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Bulk and Shear Viscosities of a Polydisperse Hard-Sphere Fluid

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The bulk and shear viscosity expressions for a multicomponent hard-sphere mixture in the Enskog transport theory are generalized to the polydisperse limit. The effect of polydispersity is expressed in terms of correction factors to the monodisperse fluid results. These correction factors have been evaluated for both a log-normal size distribution with the mass–size relation of a power-law form and a log-normal mass distribution with fixed particle size, which is the continuous limit of "isotopes."

KEY WORDS: Bulk viscosity, shear viscosity; hard-sphere fluid; polydisperse; Enskog transport theory.

1. INTRODUCTION

The transport properties (shear and bulk viscosities, thermal conductivity, mutual and thermal diffusion coefficients) of dense multicomponent hard-sphere fluid mixtures have been obtained by Cohen and co-workers$^{(1)}$ in the revised Enskog theory (RET). The RET is an improvement of standard Enskog theory (SET) in that it takes as input the radial distribution function at contact between two colliding spheres (usually known as the contact value) evaluated as a functional of the local density field for a nonuniform system at equilibrium, while the SET requires as input the contact value of the radial distribution function for a uniform system evaluated as a function of the local density field at some particular point, typically the midpoint of the line joining the centers of the two colliding spheres. The

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RET leads to a description of mutual diffusion that is consistent with irreversible thermodynamics,$^{(2)}$ while the SET does not.$^{(3)}$ The RET results of Cohen and co-workers have been recently extended by us$^{(4)}$ to the study of shear viscosity of polydisperse hard-sphere fluids. A polydisperse hard-sphere fluid is an infinite-species limit of the multicomponent hard-sphere mixture in that the size and mass of the particle satisfy some continuous distributions. In our previous study$^{(4)}$ (hereafter refered to as I), explicit expression of shear viscosity was given for a distribution of particle size with the mass–size relation of a power-law form as the solution of a set of linear integral equations. For the special case of equal-mass particles, analytic solution to this set of linear integral equations was obtained. It was shown that a simple Gaussian quadrature method can be used to evaluate numerically the shear viscosity. Here we further extend our study to the bulk viscosity. We shall also study both the shear and bulk viscosities in a continuous analog of isotopic fluids, i.e., a polydisperse fluid with a continuous distribution of mass with the particle size constant.

2. POLYDISPERSITY IN SIZE OF PARTICLES

Expressions for the shear viscosity η and the bulk viscosity κ are the same in the RET and SET for a ν-component dense hard-sphere mixture.$^{(1)}$ In the Nth Enskog approximation (i.e., when N Sonine polynomials are included in the Sonine polynomial expansion that is used in the Chapman–Enskog method of solution; see ref. 5), η and κ are given by$^{(1)}$

$$\eta(N)=\frac{1}{2}k_{\mathrm{B}}T\sum_{i=1}^{\nu}x_iH_ib_{i0}(N)+\frac{4}{15}n^2(\pi k_{\mathrm{B}}T)^{1/2}\sum_{i=1}^{\nu}\sum_{j=1}^{\nu}(2M_{ij}m_j)^{1/2}x_ix_j\sigma_{ij}^4\chi_{ijc} \tag{2.1}$$

$$\kappa(N)=\frac{5}{2}k_{\mathrm{B}}T\sum_{i=1}^{\nu}x_i(H_i-1)\,h_{i1}(N)+\frac{4}{9}n^2(\pi k_{\mathrm{B}}T)^{1/2}\sum_{i=1}^{\nu}\sum_{j=1}^{\nu}(2M_{ij}m_j)^{1/2}x_ix_j\sigma_{ij}^4\chi_{ijc} \tag{2.2}$$

where k_{B} is Boltzmann's constant, T is the absolute temperature, x_i is the mole fraction of the ith species, $b_{i0}(N)$ and $h_{i1}(N)$ are the coefficients of Sonine polynomial expansions and are therefore different for different N used, and H_i ($i=1, 2,..., \nu$) are given by

$$H_i=1+\frac{8\pi}{15}n\sum_{j=1}^{\nu}x_jM_{ji}\sigma_{ij}^3\chi_{ijc} \tag{2.3}$$

