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A Mean-Field Theory of Suspension Viscosity

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ABSTRACT: Hydrodynamic scattering theory is used to calculate the effective viscosity of a fluid through which spherical scattering centers are randomly dispersed. When the spheres are free to move, the system is a suspension. When the spheres are immobile, they mimic a porous medium. Calculations are performed for an arbitrary slip boundary condition at the fluid–sphere interface.

1. Introduction

A mean-field theory is proposed for the effective viscosity of a fluid permeated by a random distribution of spherical particles, freely suspended in one case and immobilized in another. Our approach is based on hydrodynamic multiple scattering theory. Calculations are performed for an arbitrary slip boundary condition at the fluid–sphere interface. We believe that the technique presented here is more straightforward and physically appealing than that which previously has been used.

In section 2 the Einstein suspension problem is analyzed from the point of view of hydrodynamic scattering theory. Section 3 is devoted to the problem of flow through a randomly distributed array of stationary obstacles, a model that often has been used for porous media.

2. The Suspension

We consider a stationary, incompressible flow perturbed by the presence of a single sphere of radius a, which is permitted to translate and rotate freely in the surrounding Newtonian fluid. The position vector of this sphere will be denoted by the symbol $\mathbf{R}$ and that of an arbitrary field point by $\mathbf{r}$. $\rho = \mathbf{r} - \mathbf{R}$ is the vector extending from the center of the sphere to the field point. The perturbation of the velocity field appropriate to an arbitrary slip boundary condition is given by the expression (for example, see p 249 of Batchelor[1])

$$\delta\mathbf{w}(\rho|\mathbf{R}) = -\frac{1-\lambda}{1+2\lambda}\,\frac{5}{2}\,\frac{a^3}{\rho^2}\hat{\rho}\hat{\rho}\cdot\underline{\underline{\alpha}}^\circ{}_S(\mathbf{R})\cdot\hat{\rho} - \frac{1-3\lambda}{1+2\lambda}\,\frac{a^5}{\rho^4}\left[\underline{\underline{\alpha}}^\circ{}_S(\mathbf{R})\cdot\hat{\rho} - \frac{5}{2}\hat{\rho}\hat{\rho}\cdot\underline{\underline{\alpha}}^\circ{}_S(\mathbf{R})\cdot\hat{\rho}\right] \quad (2.1)$$

provided that $|\rho| \geq a$. Here $\hat{\rho}$ is the unit vector $\rho/|\rho|$. The value of the slip coefficient λ can vary from $\lambda = 0$ for the stick boundary condition at the surface of the sphere to $\lambda = 1/3$ for perfect slip. The symbol $\alpha^\circ{}_S(\mathbf{R})$ appearing in eq 1 is the symmetric rate of strain tensor associated with the original unperturbed flow $\mathbf{w}^\circ(\mathbf{R})$, viz.

$$[\underline{\underline{\alpha}}^\circ{}_S(\mathbf{R})]_{ij} = \tfrac{1}{2}[\partial w^\circ{}_i/\partial X_j + \partial w^\circ{}_j/\partial X_i] \quad (2.2)$$

with X_i denoting a Cartesian component of $\mathbf{R}$. Strictly speaking, the formula 2.1 is valiid only if the rate of strain varies negligibly over distances comparable to the size of the sphere, i.e., only if $\alpha^\circ{}_S(\mathbf{R} + \mathbf{a}) \approx \alpha^\circ{}_S(\mathbf{R})$.

We now rewrite the perturbation $\delta\bar{\mathbf{w}}(\rho|\mathbf{R})$ in the form $\underline{\underline{B}}(\rho)\colon \nabla_R\mathbf{w}^\circ(\mathbf{R})$ with $\underline{\underline{B}}(\rho)$ the third-rank tensor defined (for $|\rho| \geq a$) by the formula

$$\underline{\underline{B}}(\rho) = -\frac{1-\lambda}{1+2\lambda}\,\frac{5a^3}{2}\left(\frac{1}{\rho^2}\hat{\rho}\hat{\rho}\hat{\rho}\right) - \frac{1-3\lambda}{1+2\lambda}\,\frac{a^5}{2}\nabla_\rho\left(\frac{1}{\rho^3}\hat{\rho}\hat{\rho}\right) \quad (2.3)$$

The fluid velocity at the location $\mathbf{r}$ is then given by the expression

$$\mathbf{w}(\mathbf{r};\mathbf{R}) = \mathbf{w}^\circ(\mathbf{r}) + \underline{\underline{B}}(\mathbf{r}-\mathbf{R})\colon \nabla_R\mathbf{w}^\circ(\mathbf{R}) \quad (2.4)$$

Because the interior of the sphere is not accessible to the fluid, eq 2.4 is applicable only if $|\mathbf{r} - \mathbf{R}| \geq a$.

