Bulk properties of two-phase disordered media. IV. Mechanical properties of suspensions of penetrable spheres at nondilute concentrations

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We derive rigorous upper and lower bounds on the bulk and shear moduli of suspensions of spheres of variable penetrability distributed throughout a matrix (or fluid), for all possible phase property values, through second order in the sphere volume fraction ϕ_2. The bounds, at the very least, capture the salient qualitative features that come into play when particles overlap, and, in some instances, are shown to be quantitatively very sharp. Among other results, we use these bounds to obtain good estimates of the bulk and expansion viscosities of an incompressible fluid containing spherical air bubbles and thus extend the corresponding results of Taylor in which pair interactions were neglected.

I. INTRODUCTION

In previous articles[1–3] (henceforth denoted by I, II, and III, respectively), we studied the problem of determining the effective electrical conductivity (and mathematically analogous properties) of suspensions of spheres. This work is concerned with the prediction of mechanical properties (e.g., elastic moduli and viscosities) of suspensions of spheres at nondilute concentration by considering interactions between pairs of particles. Specifically, for some general effective property κ^* we seek to study the following relation:

$$\frac{\kappa^*}{\kappa_1} = 1 + a_1\phi_2 + a_2\phi_2^2, \tag{1}$$

where κ_i and ϕ_i is the property value and volume fraction associated with the ith phase ($i = 1,2$), respectively. Here we take phase 1 to be the matrix (which may either be an elastic material or a fluid) and phase 2 to be the included or particle phase.

The first-order coefficient a_1 depends upon the individual phase property values and the solution of the boundary-value problem for an isolated sphere in an infinite matrix (or fluid), and hence does not contain information about the local structure of the medium. The second-order coefficient a_2 not only involves the same information contained in a_1 but depends upon the solution to the two-sphere boundary-value problem and the low-density limit of the radial (or pair) distribution function $g_0(r)$.

The analysis of mechanical properties of suspensions originated with Einstein,[4] who calculated the effective shear viscosity of a very dilute suspension of equisized rigid spheres in an incompressible fluid and found that $a_1 = 5/2$ for such a system. By mathematical analogy, $a_1 = 5/2$ for the problem of determining the shear modulus of a composite consisting of rigid spheres in an incompressible matrix. This analogy fails to hold for the second-order coefficient a_2 since the distributions of the particles in the two cases are different. In the case of a fluid suspension, the bulk motion will strongly affect $g_0(r)$, whereas in the elasticity problem the infinitesimal applied strain has negligible effect on $g_0(r)$.

In recent years, a large number of papers have dealt with the calculation of the second-order coefficient a_2 for various mechanical properties of suspensions of impenetrable spheres in which the average coordination number (i.e., average number of spheres physically touching each sphere) is implicitly taken to be zero.[5–9] Although exact results for a_2 of such systems have been obtained for the effective bulk modulus for all phase property values, analogous results for the effective shear modulus (due to the difficulty of solving the interaction problem for two elastic spheres in a strain field) have been presented only for the limiting cases of rigid particles and cavities.[9]

Of particular interest is the extent to which the connectedness of pairs of inclusions influences a_2 and hence κ^*. Connectedness shall be introduced by allowing the spheres to be penetrable to one another in varying degrees. Such sphere distributions may serve as useful models of certain polymer solutions, porous media, sintered materials, and composite materials: media characterized by a nonzero average coordination number. To our knowledge, the effect of interparticle overlap on a_2 for the elasticity problem has heretofore not been investigated. This is due to the fact that it is a nontrivial task to exactly obtain the solution to the boundary-value problem for two overlapping spheres. Short of finding this exact solution, the next best means of studying and estimating a_2 for penetrable spheres, for all possible phase property values, is to derive bounds on a_2, as shown below.

The purpose of this note is to study the effect of interparticle overlap on a_2 for various mechanical properties of suspensions. This is accomplished by first obtaining bounds on

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a_2 for the bulk and shear moduli of a suspension of spheres distributed with arbitrary degree of penetrability. The bounds on the second-order coefficient, at the very least, capture the essential qualitative features that come into play when particles overlap, for a wide range of phase property values. In certain instances, the bounds on the elastic moduli are shown to be quantitatively very sharp. From these results, sharp bounds on the bulk viscosity and expansion viscosity are derived for an incompressible fluid containing air bubbles.