Here n is the total particle number density, χ_{ijc} is the contact value, $M_{ij} = m_i/(m_i + m_j)$ with m_i the mass per particle of species i, and $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ with σ_i the particle size (diameter) of species i. The Sonine coefficients are to be solved from the equations

$$\sum_{q=0}^{N-1} \left[b_{iq}(N) \sum_{j=1}^{v} x_j B_{ij2}^{pq'} \chi_{ijc} + \sum_{j=1}^{v} x_j B_{ij2}^{pq''} \chi_{ijc} b_{jq}(N) \right] = 5H_i \, \delta_{p0} \tag{2.4}$$

for $p = 0, 1, \ldots, N-1$ and $i = 1, 2, \ldots, v$; and

$$\sum_{q=1}^{N-1} \left[h_{iq}(N) \sum_{j=1}^{v} x_j B_{ij0}^{pq'} \chi_{ijc} + \sum_{j=1}^{v} x_j B_{ij0}^{pq''} \chi_{ijc} h_{jq}(N) \right] = T_i \, \delta_{p1} \tag{2.5}$$

for $p = 1, 2, \ldots, N-1$ and $i = 1, 2, \ldots, v$, with

$$\sum_{i=1}^{v} x_i h_{i1}(N) = 0 \tag{2.6}$$

The partial bracket integrals $B_{ijl}^{pq'}$ and $B_{ijl}^{pq''}$ were first given by Lindenfeld and Shizgal$^{(6)}$ and were included in the Appendix of I. Those relevant to κ ($l = 0$) have particularly simple forms. We thus include them in the Appendix. In Eqs. (2.4) and (2.5), δ_{ij} is the Kronecker delta. The T_i ($i = 1, 2, \ldots, v$) are given by

$$T_i = 1 + \frac{5}{2} (H_i - 1) - \frac{P}{nk_B T} \tag{2.7}$$

where P is the pressure and the equation of state is given by the virial theorem:

$$\frac{P}{nk_B T} = 1 + \frac{2\pi}{3} n \sum_{i=1}^{v} \sum_{j=1}^{v} x_i x_j \sigma_{ij}^3 \chi_{ijc} \tag{2.8}$$

For the contact value χ_{ijc}, we use the highly accurate Carnahan–Starling formula proposed by Mansoori *et al.*,$^{(7)}$

$$\chi_{ijc} = Z^{-3} \left[Z^2 + \frac{3\sigma_i \sigma_j}{\sigma_i + \sigma_j} Z Z_2 + 2 \left(\frac{\sigma_i \sigma_j}{\sigma_i + \sigma_j} \right)^2 Z_2^2 \right] \tag{2.9}$$

where

$$Z_i = \frac{\pi}{6} n \sum_{j=1}^{v} x_j \sigma_j^i, \qquad i = 1, 2, 3; \qquad Z = 1 - Z_3 \tag{2.10}$$

It is clear that Z_3 is equal to the volume fraction of the fluid mixture. Before we take the polydisperse limit, we note that Eq. (2.5) is not a set of independent equations. This comes from the fact that $\sum_{i=1}^{\nu} x_i T_i = 0$. This explains why an additional equation (2.6) is required to uniquely determine $h_{i1}(N)$. While the lowest-order Enskog approximation ($N=1$) is adequate for the shear viscosity η in the sense of yielding the full Enskog result to within a few percent, the second Enskog approximation ($N=2$) is required to obtain the same level of accuracy for the bulk viscosity κ.⁽⁸⁾

The limiting procedure of going from a multicomponent mixture to a polydisperse fluid has been described in I. We consider here a polydisperse hard-sphere fluid with a continuous distribution $f(R)$ of its particle size R, and a mass as a function of R, $m = m(R)$. The moments of $f(R)$ are defined by

$$f_i = \int_0^\infty f(R)\, R^i\, dR, \qquad i = 0, 1,.... \tag{2.11}$$

In particular, $f_0 = 1$, $f_1 = \bar{R}$ is the mean particle size, $f_2 = \sigma_R^2 + \bar{R}^2$, where $\sigma_R^2 = \int_0^\infty f(R)(R - \bar{R})^2\, dR$ defines the standard deviation from the mean σ_R. The polydispersity index s is given by $s = \sigma_R / \bar{R}$.

In the polydisperse limit, Eqs. (2.1) and (2.2) become

$$\eta = \tfrac{1}{2} k_B T I_\eta + \tfrac{4}{15} n^2 (\pi k_B T)^{1/2} J_\eta \tag{2.12}$$

$$\kappa = \tfrac{5}{2} k_B T I_\kappa + \tfrac{4}{9} n^2 (\pi k_B T)^{1/2} J_\kappa \tag{2.13}$$

with

$$I_\eta = \int_0^\infty f(R)\, H(R)\, b_0(R)\, dR \tag{2.14}$$

$$I_\kappa = \int_0^\infty f(R)[H(R) - 1]\, h_1(R)\, dR \tag{2.15}$$

and

$$J_\eta = J_\kappa = \frac{1}{16} \int_0^\infty \int_0^\infty f(R)\, f(R') \times [2M(R, R')\, m(R')]^{1/2} (R + R')^4 \chi_c(R, R')\, dR'\, dR \tag{2.16}$$