The relation 2.4 provides a specific example of a more general rule of hydrodynamic scattering theory, according to which, for an arbitrary unperturbed flow $\mathbf{w}^\circ(\mathbf{R})$ and for an arbitrary boundary condition on the surface of the target, there exists a linear functional relationship between the "incoming" (unperturbed) flow and the perturbation $\delta\mathbf{w}$ resulting from the presence of the target. This relationship can be expressed in the form

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$$\mathbf{w}(\mathbf{r};\mathbf{R}) = \mathbf{w}^\circ(\mathbf{r}) + \int \mathrm{d}\mathbf{r}'\, \underline{\underline{\mathrm{T}}}(\mathbf{r}|\mathbf{r}')\cdot\mathbf{w}^\circ(\mathbf{r}') \qquad (2.5)$$

The hydrodynamic response tensor $\underline{\underline{\mathrm{T}}}(\mathbf{r}|\mathbf{r}')$ generally depends both on the type of incoming flow and on the properties of the target. For the particular case of a suspended sphere it is given by the expression

$$\underline{\underline{\mathrm{T}}}_S(\mathbf{r}|\mathbf{r}') = -H(a - |\mathbf{R} - \mathbf{r}'|)\delta(\mathbf{r}' - \mathbf{r})\underline{\underline{\mathrm{I}}} + H(|\mathbf{r} - \mathbf{r}'| - a)\delta(\mathbf{r}' - \mathbf{R})\underline{\underline{\mathrm{B}}}(\mathbf{r} - \mathbf{r}')\cdot\nabla_{r'} \qquad (2.6)$$

with $H(x)$ denoting the unit step function, $H(x) = 1$ for $x \geq 0$ and $H(x) = 0$ for $x < 0$. The tensor given by eq 2.6 has been constructed so that $\mathbf{w}(\mathbf{r};\mathbf{R}) = 0$ for $|\mathbf{r} - \mathbf{R}| < a$.

Equation 2.5 is valid when the flow is scattered by a single suspended sphere. When more are present, it is necessary to take into account their mutual interactions which propagate through the supporting medium. Thus, the flow incident upon one of the spheres consists not only of the externally imposed flow $\mathbf{w}^\circ(\mathbf{R})$ but also of the sum of perturbations caused by all the others. In the present paper we use a mean-field approximation to this multiple scattering problem, which totally neglects dynamic correlations among the scattering centers. To this approximation, the mean velocity field of a fluid containing suspended particles is determined self-consistently by the integral equation

$$\mathbf{w}(\mathbf{r}) = \mathbf{w}^\circ(\mathbf{r}) + \int \mathrm{d}\mathbf{r}'\, n(\mathbf{r}')H(|\mathbf{r} - \mathbf{r}'| - a)\underline{\underline{\mathrm{B}}}(\mathbf{r} - \mathbf{r}'):\nabla_{r'}\mathbf{w}(\mathbf{r}') \qquad (2.7)$$

Here $n(\mathbf{r})$ is the probability density for the center of a sphere to lie at the location $\mathbf{r}$. For a homogeneous distribution $n(\mathbf{r})$ is equal to c, the average number density of suspended spheres.