II. LOW-DENSITY BOUNDS ON THE ELASTIC MODULI

Third-order bounds on the effective conductivity of a dispersion of spheres have been shown to yield useful estimates of this property through second order in the sphere volume fraction ϕ_2.[2,3] By third-order bounds we generally mean those bounds which are exact through third order in the difference of the phase property values (i.e., $\kappa_2-\kappa_1$). Beran and Molyneux (BM)[10] and McCoy[11] have derived such bounds for the effective bulk modulus K^* and shear modulus G^* of composites, respectively.

The BM bounds on K^* are given by

$$K_L^* \leqslant K^* \leqslant K_U^*, \tag{2}$$

where

$$K_U^* = \left[\langle K\rangle - \frac{3\phi_1\phi_2(K_2-K_1)^2}{3\langle\widetilde{K}\rangle + 4\langle G\rangle_\zeta}\right], \tag{3}$$

$$K_L^* = \left[\langle 1/K\rangle - \frac{4\phi_1\phi_2(1/K_2-1/K_1)^2}{4\langle 1/\widetilde{K}\rangle + 3\langle 1/G\rangle_\zeta}\right]^{-1}, \tag{4}$$

$$\zeta_1 = \frac{9}{2\phi_1\phi_2} I[S_3(r,s,\mu)], \tag{5}$$

$$\zeta_2 = 1-\zeta_1, \tag{6}$$

and where I is the integral operator defined by

$$I[\ ] = \lim_{L\to\infty}\lim_{\Delta\to 0}\int_\Delta^L \frac{dr}{r}\int_\Delta^L \frac{ds}{s}\int_{-1}^{1} d\mu[\ ]P_2(\mu). \tag{7}$$

Here $S_3(r,s,\mu)$ is the three-point probability function which gives the probability of finding the vertices of a triangle, with sides of length r and s and included angle $\cos^{-1}(\mu)$, in phase 1; $P_2(\mu)$ is the Legendre polynomial of order two. For any arbitrary property κ, $\langle\kappa\rangle = \kappa_1\phi_1+\kappa_2\phi_2$, $\langle\widetilde{\kappa}\rangle = \kappa_1\phi_2+\kappa_2\phi_1$, and $\langle\kappa\rangle_\zeta = \kappa_1\zeta_1+\kappa_2\zeta_2$. To summarize, the BM bounds on K^* depend not only upon K_1, K_2, G_1, G_2, and ϕ_2, but on a microstructural parameter $\zeta_1(=1-\zeta_2)$ which is an integral over the three-point probability function.

The McCoy bounds on G^* are given by

$$G_L^* \leqslant G^* \leqslant G_U^*, \tag{8}$$

where

$$G_U^* = \left[\langle G\rangle - \frac{6\phi_1\phi_2(G_2-G_1)^2}{6\langle\widetilde{G}\rangle + \theta}\right] \tag{9}$$

and

$$G_L^* = \left[\langle 1/G\rangle - \frac{\phi_1\phi_2(1/G_2-1/G_1)^2}{\langle 1/\widetilde{G}\rangle + 6\Xi}\right]^{-1}. \tag{10}$$

The quantities θ and Ξ depend not only upon K_1, K_2, G_1, G_2, ϕ_2, ζ_2, but on another three-point parameter defined by

$$\eta_1 = \frac{5}{21}\zeta_1 + \frac{150}{7\phi_1\phi_2}J[S_3(r,s,\mu)], \tag{11}$$

$$\eta_2 = 1-\eta_1, \tag{12}$$

where

$$J[\ ] = \lim_{L\to\infty}\lim_{\Delta\to 0}\int_\Delta^L \frac{dr}{r}\int_\Delta^L \frac{ds}{s}\int_{-1}^{1} d\mu[\ ]P_4(\mu). \tag{13}$$

Here $P_4(\mu)$ is the Legendre polynomial of order four. The parameters ζ_i and η_i lie in the closed interval [0,1]. Both θ and Ξ are linear in ζ_i and η_i and are given explicitly in Ref. 12.