Here $M(R, R') = m(R)/[m(R) + m(R')]$, and $\chi_c(R, R')$ is the contact value given by the approximate Carnahan–Starling formula⁽⁴⁾:

$$\chi_c(R, R') = Z^{-3} \left[Z^2 + \frac{3RR'}{R + R'} Z Z_2 + 2 \left(\frac{RR'}{R + R'} \right)^2 Z_2^2 \right] \tag{2.17}$$

with

$$Z_i = \frac{\pi}{6} n f_i, \qquad i = 0, 1, 2, 3; \quad Z = 1 - Z_3 \tag{2.18}$$

Note that the volume fraction of a polydisperse fluid

$$\phi = Z_3 = \frac{\pi}{6} n f_3 \tag{2.19}$$

is related to the reduced density

$$n^* = \frac{\pi}{6} n \bar{R}^3 \tag{2.20}$$

by

$$\phi = n^* \frac{f_3}{\bar{R}^3} \tag{2.21}$$

Only in the monodisperse limit is ϕ equal to n^*. In Eqs. (2.14) and (2.15), $H(R)$ is given by

$$H(R) = 1 + \frac{\pi}{15} n \int_0^\infty f(R')[1 - M(R, R')] \times (R + R')^3 \chi_c(R, R')\, dR' \tag{2.22}$$

and $b_0(R)$, $h_1(R)$ are to be determined from

$$\sum_{q=0}^{N-1} \left[\int_0^\infty K_{pq2}(R, R')\, b_q(R')\, dR' + g_{pq2}(R)\, b_q(R) \right] = 5H(R)\, \delta_{p0} \tag{2.23}$$

for $p = 0, 1, \ldots, N-1$; and

$$\sum_{q=1}^{N-1} \left[\int_0^\infty K_{pq0}(R, R')\, h_q(R')\, dR' + g_{pq0}(R)\, h_q(R) \right] = T(R)\, \delta_{p1} \tag{2.24}$$

for $p = 1, 2, \ldots, N-1$, with

$$\int_0^\infty f(R)\, h_1(R)\, dR = 0 \tag{2.25}$$

Here

$$K_{pql}(R, R') = f(R')\, B''_{pql}(R, R')\, \chi_c(R, R') \tag{2.26}$$

$$g_{pql}(R) = \int_0^\infty f(R')\, B'_{pql}(R, R')\, \chi_c(R, R')\, dR' \tag{2.27}$$

for $l=0$, 2, and

$$T(R)=1+\frac{5}{2}[H(R)-1]-\frac{P}{nk_{\mathrm{B}}T} \tag{2.28}$$

where the equation of state is given by the virial theorem as

$$\frac{P}{nk_{\mathrm{B}}T}=1+\frac{\pi}{12}n\int_0^{\infty}\int_0^{\infty}f(R)\,f(R')$$

$$\times(R+R')^3\,\chi_c(R,R')\,dR'\,dR \tag{2.29}$$

We note that the set of linear integral equations (2.24) is not independent. Equation (2.25) must be included to obtain unique solution of $h_1(R)$. The $T(R)$ satisfies the equation

$$\int_0^{\infty}f(R)\,T(R)\,dR=0 \tag{2.30}$$

The partial bracket integrals $B'_{pql}(R,R')$ and $B''_{pql}(R,R')$ are the polydisperse generalizations of $B_{ijl}^{pq'}$ and $B_{ijl}^{pq''}$ and were given in the Appendix of I. Those relevant to κ $(l=0)$ have particularly simple forms and are included in the Appendix.

In the monodisperse limit, we expect to recover the well-known Enskog expression of κ. For a monodisperse hard-sphere fluid with size $\bar{R}$, mass $\bar{m}$, and volume fraction ϕ, which now is qual to n^*, we have simply

$$f(R)=\delta(R-\bar{R}) \tag{2.31}$$

This gives, from Eqs. (2.15), (2.16), and (2.25), that $h_1(\bar{R})=0$, $I_\kappa=0$, and

$$J_\kappa=\bar{m}^{1/2}\bar{R}^4\chi_c \tag{2.32}$$

where $\chi_c=\chi_c(\bar{R},\bar{R})$ is the contact value that, from Eq. (2.17), is given by the Carnahan–Starling formula

$$\chi_c=\frac{1-\phi/2}{(1-\phi)^3} \tag{2.33}$$

Hence we recovered the Enskog expression:

$$\kappa=\frac{16}{\pi}\frac{\phi^2}{\bar{R}^2}\left(\frac{\bar{m}k_{\mathrm{B}}T}{\pi}\right)^{1/2}\chi_c \tag{2.34}$$