The physical interpretation of eq 2.7 is simple; the average velocity field of the fluid is the sum of the externally imposed flow $\mathbf{w}^\circ(\mathbf{r})$ and the perturbation generated by the randomly distributed particles. The Fourier transform of eq 2.7 can be written as

$$\tilde{\mathbf{w}}(\kappa) = \tilde{\mathbf{w}}^\circ(\kappa) + c\tilde{\underline{\underline{\mathrm{G}}}}(\kappa)\cdot\tilde{\mathbf{w}}(\kappa) \qquad (2.8)$$

wherein

$$\tilde{\mathbf{w}}(\kappa) = \int \mathrm{d}\mathbf{r}\, \exp(-i\kappa\cdot\mathbf{r})\mathbf{w}(\mathbf{r}) \qquad (2.9)$$

and

$$\tilde{\underline{\underline{\mathrm{G}}}}(\kappa) = \int \mathrm{d}\mathbf{r}\, \exp(-i\kappa\cdot\mathbf{r})H(|\mathbf{r}| - a)\underline{\underline{\mathrm{B}}}(\mathbf{r})\cdot i\kappa \qquad (2.10)$$

The integral defined by eq 2.10 is convergent and exists for all values of the wave vector $\boldsymbol{\kappa}$.

We now assume that the unperturbed flow $\tilde{\mathbf{w}}^\circ(\kappa)$ is incompressible and generated by an external force density $\tilde{\mathbf{f}}(\kappa)$. Consequently

$$\tilde{\mathbf{w}}^\circ(\kappa) = \frac{1}{\eta_0\kappa^2}(\underline{\underline{\mathrm{I}}} - \hat{\kappa}\hat{\kappa})\cdot\tilde{\mathbf{f}}(\kappa) \qquad (2.11)$$

with η_0 the viscosity of pure solvent. Since the mean flow field $\tilde{\mathbf{w}}(\kappa)$ must also be incompressible, the solution of eq 2.8 can be written as

$$\tilde{\mathbf{w}}(\kappa) = \frac{1}{\eta_0\kappa^2[1 - c\tilde{G}_\perp(\kappa)]}(\underline{\underline{\mathrm{I}}} - \hat{\kappa}\hat{\kappa})\cdot\tilde{\mathbf{f}}(\kappa) \qquad (2.12)$$

The function $\tilde{\mathrm{G}}_\perp(\kappa)$ appearing in this expression is the transverse component of $\tilde{\underline{\underline{\mathrm{G}}}}(\kappa)$ defined according to

$$\tilde{\underline{\underline{\mathrm{G}}}}(\kappa) = \mathrm{G}_\parallel(\kappa)\hat{\kappa}\hat{\kappa} + \mathrm{G}_\perp(\kappa)(\underline{\underline{\mathrm{I}}} - \hat{\kappa}\hat{\kappa}) \qquad (2.13)$$

It is given explicitly by the formula

$$G_\perp(\kappa) = -\frac{15}{2}\left(\frac{4}{3}\pi a^3\right)\frac{1-\lambda}{1+2\lambda}[\Omega^{-3}(\sin\Omega - \Omega\cos\Omega)] + \frac{3}{2}\left(\frac{4}{3}\pi a^3\right)\frac{1-3\lambda}{1+2\lambda}\left[\Omega^{-3}(-3\sin\Omega + 2\Omega^2\sin\Omega + \Omega^4\sin\Omega + 3\Omega\cos\Omega - \Omega^3\cos\Omega) + \Omega^2\int_\Omega^\infty \mathrm{d}x\, x^{-1}\cos x\right] \qquad (2.14)$$

with $\Omega = \kappa a$.

In general, the effective viscosity defined by

$$\eta^{\mathrm{eff}}(\kappa) = \eta_0[1 - c\tilde{G}_\perp(\kappa)] \qquad (2.15)$$

is a function of the dimensionless wavenumber $\Omega = \kappa a$. However, we assumed at the beginning that the velocity varied little over distances comparable to the radius of a sphere. Therefore, it is consistent to adopt the Navier–Stokes effective fluid approximation and take the limit $\kappa a \to 0$. This leads from eq 2.14 and 2.15 to the formula

$$\eta^{\mathrm{eff}} = \eta_0\left[1 + \left(\frac{5}{2}\,\frac{1-\lambda}{1+2\lambda}\right)\phi\right] \qquad (2.16)$$

for the viscosity of a dilute suspension of volume fraction $\phi = ((4/3)\pi a^3)c$. Equation 2.16 is a generalization of the Einstein formula appropriate to an arbitrary slip boundary condition at the sphere–solvent interface. According to this formula, the second virial coefficient of the suspension viscosity varies between the values of 1 for perfect slip ($\lambda = 1/3$) and 2.5 for no slip ($\lambda = 0$).

