion seems to be available at this time.

3) Improvement of MCSL

Noting that the deviation of Y_{12}^{MCSL} from the exact Y_{12} is small in the region $0 < q \le 1$ and is vanishing at $q = 1$, we may write

$$\frac{Y_{12}(q)}{Y_{12}^{MCSL}(q)} = C(q) = C_0 + C_1(q-1)$$

To determine C_0, C_1, we exploit two conditions

i) at $q = 1$, $Y_{12}(q=1) = Y_{11} = Y_{11}^{CS}$

$$C = 1 = C_0$$

ii) at $q = 0$, $Y_{12}(q=0) = 1 + 4\xi_1 Y_{11}$

$$C_0 - C_1 = 1 + 4\xi Y_{11}/Y_{12}^{MCSL}(q=0)$$

We find

$$\frac{Y_{12}(q)}{Y_{12}^{MCSL}(q)} = \frac{1 + 4\xi_1 Y_{11}}{Y_{12}^{MCSL}(q=0)} + \left[1 - \left(\frac{1 + 4_1 Y_{11}}{Y_{12}^{MCSL}(q=0)}\right)\right]q$$

$$Y_{12}(q) = \left[\frac{(1-\xi_1)^3 + 4\xi_1(1 - \frac{1}{2}\xi_1)}{1 + \xi_1} + \left\{1 - \frac{(1-\xi_1)^3 + 4\xi_1(1 - \frac{1}{2}\xi_1)}{1 + \xi_1}\right\}q\right]$$

$$\times\ (1-\xi_1)^{-3}\left\{1 + [(1+q^{-1}) - 1]\xi_1\right\}\left\{1 + [2(1+q)^{-1} - 1]\xi_1\right\}$$

It is worthwhile noting that this correction yields rigorously the result $M = 1$ in the limit $q \to 0$, where M is the mixing parameter under the mixing condition of fixed temperature and pressure defined in ref. [22]:

$$M = \lim_{\xi_2 \to 0} \frac{\xi_1^{\,0} - \xi_1}{\xi_2 \xi_1^{\,0}}$$

where $\xi_1^{\,0}$, ξ_1 is the volume fraction of the solvent beforeeand after mixing the solute, respectively. Physically this expresses the fact that the overall volume increase by mixing is identical to the volume of the solute mixed.

ACKNOWLEDGMENTS

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TABLE 1. Our results in comparison with MD[17] results and the work of Hynes, et al.[6] (HKW). D_E is the Enskog value of D, the self-diffusion coefficient; ξ_1 is $\pi\rho_1\sigma_{11}^3/6$ where ρ_1 is solvent number density and σ_{11} is solvent-particle diameter. The σ_{11}^* is effective solvent-particle diameter. Column A refers to our result obtained by using an effective collisional diameter only; B refers to our final result obtained by using the effective reduced mass as well as the effective diameter.

ξ_1	$\beta = \sigma_{11}^*/\sigma_{11}$	$(D/D_E)^{HKW}$	$(D/D_E)^{MD}$	(D/D_E) THIS WORK	
				A	B
0	1.191	1		0.833	1.00
0.0074	1.190	1.030	1.02	0.852	1.017
0.037·	1.185	1.156	1.04	0.935	1.093
0.247	1.135	1.711	1.34	1.261	1.380
0.370	1.107	1.635	1.27	1.107	1.207
0.411	1.099	1.608	1.15	1.057	1.153
0.463	1.088	1.437	0.84	0.865	0.955
0.494	1.082	1.280	0.58	0.698	0.784

TABLE 2.   The ratio $1 + 4Y_{11}/Y_{12}(q=0)$ given by the
two approximations noted in the text.

ξ_1	MCSL	PY
0	1	1
0.01	1.0001	1.0003
0.1	1.0082	1.0250
0.2	1.0267	1.0857
0.3	1.0485	1.1687
0.4	1.0686	1.2667
0.5	1.0833	1.3750

FIGURE CAPTIONS

Figure 1. The coefficient of self-diffusion given in terms of the
Enskog value D_E. The full curve shows the result of our
final approximation B in which the solvent-solute collision
is described by an effective reduced mass as well as an
effective collision diameter. The dashed curve gives the
result of Hynes, et al.[6] (HKW) and the circles show the
molecular-dynamics value.[17]