The form of the approximation formula (2.17) for $\chi_c(R,R')$ leads to a couple of interesting analytic consequences. First, we note that if we substitute Eq. (2.17) into the equation of state (2.29), the integration can be easily performed to yield

$$\frac{P}{k_B T} = \frac{6}{\pi} Z^{-3}[Z_0 Z^2 + 3Z_1 Z_2 Z + 3Z_2^3 - Z_2^3 Z_3] \tag{2.35}$$

(This equation of state for a polydisperse hard-sphere fluid was obtained earlier by Salacuse and Stell$^{(9)}$ from direct generalization of its finite-component mixture version.) Second, in the special case of equal-mass particles, the partial bracket integrals are functions of $(R+R')^2$ only. Use of Eq. (2.17) makes the kernel $K_{pql}(R, R')$ degenerate. Therefore, the integral equations for the Sonine coefficients can be solved analytically, which leads to simple algebraic expressions for the transport coefficients. Detailed results have been given for η in I. For κ the procedure is similar and just as straightforward. We note here that although this analyticity is the consequence of using the approximate Carnahan–Starling formula (2.17), it becomes exact in the dilute-gas limit, where Eq. (2.17) becomes exact.

For general mass–size relations, however, the integral equations for the Sonine coefficients in general have to be solved numerically. A mass–size relation of a power-law form appears in many physical situations and has been considered in I. It assumes that

$$m(R) = \bar{m}\,\frac{R^d}{f_d} \tag{2.36}$$

where $\bar{m}$ is the average mass per particle, defined by

$$\bar{m} = \int_0^\infty m(R)\, f(R)\, dR \tag{2.37}$$

The exponent d is essentially the fractal dimension of the system. The f_d is the generalized dth moment given by Eq. (2.11) in which i is set to d. The equal-mass particle case simply corresponds to $d = 0$. The size distribution we consider here is the log-normal distribution,$^{(10)}$ a two-parameter function defined by

$$f(R) = \frac{1}{\beta(2\pi)^{1/2} R} \exp - \left[\frac{\ln(R/R_0)}{\beta\sqrt{2}}\right]^2 \tag{2.38}$$

where $\beta > 0$ is related to the polydispersity index by $\beta = [\ln(s^2 + 1)]^{1/2}$, and R_0 is the particle size that maximizes the exponent and is related to $\bar{R}$ by $\bar{R} = R_0 \exp(\beta^2/2)$. The moments are

$$f_i = R_0^i \exp(i^2\beta^2/2), \qquad i = 0, 1, 2,... \tag{2.39}$$

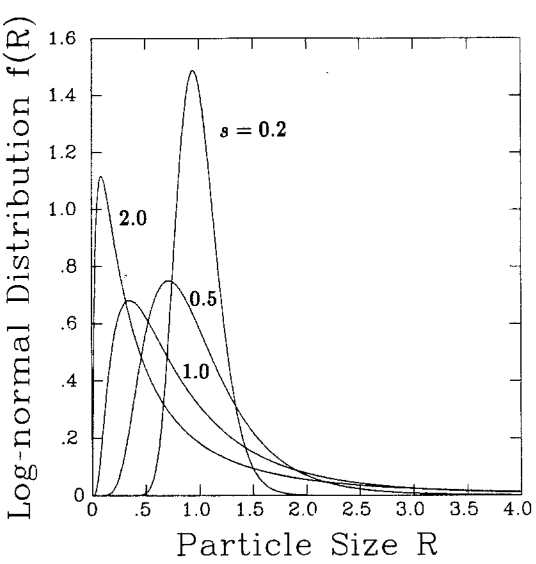

Fig. 1. Log-normal size distribution for a number of values of the polydisperse index *s*.

Figure 1 shows the log-normal distribution for a number of values of the polydispersity index *s*, with $\bar{R}$ set to unity without loss of generality. It is seen that for low polydispersity ($s < 20\%$), the log-normal distribution is very much like a Gaussian. As *s* increases, smaller particles become more probable.