We would like to point out here that while the Einstein result (eq 2.16) itself is well-known, the relation is most often derived from an analysis of the rate of dissipation (per unit volume) due to the particles of the suspension. In this method calculations must be performed with care, since it involves integrals that are not absolutely convergent.[1,2,3] Also, some uncertainties have arisen[4] about the proper interpretation of the results of these calculations. The method proposed here is free from such ambiguities. Since it is almost impossible to give proper credit to the many works that have been done on this subject, we direct interested readers to two review papers, ref 3 and 5.

Strictly speaking, the theory cannot be extended to more concentrated solutions without conducting a careful analysis of the interparticle correlations that have been ignored in the mean-field approximation. However, we can obtain a rough estimate of the concentration dependence of the effective viscosity by using the mean-field theory to compute the increment of viscosity that results from adding a small amount of solute to a fluid with the effective viscosity $\eta^{\mathrm{eff}}(\phi)$. Thus, for a small change of concentration we obtain the result

$$\eta^{\mathrm{eff}}(\phi + \delta\phi) = \eta^{\mathrm{eff}}(\phi)\left[1 + \left(\frac{5}{2}\,\frac{1-\lambda}{1+2\lambda}\right)\delta\phi\right]$$

or

$$\frac{\mathrm{d}}{\mathrm{d}\phi}\ln\eta^{\mathrm{eff}}(\phi) = \left(\frac{5}{2}\,\frac{1-\lambda}{1+2\lambda}\right) \qquad (2.17)$$

The solution of this differential equation which satisfies the boundary condition $\eta^{\mathrm{eff}}(0) = \eta_0$ is the Arrhenius-type[6] function

$$\eta^{\mathrm{eff}}(\phi) = \eta_0\exp\left[\left(\frac{5}{2}\,\frac{1-\lambda}{1+2\lambda}\right)\phi\right] \qquad (2.18)$$

This same result (with $\lambda = 0$) has been obtained previously by Vand[7] and Mooney,[8] using entirely different methods of derivation. The latter author also introduced corrections due to particle correlations, which significantly improved the agreement with experimental data.

3. Flow through a Fixed Array of Obstacles

The calculational procedure developed in the preceding section can be applied to fluid flow through a *stationary* array of spherical particles. The flow distortions caused by these immobilized scattering centers are more complicated than those produced by freely moving suspended particles. To be more specific, we begin by considering a single sphere, located at the position $\mathbf{R}$ within a homogeneous flow $\mathbf{w}^\circ(\mathbf{r})$. In the neighborhood of this obstacle the unperturbed flow field can be written as the sum

$$\begin{aligned}\mathbf{w}^\circ(\mathbf{r}) &= \mathbf{w}^\circ(\mathbf{R}) + (\mathbf{r}-\mathbf{R})\cdot\nabla_R\mathbf{w}^\circ(\mathbf{R}) \\ &= \mathbf{w}^\circ(\mathbf{R}) + (\mathbf{r}-\mathbf{R})\cdot\underline{\underline{\alpha}}^\circ{}_\mathrm{S}(\mathbf{R}) + (\mathbf{r}-\mathbf{R})\cdot\underline{\underline{\alpha}}^\circ{}_\mathrm{A}(\mathbf{R})\end{aligned} \quad (3.1)$$

consisting of a uniform flow $\mathbf{w}^\circ(\mathbf{R})$, a contribution associated with the symmetric rate of strain $\underline{\underline{\alpha}}^\circ{}_\mathrm{S}(\mathbf{R})$, and a term proportional to

$$[\underline{\underline{\alpha}}^\circ{}_\mathrm{A}(\mathbf{R})]_{ij} = \tfrac{1}{2}[\partial w^\circ{}_i/\partial X_j - \partial w^\circ{}_j/\partial X_i] \quad (3.2)$$

the antisymmetric part of the velocity gradient tensor.