Figure 2. The ratio of the friction coefficient ζ to the Stokes
value ζ_S for the size ratio $0 < \sigma_{11}/\sigma_{22} \leq 1$, at solvent
volume fraction $\xi_1 = 0.4$. The full curves represent our
result for several values of δ, where δ is defined through
$m_1/m_2 = (\sigma_{11}/\sigma_{22})^\delta$. The dotted line gives the result of
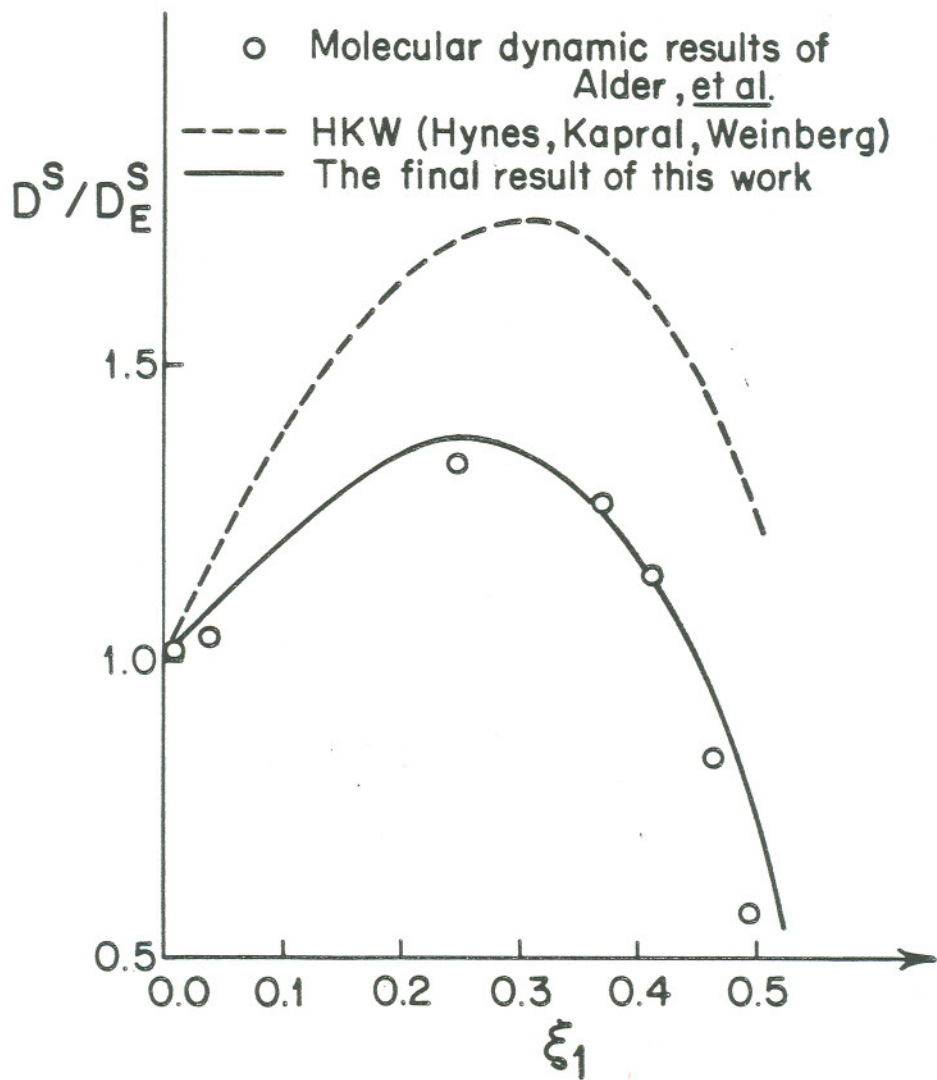HKW for the case $\delta = 3$.