A simple numerical method we use is the Gauss–Hermite quadrature. For any function $F(R)$, we have

$$\int_0^\infty f(R)\, F(R)\, dR = \frac{1}{\sqrt{\pi}} \sum_{i=1}^{L} w_i F(R_i) \tag{2.40}$$

where L is the number of quadrature points,

$$R_i = \bar{R} \exp(x_i \beta \sqrt{2} - \beta^2/2) \tag{2.41}$$

and w_i, x_i are the weight factors and abscissas for the weight function $\exp(-x^2)$ in $(-\infty, +\infty)$, respectively. Thus the integral equations (2.23)–(2.25) are made into linear algebraic equations for the Sonine coefficients evaluated at the quadrature points, solutions of which are then substituted into expressions for the transport coefficients, again using the same quadrature method. It has been found that convergence is fast. For the region of high ϕ, *s*, and *d*, use of 18 quadrature points in our study gives an accuracy within 1% for the bulk viscosity. For the shear viscosity and other regions of interest, the convergence is even faster. Our calculations are in the first Enskog approximation for η and in the second Enskog approximation for κ.

We can present our results as corrections to the monodisperse-fluid results. We define the correction factors as

$$f_\alpha = \frac{\alpha}{\alpha(s=0)} \tag{2.42}$$

where $\alpha = \eta$ or κ. The f_α thus defined is a function of ϕ, s, and d. Here $\alpha(s=0)$ is the monodisperse limiting result of α in a fluid with the same volume fraction ϕ, particle size $\bar{R}$, and mass $\bar{m}$. The quantity $\kappa(s=0)$ has been given by Eq. (2.34), while $\eta(s=0)$ in the first Enskog approximation is given by

$$\eta(s=0) = \frac{1}{\chi_c}\left[\left(1+\frac{8}{5}\phi\chi_c\right)^2 + \frac{768}{25\pi}\phi^2\chi_c^2\right]\eta_0 \tag{2.43}$$

where $\eta_0 = (5/16\bar{R}^2)(\bar{m}k_B T/\pi)^{1/2}$ is the dilute-gas limit of $\eta(s=0)$. The monodisperse case $(s=0)$ corresponds to $f_\eta = f_\kappa = 1$ for all ϕ and d. We wish to point out that f_η thus defined differs from that in I in that the latter is the correction factor to the monodisperse dilute gas. The two become the same only in the dilute-gas limit.

Numerical results for f_η and f_κ vs. s are presented in Figs. 2 and 3,

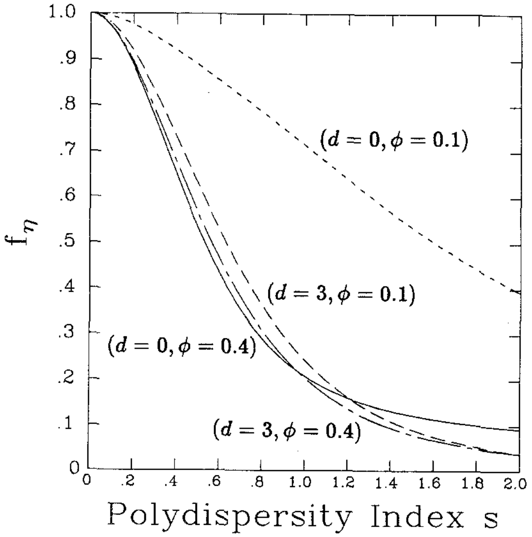

Fig. 2. Polydispersity in size: f_η vs. s for $d=0$, $\phi=0.1$ (- -); $d=0$, $\phi=0.4$ (—); $d=3$, $\phi=0.1$ (– –); and $d=3$, $\phi=0.4$ (— - —). The mean particle diameter $\bar{R}$ is held fixed.

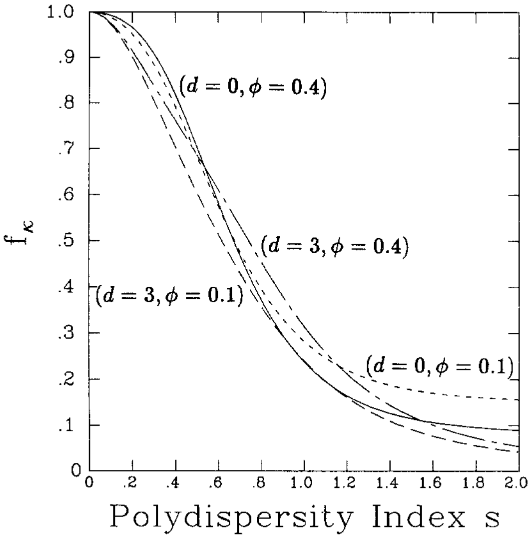

Fig. 3. Same as Fig. 2, but for f_κ.