The flow distortion caused by the obstacle is the sum of three parts, one specific to each of the terms in eq 3.1. The contribution from the second of these is $\delta\mathbf{w}_\mathrm{S}(\mathbf{r};\mathbf{R}) = \underline{\underline{\mathrm{B}}}(\mathbf{r}-\mathbf{R}){:}\nabla_R\mathbf{w}^\circ(\mathbf{R})$, the function considered in the preceding section. We proceed now to the other two. According to Lamb,[9] the perturbation that results from placing an immobilized sphere in a spatially uniform flow is given by the expression (for $|\rho| = |\mathbf{r}-\mathbf{R}| \geq a$)

$$\delta\mathbf{w}_\mathrm{U}(\rho|\mathbf{R}) = -(1-\lambda)\left[\frac{3}{4}\frac{a}{\rho}(\underline{\underline{\mathrm{I}}} + \hat{\rho}\hat{\rho}) + \frac{1}{4}\frac{1-3\lambda}{1-\lambda}\left(\frac{a}{\rho}\right)^3(\underline{\underline{\mathrm{I}}} - 3\hat{\rho}\hat{\rho})\right]\cdot\mathbf{w}^\circ(\mathbf{R}) = -\xi\underline{\underline{\mathrm{A}}}(\rho)\cdot\mathbf{w}^\circ(\mathbf{R}) \quad (3.3)$$

Here, $\xi = 6\pi\eta_0 a(1-\lambda)$ is the Stokes friction coefficient for a slip coefficient λ, and $\underline{\underline{\mathrm{A}}}(\rho)$ is related by the formula

$$\underline{\underline{\mathrm{A}}}(\rho) = \underline{\underline{\mathrm{O}}} + \frac{a^2}{6}\frac{1-3\lambda}{1-\lambda}\nabla_\rho{}^2\underline{\underline{\mathrm{O}}} \quad (3.4)$$

to the Oseen tensor

$$\underline{\underline{\mathrm{O}}}(\rho) = \frac{1}{8\pi\eta_0\rho}(\underline{\underline{\mathrm{I}}} + \hat{\rho}\hat{\rho}) \quad (3.5)$$

The hydrodynamic response tensor for this scattering of a uniform flow is (compare eq 2.6)

$$\underline{\underline{\mathrm{T}}}_\mathrm{U}(\mathbf{r}|\mathbf{r}') = -H(a - |\mathbf{R}-\mathbf{r}'|)\delta(\mathbf{r}'-\mathbf{r})\underline{\underline{\mathrm{I}}} - \xi H(|\mathbf{r}-\mathbf{r}'| - a)\delta(\mathbf{r}'-\mathbf{R})\underline{\underline{\mathrm{A}}}(\mathbf{r}-\mathbf{r}') \quad (3.6)$$

The perturbation associated with the (constant) antisymmetric part of the velocity gradient is not difficult to determine. We find that it can be written in the form

$$\delta\mathbf{w}_\mathrm{A}(\rho|\mathbf{R}) = -2\frac{1-3\lambda}{2+3\lambda}\left(\frac{a}{\rho}\right)^3(\rho\cdot\underline{\underline{\alpha}}^\circ{}_\mathrm{A}(\mathbf{R})) = \underline{\underline{\mathrm{C}}}(\rho){:}\nabla_R\mathbf{w}^\circ(\mathbf{R}) \quad (3.7)$$

with $\underline{\underline{\mathrm{C}}}$ denoting the third-rank tensor with components

$$\mathrm{C}_{ijk} = -\frac{1-3\lambda}{2+3\lambda}\left(\frac{a}{\rho}\right)^3(\rho_k\delta_{ij} - \rho_j\delta_{ik}) \quad (3.8)$$

The corresponding hydrodynamic response tensor is

$$\underline{\underline{\mathrm{T}}}_A(\mathbf{r}|\mathbf{r}') = -H(a - |\mathbf{R}-\mathbf{r}'|)\delta(\mathbf{r}'-\mathbf{r})\underline{\underline{\mathrm{I}}} + H(|\mathbf{r}-\mathbf{r}'| - a)\delta(\mathbf{r}'-\mathbf{R})\underline{\underline{\mathrm{C}}}(\mathbf{r}-\mathbf{r}')\cdot\nabla_{r'} \quad (3.9)$$