The bounds (2) and (8) actually represent the simplified forms of the BM and McCoy bounds obtained by Milton.[12] These bounds improve upon the corresponding Hashin–Shtrikman[13] and Walpole[14] second-order bounds on K^* and G^* and hence do not include three-point information (i.e., ζ_i and η_i).

For suspensions of spheres, the BM and McCoy bounds expanded through second order in ϕ_2 are given by

$$\frac{K_U^*}{K_1} = 1 + k_1\phi_2 + k_2^U\phi_2^2, \tag{14}$$

$$\frac{K_L^*}{K_1} = 1 + k_1\phi_2 + k_2^L\phi_2^2, \tag{15}$$

$$\frac{G_U^*}{G_1} = 1 + g_1\phi_2 + g_2^U\phi_2^2, \tag{16}$$

$$\frac{G_L^*}{G_1} = 1 + g_1\phi_2 + g_2^L\phi_2^2, \tag{17}$$

where

$$k_1 = \frac{(\alpha-1)(4\gamma_1+3)}{4\gamma_1+3\alpha}, \tag{18}$$

$$g_1 = \frac{5(\beta-1)(4\gamma_1+3)}{3(2\beta+3)+4\gamma_1(3\beta+2)}, \tag{19}$$

$$k_2^U = \frac{3(\alpha-1)^2[4\gamma_1+3+4e_1\gamma_1(\beta-1)]}{(4\gamma_1+3\alpha)^2}, \tag{20}$$

$$k_2^L = \frac{3(\alpha-1)^2[\beta(4\gamma_1+3)+4e_1\gamma_1(\beta-1)]}{\beta(4\gamma_1+3\alpha)^2}, \tag{21}$$

$$g_2^U = \frac{6(\beta-1)^2\{5(2\gamma_1+1)(4\gamma_1+3)+5e_1\gamma_1[3\gamma_1(\beta-1)+2(\alpha+\beta-2)]+f_1(\beta-1)(\gamma_1+3)^2\}}{[3(2\beta+3)+4\gamma_1(3\beta+2)]^2}, \tag{22}$$

and

$$g_2^L = \frac{6(\beta-1)^2\{5(2\gamma_1+1)(4\gamma_1+3)+5e_1\gamma_1[3\gamma_1(1-1/\beta)-2(1/\alpha+1/\beta-2)]+f_1(1-1/\beta)(\gamma_1+3)^2\}}{[3(2\beta+3)+4\gamma_1(3\beta+2)]^2}. \tag{23}$$

Assuming that the parameters ζ_2 and η_2 can be expanded in powers of ϕ_2, the coefficients e_1 [appearing in Eqs. (20)–(23)] and f_1 [appearing in Eqs. (22) and (23)] are defined through the relations

$$\zeta_2 = e_1\phi_2 + O(\phi_2^2), \quad (24)$$

$$\eta_2 = f_1\phi_2 + O(\phi_2^2). \quad (25)$$

As described below, the coefficients e_1 and f_1 depend upon the zero-density limit of the radial distribution function $g_0(r)$. In Eqs. (18)–(23),

$$\alpha = \frac{K_2}{K_1}; \quad \beta = \frac{G_2}{G_1}; \quad \gamma_i = \frac{G_i}{K_i}(i = 1,2).$$

Only three of these ratios are independent since $\alpha\gamma_2 = \beta\gamma_1$. Moreover, because $\gamma_i = (3 - 6\nu_i)/(2\nu_i + 2)$, where ν_i is Poisson's ratio for the ith phase $(0 \leqslant \nu_i \leqslant 0.5)$, then $0 \leqslant \gamma_i \leqslant 1.5$.

It is important to note that the low-density bounds on K^* [(14) and (15)] and on G^* [Eqs. (16) and (17)] are exact through first order in ϕ_2. Hence, the actual second-order coefficients k_2 and g_2 are bounded by $k_2^L \leqslant k_2 \leqslant k_2^U$ and $g_2^L \leqslant g_2 \leqslant g_2^U$.