respectively, for a number of d and ϕ values. It is seen that an increase of polydispersity reduces both the bulk and shear viscosities. This can be understood from Eq. (2.21) in the following way: as the system becomes more polydisperse, the total number density of particles decreases and smaller particles become more probable, which effectively slows down momentum transfer. The decrease of shear viscosity becomes faster, for a system with fixed fractal dimension, as the volume fraction is increased. The opposite trend is observed for the bulk viscosity, except that at low fractal dimensions and high polydispersities ($s > 70\%$), the same behavior as in the case of shear viscosity appears. As the volume fraction is lowered, the decrease of momentum transfer becomes faster for systems with higher fractal dimension. As volume fraction increases, the opposite trend is observed for shear viscosity in the low- and medium-polydispersity regions ($s < 90\%$), and for bulk viscosity in the medium- and high-polydispersity regions (s between 55% and 150%). As can be seen from our figures, the effect of size polydispersity can bring both the shear and bulk viscosities down as much as 95% for large s.

3. POLYDISPERSITY IN MASS OF PARTICLES

An interesting situation not covered so far is when all particles have the same size R but a continuous mass distribution $f(m)$. This limiting case of "isotopes" is especially relevant to some problems associated with polymers. The approach to the polydisperse results in this case is similar to the corresponding derivation in terms of size distribution, but the resulting equations are much simpler.

The η and κ are again given by Eqs. (2.12) and (2.13), respectively, but now with

$$I_\eta = \int_0^\infty f(m)\, H(m)\, b_0(m)\, dm \tag{3.1}$$

$$I_\kappa = \int_0^\infty f(m)[H(m) - 1]\, h_1(m)\, dm \tag{3.2}$$

and

$$J_\eta = J_\kappa = R^4 \chi_c \int_0^\infty \int_0^\infty f(m)\, f(m') \times [2M(m, m')m']^{1/2}\, dm'\, dm \tag{3.3}$$

where $M(m, m') = m/(m + m')$, and χ_c is given by Eq. (2.33), since now the volume fraction ϕ is simply equal to $n^* = (\pi/6)\, nR^3$. The $H(m)$ is given by

$$H(m) = 1 + \frac{16}{5} n^* \chi_c \int_0^\infty f(m')[1 - M(m, m')]\, dm' \tag{3.4}$$

The Sonine coefficients $b_0(m)$ and $h_1(m)$ are to be determined from a set of linear integral equations identical in form to Eqs. (2.23)–(2.25) but with R replaced by m, and with

$$K_{pql}(m, m') = \chi_c f(m')\, B''_{pql}(m, m') \tag{3.5}$$

$$g_{pql}(m) = \chi_c \int_0^\infty f(m')\, B'_{pql}(m, m')\, dm' \tag{3.6}$$

Expressions for the partial bracket integrals $B'_{pql}(m, m')$ and $B''_{pql}(m, m')$ are given in the Appendix. The equation of state in this case is simply given by

$$\frac{P}{nk_{\mathrm{B}}T} = 1 + 4n^* \chi_c \tag{3.7}$$

The mass distribution we consider here is again the log-normal distribution defined by Eq. (2.38), but with R replaced by m. The numerical method we use to solve the integral equations is the same quadrature used

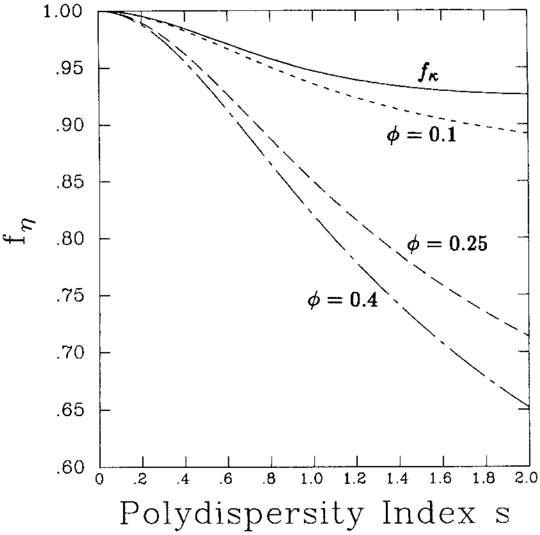

Fig. 4. Polydispersity in mass: f_κ vs. s (—); f_η vs. s for $\phi = 0.1$ (--); $\phi = 0.25$ (– –); and $\phi = 0.4$ (— - —). The particle diameter R is the same for all particles, and the mean particle mass $\bar{m}$ is held fixed.

in the previous section, with R replaced by m in Eqs. (2.40) and (2.41). However, the convergence of the quadrature method in this case is much faster. Only a few quadrature points are needed to reach 1% accuracy. Our calculations are again in the first Enskog approximation for η and in the second Enskog approximation for κ.