By combining these results we obtain the mean-field equation

$$\mathbf{w}(\mathbf{r}) = \mathbf{w}^\circ(\mathbf{r}) + c\int d\mathbf{r}'\, H(|\mathbf{r}-\mathbf{r}'| - a) \times [-\xi\underline{\underline{\mathrm{A}}}(\mathbf{r}-\mathbf{r}') + \underline{\underline{\mathrm{B}}}(\mathbf{r}-\mathbf{r}')\cdot\nabla_{r'} + \underline{\underline{\mathrm{C}}}(\mathbf{r}-\mathbf{r}')\cdot\nabla_{r'}]\cdot\mathbf{w}(\mathbf{r}') \quad (3.10)$$

for the velocity of a fluid permeated by a random distribution of immobilized spheres. The Fourier transform of eq 3.10 is of the same form as eq 2.8 but with $\tilde{\underline{\underline{\mathrm{G}}}}(\kappa)$ defined by

$$\tilde{\underline{\underline{\mathrm{G}}}}(\kappa) = \int d\mathbf{r}\, \exp(-i\kappa\cdot\mathbf{r})H(|\mathbf{r}| - a)[-\xi\underline{\underline{\mathrm{A}}}(\mathbf{r}) + \underline{\underline{\mathrm{B}}}(\mathbf{r})\cdot i\kappa + \underline{\underline{\mathrm{C}}}(\mathbf{r})\cdot i\kappa] \quad (3.11)$$

in place of eq 2.10. As in the case of the suspension, it is the transverse component of $\tilde{\underline{\underline{\mathrm{G}}}}(\kappa)$ that determines the effective viscosity. This quantity is the sum of three parts

$$\tilde{G}_{\mathrm{A}_\perp}(\kappa) = -\frac{\xi}{2\eta_0\kappa^2}[\Omega^{-1}(\sin\Omega + \Omega\cos\Omega)] + \pi a^3(1-3\lambda)[\Omega^{-3}(\sin\Omega - \Omega\cos\Omega)] \quad (3.12)$$

$$\tilde{G}_{\mathrm{C}_\perp}(\kappa) = -4\pi a^3\frac{1-3\lambda}{2+3\lambda}[\Omega^{-1}\sin\Omega] \quad (3.13)$$

and $\tilde{G}_{\mathrm{B}_\perp}(\kappa)$, given by eq 2.14. Thus, the long wavelength limit of the effective viscosity $\eta^\mathrm{eff}(\kappa) = \eta_0[1 - c\tilde{G}_\perp(\kappa)]$ is given by the expression

$$\eta^\mathrm{eff} = \eta^0\left[1 + \phi\left\{\frac{5}{2}\frac{1-\lambda}{1+2\lambda} + 3\frac{1-3\lambda}{2+3\lambda} - \frac{1}{4}(1-3\lambda)\right\}\right] \quad (3.14)$$

The second virial coefficient of this viscosity varies from 3.75 for the stick boundary condition to 1 for perfect slip.

The equation of motion for the stationary flow is the Brinkman–Debye–Navier–Stokes equation

$$\begin{aligned}\eta^\mathrm{eff}\kappa^2\tilde{\mathbf{w}}(\kappa) + i\kappa\tilde{p}(\kappa) + \xi c\tilde{\mathbf{w}}(\kappa) &= \tilde{\mathbf{f}}(\kappa) \\ i\kappa\cdot\tilde{\mathbf{w}}(\kappa) &= 0\end{aligned} \quad (3.15)$$

so that the screening length (L) of the hydrodynamic interaction depends on the friction coefficient ξ according to the formula

$$L^2 = \eta^\mathrm{eff}/\xi c \quad (3.16)$$

These same equations, eq 3.15 but without the term $\xi c\tilde{\mathbf{w}}$ and with an effective viscosity given by eq 2.16 instead of eq 3.14, govern the flow of the suspension, treated in section 2.

The effective viscosity of a fluid containing fixed spherical obstacles has been calculated previously by Lundgren,[10] Freed and Muthukumar,[11] and Kapral and Bedeaux.[12] The system studied by the third pair of authors incorporated a regular crystalline array of obstacles instead of the random array treated here. The second virial coefficient of viscosity obtained by Lundgren and by Kapral and Bedeaux was equal to the Einstein value of 2.5, appropriate to the viscosity of a suspension with stick boundary condition. Freed and Muthukumar obtained the value of 4, which (according to our formula 3.14) is correct when the rotations of the spheres are suppressed. Although all of these authors used methods very different from ours, we believe that the results of Freed and Muthukumar would have agreed with ours had they taken into account the flow distortion associated with $\underline{\underline{\alpha}}^\circ{}_\mathrm{A}$ (which produces the last term of eq 3.14). So far as we are aware, all previous calculations have been restricted to the stick boundary condition $\lambda = 0$.