Consider the computation of k_2^L, k_2^U, g_2^L, and g_2^U for partially penetrable spheres in the permeable-sphere (PS) model.[16] In the PS model spheres of radius R are assumed to be noninteracting when nonintersecting (i.e., when $r > 2R$, where r is the distance between sphere centers), with probability of intersecting given by a radial distribution function $g(r)$, that is, $1 - \lambda$, $0 \leqslant \lambda \leqslant 1$, independent of r, when $r < 2R$. Therefore, $\lambda = 0$ and $\lambda = 1$ correspond to the extreme limits of fully penetrable and totally impenetrable spheres, respectively. In order to calculate the bounds on the second-order coefficients k_2 and g_2 as a function of the impenetrability parameter λ, we must evaluate the coefficients e_1 and f_1 defined by Eqs. (24) and (25). Such a calculation involves the use of the low-density expansion of the three-point matrix probability function S_3 in conjunction with Eqs. (5)–(7) and Eqs. (11)–(13). The integral e_1 was already computed in II for the PS model using a spherical-harmonics expansion technique.[17] In light of this we merely present the final results:

$$e_1 = 0.210\,68 + 0.350\,78(1 - \lambda), \quad (26)$$

$$f_1 = 0.482\,74 + 0.264\,07(1 - \lambda). \quad (27)$$

Equation (27) for f_1 in the PS model has heretofore not been given. For the special case of totally impenetrable spheres $(\lambda = 1)$, f_1 has been evaluated analytically elsewhere.[18] The first terms in both Eqs. (26) and (27) give the contributions to e_1 and f_1, respectively, for a reference system of totally impenetrable spheres which possesses a radial distribution function, which in the zero-density limit, is equal to zero for $r < 2R$ and unity otherwise. The second terms in Eqs. (26) and (27), therefore, give the contributions to e_1 and f_1, respectively, in excess of the reference system value, due to interparticle overlap (see I–III).

Interestingly, for the case of fully penetrable spheres $(\lambda = 0)$, the linear expressions (24) and (25) provide remarkably good approximations of the exact ζ_2 and η_2, respectively, over the whole range of the sphere volume fraction. For example, Table I compares Eq. (25) for $\lambda = 0$ (with $f_1 = 0.746\,81$) as a function of ϕ_2 with the exact evaluation of η_2 for the entire range of ϕ_2 obtained by Torquato, Stell, and Beasley.[19] It is seen that ζ_2 and η_2 for $\lambda = 0$ are essentially determined by the zero-density limit of the radial distribution function $g_0(r)$. The reason for this is that fully penetrable spheres, because of the absence of exclusion volume effects, are characterized by a relatively high degree of "randomness."[20]

For cases in which the phase properties are not very different (e.g., $1 < \beta < 10$), the upper and lower bounds on k_2 and g_2 are generally sufficiently close to one another to provide good estimates of the second-order coefficients. As the difference between the phase properties increases, the bounds, as is well known, diverge from one another. This, however, does not mean that the bounds become useless for such cases. For reasons similar to these given in II and III, the lower bounds k_2^L and g_2^L will provide an estimate of k_2 and g_2, respectively, for the case of a suspension of spheres in a weaker matrix. If the converse is true, the upper bounds k_2^U and g_2^U yield estimates of the second-order coefficients.

In Fig. 1 we plot the lower bound k_2^L for $\alpha > 1$ and the upper bound k_2^U for $\alpha < 1$, for $\lambda = 0$, 0.5, and 1. Here $\gamma_1 = \gamma_2 = 0.5$ and hence $\alpha = \beta$. Figure 2 gives the analogous curves for the second-order coefficient associated with the shear modulus. It is seen that increasing the degree of interparticle overlap (decreasing the impenetrability parameter λ), for $\alpha = \beta > 1$, increases the value of k_2^L or g_2^L. It is expected that the actual second-order coefficients will behave in a similar fashion since the stiffer material forms a "more continous" phase as $\lambda \to 0$. Similarly, decreasing the impenetrability parameter λ, for $\alpha = \beta < 1$, decreases the value of k_2^U or g_2^U. Again, this is not surprising since the weaker material here is the one that forms the more continuous phase.