Our results are presented as correction factors defined by Eq. (2.42). The f_η is a function of the volume fraction ϕ and the polydispersity index s of the mass distribution. The f_κ, however, can be easily shown to be a function of s only. The density dependence of the bulk viscosity is accounted for completely by its monodisperse expression (2.34). Results of f_η vs. s for a number of volume fractions and f_κ vs. s are shown in Fig. 4. The monodisperse case ($s = 0$) corresponds to $f_\eta = f_\kappa = 1$ for all ϕ. It is seen that, as in the size distribution case, the effect of polydispersity is to reduce the momentum transfer, because as polydispersity increases, lighter particles become more probable. The decrease of shear viscosity becomes faster as the volume fraction increases.

4. DISCUSSION

We have presented in this paper an extension of our work in I to the bulk viscosity of a polydisperse hard-sphere fluid and to the bulk and shear viscosities in the interesting situation of a continuous mass distribution with fixed particle size. Although our numerical results shown here are only for a log-normal distribution, any reasonable distribution (such as the Schulz or gamma distribution and the Gaussian distribution) gives similar behavior. For a Schulz distribution, we have found that in the low-polydispersity region (up to $s = 26\%$), the difference between the shear viscosities using the log-normal and Schulz distributions is less than 0.4%.

The results of shear and bulk viscosities presented here diverge at volume fraction equal to one. This artifact results from using the approximate Carnahan–Starling formula (2.17) for the contact value, which is increasingly inaccurate at high volume fractions. The exact contact value can be expected to diverge at a close-packing density with a volume fraction less than one. Moreover, for a sufficiently low degree of polydispersity, one expects a transition(11) into an ordered state at an even lower volume fraction, beyond which Eq. (2.17) is no longer accurate. If one instead follows the metastable disordered state above this volume fraction, one expects to approach a glass transition signaled by a striking increase in the shear viscosity.(12) At present it is unclear whether one should also expect a striking increase in the metastable contact value as one approaches such a transition. If so, then the Enskog shear and bulk viscosities would also show a glass-transition anomaly that will not appear as long as Eq. (2.17) is used. In any case, because of the neglect of velocity correlations, the Enskog theory results presented here cannot be expected to be of high quantitative accuracy for volume fractions beyond about 30%.

APPENDIX. PARTIAL BRACKET INTEGRALS FOR $l = 0$

Those partial bracket integrals appearing in the bulk viscosity expression have particularly simple forms. For a multicomponent hard-sphere mixture, we have

$$
\begin{aligned}
B_{ij0}^{pq'} = 2\sigma_{ij}^2 \left(\frac{2k_B T}{m_i} \right)^{1/2} & \sum_{n=0}^{\tilde{p}} \sum_{s=0}^{\tilde{p}-n} \sum_{m=0}^{\tilde{p}-n-s} 4^n \frac{(s+n+1)!}{(n+1)!\, s!} \\
& \times \frac{\Gamma(p+q-2s-2n-m-1/2)}{(p-m-s-n)!\,(q-m-s-n)!\, m!} B_{n0}^{(1)} \\
& \times M_{ij}^n M_{ji}^{p+q-2m-2s-n-1/2} (M_{ij} - M_{ji})^{m+2s} \qquad \text{(A1)}
\end{aligned}
$$

$$
\begin{aligned}
B_{ij0}^{pq''} = 2\sigma_{ij}^2 \left(\frac{2k_B T}{m_i} \right)^{1/2} & M_{ij}^q M_{ji}^{p-1/2} \\
& \times \sum_{n=0}^{\tilde{p}} 4^n \frac{\Gamma(p+q-2n-1/2)}{(p-n)!\,(q-n)!} B_{n0}^{(2)} \qquad \text{(A2)}
\end{aligned}
$$

where

$$B_{n0}^{(1)} = -\frac{n}{2} \tag{A3}$$

$$B_{n0}^{(2)} = \tfrac{1}{2}(1-\delta_{n0}) \tag{A4}$$

and $\tilde{p} = \min(p, q)$. In the polydisperse limit, these become

$$\begin{aligned} B'_{pq0}(R, R') = {} & \left(\frac{k_{\mathrm{B}}T}{2}\right)^{1/2} \frac{(R+R')^2}{[m(R)]^{1/2}} \sum_{n=0}^{\tilde{p}} \sum_{s=0}^{\tilde{p}-n} \sum_{m=0}^{\tilde{p}-n-s} 4^n \frac{(s+n+1)!}{(n+1)!\, s!} \\ & \times \frac{\Gamma(p+q-2s-2n-m-1/2)}{(p-m-s-n)!\,(q-m-s-n)!\, m!} B_{n0}^{(1)} \\ & \times [M(R, R')]^n [1-M(R, R')]^{p+q-2m-2s-n-1/2} \\ & \times [2M(R, R')-1]^{m+2s} \end{aligned} \tag{A5}$$