It is conventional to hope that results obtained from the analysis of this fixed-sphere problem will be applicable to flow through a porous medium. An example appropriate to the field of polymer physics is a gel, provided that its polymeric constituents can be treated as a rigid assembly of nonrotating, nontranslating spherical "blobs" such as those of the Kirkwood–Riseman model.[13]

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Deformation of Microphase Structures in Segmented Polyurethanes

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ABSTRACT: Microstructure deformation in three selected polyurethanes has been studied quantitatively by SAXS during macroscopic tensile strain. The results demonstrate three possible modes of response at the level of the microphase structure: a shear mode, a tensile mode, and rotation or translation of independent particles. In the shear mode, as seen in an amine-cured polyurethane, the hard-segment lamellae tilt away from the stretch direction, while the soft-segment microphase deforms in shear. In the tensile mode, exemplified by a diol-cured polyurethane, the lamellae orient normal to the stretch direction, while the soft-segment microphase deforms in tension. For a triol-cured polyurethane, the local deformation mode is not uniquely determined; results are interpreted in terms of either rotation or translation of microparticles.

Introduction

The elastomeric properties of segmented polyurethanes have long been associated[1-3] with microphase separation, the microphase rich in soft-segment units conferring elastomeric behavior while the microphase rich in hard segments provides physical cross-linking. Bonart[3] studied polyurethane morphology by small-angle X-ray scattering (SAXS) and reported preferred orientation of the periodic microphase structure as a result of tensile stretching. Cooper and co-workers[4-6] measured preferred orientation of the hard and soft segment molecular units within the microphases by infrared dichroism.

Within this context the question of hysteresis must be addressed. In polyurethane elastomers, high levels of long-term residual deformation are commonly observed after removal of stress.[7] For diol-cured elastomers, Estes et al.[4] report residual hard-segment orientation upon removal of applied tensile stress. This orientation hysteresis effect was particularly pronounced[6] in elastomers that totally lack N–H groups to participate in hydrogen bonding. In the opposite extreme, amine-cured polyurethanes, also referred to as poly(urethane ureas), possess two N–H groups per hard-segment repeat compared to one for diol-cured polyurethanes. The amine-cured polyurethanes show[8-13] a greater propensity toward microphase segregation than their diol-cured counterparts, presumably because of the larger number of possible hydrogen bonds between hard-segment chemical groups.

Desper and Schneider[8] have quantitatively characterized microphase segregation in polyurethanes in the undeformed state using methods established[14] for the slit-collimated Kratky SAXS camera. These studies have been extended to investigate the response of polyurethane microstructure to deformation. In the present work, the study of polyurethane microstructure deformation has been undertaken by using a modern SAXS instrument capable of yielding quantitative data in two dimensions. This instrument, the 10-m SAXS camera at the National Cancer for Small-Angle Scattering Research at the Oak Ridge National Laboratory, incorporates pinhole optics and a two-dimensional position-sensitive proportional counter. With the exception of preliminary studies by Abouzahr,[13] this is believed to be the first in-depth study of this kind on polyurethane microstructure deformation.

Experimental Procedures

Sample Preparation. Three polymers representing three distinct classes of polyurethanes were investigated: the first, an amine-cured polyurethane from a series previously characterized[8] in the undeformed state; the second, a triol-cured polymer; the third, a diol-cured polymer. Polymers were synthesized by a two-step process at the compositions given in Table I. For all three polymers the soft segment was poly(tetramethylene oxide) (PTMO) of molecular weight 1000. The hard segment consisted of either toluene diisocyanate (TDI, mixed isomers) or methylenebis(p-phenyl isocyanate) (MDI) reacted with either an amine (trimethyl glycol bis(p-aminobenzoate), TMAB), a triol (1,1,1-

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