III. INCOMPRESSIBLE MATRIX

A. Spherical cavities or bubbles

Here we compute the upper bounds K_U^* [Eq. (14)] for spherical but penetrable cavities $(K_2 = G_2 = 0)$ in an incompressible matrix $(K_1 = \infty, G_1$ finite) for the PS model. From this calculation we obtain corresponding results for the bulk and expansion viscosities of an incompressible fluid containing air bubbles.

For this case (as noted by Chen and Acrivos[9]), it is useful to first rewrite Eq. (14) as follows:

TABLE I. Comparison of Eq. (25) for $\lambda = 0$ (with $f_1 = 0.746\,81$) as a function of ϕ_2 with the exact evaluation of η_2 for all ϕ_2 obtained in Ref. 19.

ϕ_2	η_2 [Eq. (25) with $\lambda = 0$]	η_2 [Exact result for $\lambda = 0$]
0.1	0.075	0.075
0.3	0.224	0.222
0.5	0.373	0.367
0.7	0.523	0.512
0.9	0.672	0.658

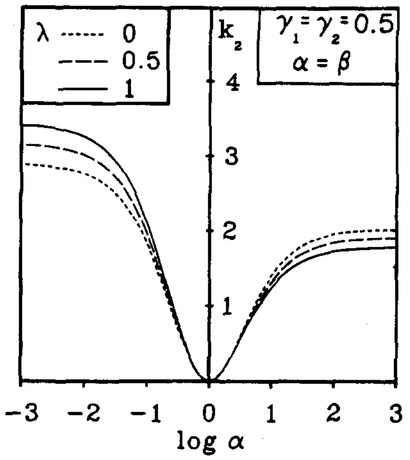

FIG. 1. Upper bound k_2^U [Eq. (20)] for $\alpha < 1$ and lower bound k_2^L [Eq. (21)] for $\alpha > 1$ in the PS model for $\lambda = 0$, 0.5, and 1. Here $\gamma_1 = \gamma_2 = 0.5$ and hence $\alpha = \beta$.

$$K_U^* = \frac{K_1}{1 - k_1\phi_2 + (k_1^2 - k_2^U)\phi_2^2 + O(\phi_2^3)}. \tag{28}$$

In the limit as $K_1 \to 0$ and $\gamma_1 \to 0$, we find

$$K_U^* = \left[\frac{3}{4G_1 + 3K_2}\phi_2 + \frac{12G_1[1 - e_1(\beta - 1)]}{(4G_1 + 3K_2)^2}\phi_2^2 + O(\phi_2^3)\right]^{-1}. \tag{29}$$

In the special case of spherical cavities in an incompressible matrix, Eq. (29) yields

$$K^* \leqslant K_U^* = \frac{4G_1}{3\phi_2} - \frac{4}{3}(1 + e_1)G_1 + O(\phi_2)$$
$$= \frac{4G_1}{3\phi_2} - \frac{4}{3}[1.210\,68 + 0.350\,78(1 - \lambda)]G_1 + O(\phi_2), \tag{30}$$

where we have used Eq. (26). Since the effective Lamé constant $\lambda_L^* = K^* - 2G^*/3$ and $G^* = G_1 + O(\phi_2)$, then we also have that

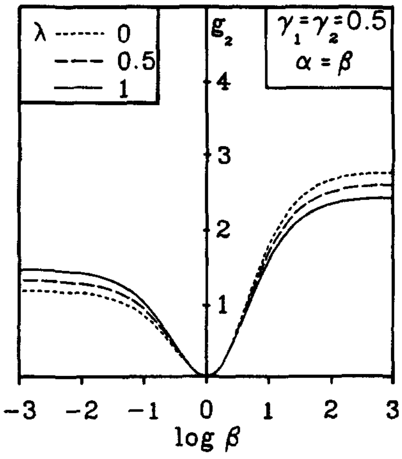

FIG. 2. Upper bound g_2^U [Eq. (22)] for $\beta < 1$ and lower bound g_2^L [Eq. (23)] for $\beta > 1$ in the PS model for $\lambda = 0$, 0.5, and 1. Here $\gamma_1 = \gamma_2 = 0.5$ and hence $\alpha = \beta$.

$$\lambda_L^* \leqslant \frac{4G_1}{3\phi_2} - (2 + \frac{4}{3}e_1)G_1 + O(\phi_2)$$
$$= \frac{4G_1}{3\phi_2} - [2.280\,91 + 0.467\,71(1 - \lambda)]G_1 + O(\phi_2). \tag{31}$$