$$\begin{aligned} B''_{pq0}(R, R') = {} & \left(\frac{k_{\mathrm{B}}T}{2}\right)^{1/2} \frac{(R+R')^2}{[m(R)]^{1/2}} [M(R, R')]^q \\ & \times [1-M(R, R')]^{p-1/2} \\ & \times \sum_{n=0}^{\tilde{p}} 4^n \frac{\Gamma(p+q-2n-1/2)}{(p-n)!\,(q-n)!} B_{n0}^{(2)} \end{aligned} \tag{A6}$$

In the second Enskog approximation ($N=2$), we need partial bracket integrals for $p=q=1$. From Eqs. (A5) and (A6), they are

$$\begin{aligned} B'_{110}(R, R') = {} & 2(2\pi k_B T)^{1/2} \frac{(R+R')^2}{[m(R)]^{1/2}} \\ & \times M(R, R')[1-M(R, R')]^{1/2} \end{aligned} \tag{A7}$$

$$B''_{110}(R, R') = -B'_{110}(R, R') \tag{A8}$$

For equal-mass particles, $M(R, R') = 1/2$. We thus have

$$B'_{pq0}(R, R') = A'_{pq0} \left(\frac{k_{\mathrm{B}}T}{m}\right)^{1/2} (R+R')^2 \tag{A9}$$

$$B''_{pq0}(R, R') = A''_{pq0} \left(\frac{k_{\mathrm{B}}T}{m}\right)^{1/2} (R+R')^2 \tag{A10}$$

where the constants A'_{pq0} and A''_{pq0} are

$$A'_{pq0} = \left(\frac{1}{2}\right)^{p+q} \sum_{n=0}^{\tilde{p}} 4^n \frac{\Gamma(p+q-2n-1/2)}{(p-n)!\,(q-n)!} B^{(1)}_{n0} \tag{A11}$$

$$A''_{pq0} = \left(\frac{1}{2}\right)^{p+q} \sum_{n=0}^{\tilde{p}} 4^n \frac{\Gamma(p+q-2n-1/2)}{(p-n)!\,(q-n)!} B^{(2)}_{n0} \tag{A12}$$

In particular, we have

$$A'_{110} = -A''_{110} = \sqrt{\pi} \tag{A13}$$

Finally, in the case of a mass distribution with fixed particle size R, the partial bracket integrals are given by

$$\begin{aligned} B'_{pql}(m, m') = {} & 2(2k_{\mathrm{B}}T)^{1/2} \frac{R^2}{\sqrt{m}} A_l l! \sum_{n=0}^{\tilde{p}} \sum_{s=0}^{\tilde{p}-n} \sum_{u=0}^{\tilde{p}-n-s} \\ & \times \sum_{t=0}^{l} \sum_{r=0}^{l-t} 4^n \frac{(r+s+n+t+1)!}{(n+t+1)!\,r!\,s!} \\ & \times \frac{\Gamma(p+q-2s-2n-u+l-r-t-1/2)}{(p-u-s-n)!\,(q-u-s-n)!\,(l-r-t)!\,u!} B^{(1)}_{nt} \\ & \times [M(m, m')]^{l+n-r-t} [1-M(m, m')]^{p+q+t-2u-2s-n-1/2} \\ & \times [2M(m, m')-1]^{u+r+2s} \end{aligned} \tag{A14}$$

$$\begin{aligned} B''_{pql}(m, m') = {} & 2(2k_{\mathrm{B}}T)^{1/2} \frac{R^2}{\sqrt{m}} A_l l! \, [M(m, m')]^{q+l/2} \\ & \times [1-M(m, m')]^{p+(l-1)/2} \\ & \times \sum_{n=0}^{\tilde{p}} \sum_{t=0}^{l} 4^n \frac{\Gamma(p+q-2n+l-t-1/2)}{(p-n)!\,(q-n)!\,(l-t)!} B^{(2)}_{nt} \end{aligned} \tag{A15}$$

where A_l, $B^{(1)}_{nt}$, and $B^{(2)}_{nt}$ have the same meanings as in I.

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