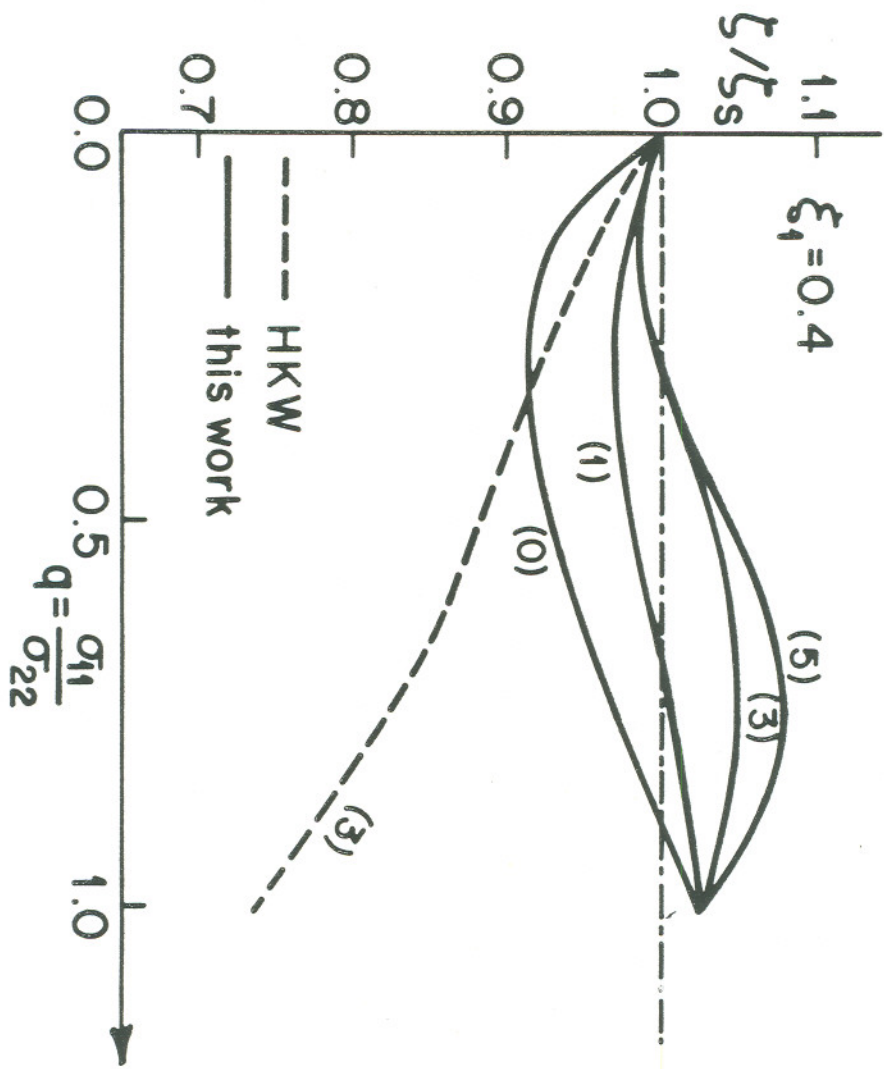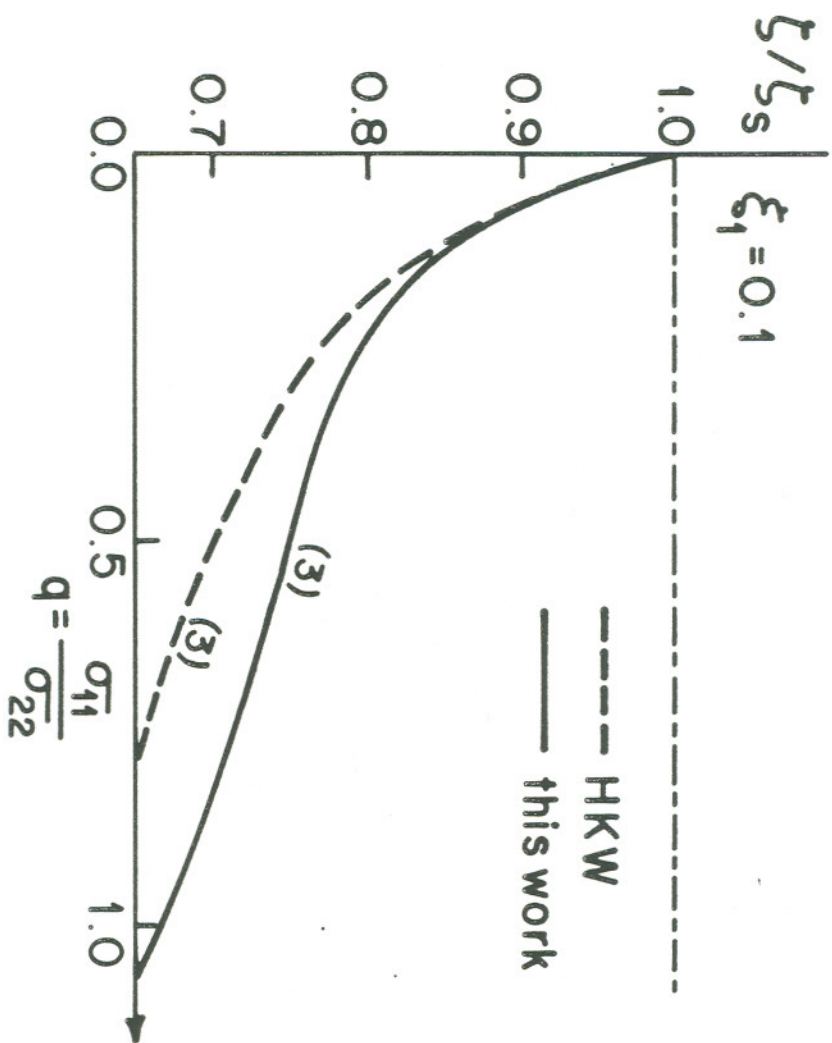Figure 3. As in Fig. 2, except that $\xi_1 = 0.1$.

Figure 1

Figure 2

Figure 3