The constant term in Eq. (31), which estimates two sphere interactions, is equal to 2.748 61 G_1 and 2.280 91G_1 for the case of fully penetrable ($\lambda = 0$) and totally impenetrable ($\lambda = 1$) cavities, respectively. Equation (31) indicates that as the degree of overlap increases, the effective Lamé constant decreases, as expected. For the special case of totally impenetrable spheres, Chen and Acrivos[9] exactly found

$$\lambda_L^* = \frac{4G_1}{3\phi_2} - 2.399G_1 + O(\phi_2). \tag{32}$$

Since the bound (31) is very sharp in this instance, it is expected that it remains sharp for all λ.

Interestingly, a composite consisting of spherical cavities in an incompressible matrix is equivalent to an incompressible fluid containing air bubbles. For a Newtonian fluid, the relationship between the stress tensor σ_{ij} and rate of strain tensor ϵ_{ij} is given by

$$\sigma_{ij} = -p\delta_{ij} + \eta\,\epsilon_{kk}\delta_{ij} + 2\mu\epsilon_{ij},$$

where p is the pressure, η is the expansion viscosity (or second coefficient of viscosity), and μ is the shear viscosity. Comparison of this expression to the linear stress–strain relation of elasticity reveals that the Lamé constant λ_L is analogous to η, G is analogous to μ, and the analog of K is the bulk viscosity $\zeta = \eta + 2\mu/3$. For this case, Taylor[21] found the expansion viscosity to be given by

$$\eta = \frac{4\mu}{3\phi_2} + O(1). \tag{33}$$

Therefore, Eq. (31) extends Taylor's results by taking into account pair interactions between spherical bubbles that penetrate one another in varying degrees.

Penetrable spherical bubbles do not exist in any stable equilibrium sense. Surface tension effects would tend to smooth out the sharp corners where the two spheres intersect. However, as demonstrated in II and III, the field induced within two overlapping spheres of radius R (whose centers are separated by a distance x) is approximately the same as the field introduced in a single ellipsoid having a major axis of length $R + x/2$ and two minor axes of length R. Therefore, for $\lambda < 1$, Eq. (31) is expected to yield useful estimates of the expansion viscosity of an incompressible fluid containing a mixture of spherical and ellipsoidal bubbles.

B. Rigid spherical particles

Consider the calculation of the lower bound G_L^* [Eq. (17)] for rigid but penetrable spherical particles ($\beta = \infty$) in an incompressible matrix ($K_1 = \infty$, G_1 finite).[22] In this limit, Eq. (17) becomes

$$\frac{G_L^*}{G_1} = 1 + \frac{5}{2}\phi_2 + \left(\frac{5}{2} + \frac{3}{2}f_1\right)\phi_2^2. \tag{34}$$

Combination of Eqs. (27) and (34) gives, in the PS model,

$$\frac{G^*}{G_1} \geqslant 1 + \frac{5}{2}\phi_2 + [3.224\,11 + 0.396\,11(1-\lambda)]\phi_2^2. \quad (35)$$

Bound (35) gives the exact first-order coefficient calculated by Einstein.[4] This equation hence extends Einstein's result for the elastic problem of rigid but penetrable spheres in an incompressible matrix by approximately accounting for pair interactions. In the extreme limits of fully penetrable and totally impenetrable spheres, the second-order coefficient is equal to 3.620 22 and 3.224 11, respectively. This supports our intuition that increasing the penetrability of rigid particles increases the effective shear modulus at the same sphere volume fraction. For rigid but totally impenetrable spheres in an incompressible matrix, Chen and Acrivos[9] exactly predict the second-order coefficient to be 5.01 (with a possible error in the third digit). The agreement between the bound (35) and the exact result[9] for G^* in this case is clearly not as good as the agreement between the bound (31) and the exact result[9] for the effective Lame constant of cavities in an incompressible matrix. Nonetheless, Eq. (35) captures the salient features that come into play when rigid particles[22] overlap. For reasons described in the Introduction, the analogy between elasticity and fluid mechanics does not hold for Eq. (35).

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