Two–point microrheology and the Electrostatic Analogy

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The recent experiments of Crocker *et al.* suggest that microrheological measurements obtained from the correlated fluctuations of widely-separated probe particles determine the rheological properties of soft, complex materials more accurately than do the more traditional particle autocorrelations. This presents an interesting problem in viscoelastic dynamics. We develop an important, simplifing analogy between the present viscoelastic problem and classical electrostatics. Using this analogy and direct calculation we analyze both the one and two particle correlations in a viscoelastic medium in order to explain this observation.

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I. INTRODUCTION

The utility of microrheology in probing the structure of soft materials has been recognized for some time[1]. This experimental technique uses the position correlations of thermally fluctuating, rigid probe particles embedded in a soft medium to measure the response of those particles to an external force[2]. From that response function one can determine the rheological properties of the material. In addition to this passive form of measurement, the response function can also be obtained directly by applying an external force to the probe beads. Such active versions of the experiment have been performed using magnetic particles[3]. It may be pointed out that sedimentation experiments used to measure the viscosity of fluids can be thought of as the zero-frequency limit of the active form of microrheology experiments.

The fundamental assumption underlying the data reduction in these measurements is the relation between the response function of a bead (rigid, spherical particle) to an externally applied force and the rheological properties of the medium in which that bead is embedded. The form of the single sphere (of radius a) response function, $\alpha^{(1,1)}(\omega)$, that is commonly used is the generalized Stokes–Einstein relation (GSER), which has the form:

$$\alpha_{ij}^{(1,1)} = \frac{1}{6\pi a G(\omega)}\delta_{ij}, \qquad (1)$$

where $G(\omega)$ is the complex shear modulus of the medium. The superscript points out that the we are considering the position response of a sphere to a force applied to that same sphere. The subscripted indices are the usual vectorial indices.

This response function owes it name to the fact that, for a Newtonian, viscous fluid where $G(\omega) = -i\omega\eta$, $\alpha^{(1,1)}$ reduces to the Stokes mobility of a sphere of radius a. A microrheological experiment in such a one–component Newtonian medium consists of measuring the position

auto-correlations of a sphere diffusing in the Newtonian fluid. These correlations are controlled by the sphere's diffusivity, which is obtained from the Stokes mobility via the Einstein relation. Thus, the measured position autocorrelations of the sphere allow one to calculate, using the response function, Eq. (1), the fluid's viscosity. This viscosity encodes all the rheology of the Newtonian fluid.

We have already examined the validity of the generalization of the GSER to a viscoelastic medium in previous articles [5, 6] and have found that in many experimental systems there is a significant frequency range over which Eq. (1) is a good approximation to the single-sphere response function. At frequencies where the single particle response function deviates significantly from Eq. (1), the breakdown of the GSER can be attributed to one of two sources: i) inertial effects at high frequencies, or ii) the effective decoupling of network and fluid dynamics at very low frequencies. We have found that inertial effects typically become significant at such high frequencies that we may safely ignore them here. Moreover, in this article, we will incorporate the appearance of non-shear modes by giving our course-grained model of a viscoelastic medium a complex, frequency–dependent bulk modulus in addition to its frequency-dependent, complex shear modulus.

Nevertheless, there still remain fundamental questions regarding the interpretation of microrheological data. In this article we address one such question: Given that the presence of the probe sphere can locally perturb the micro-structural and, therefore, the rheological properties of the medium, how can one extract information about the bulk, unperturbed medium? In other words we imagine that each probe sphere is surrounded by a pocket of perturbed material with rheological properties diferent from those of the bulk. For microrheology to be a useful experimental probe, it must be possible to extract the bulk, unperturbed viscoelastic moduli of the medium from the measured correlation functions. However, given

that the probe sphere is coupled to the bulk medium by a pocket of material whose rheological properties are modified by the introduction of that particle, one must assume that the correlations actually measure some convolution of the perturbed and bulk material properties.

The assumption of the presence of such pockets is quite reasonable in many complex liquids. The pocket, for example, may be a result of the equilibrium distribution of polymers near an impenetrable bead in solution; or it may be the result of quenched inhomogenities produced by the action of the probe during the formation of the medium. For example, in microrheological studies of polymerized F-actin, monomeric G-actin is polymerized in a solution already containing the probe particles[10]. The proximity of the probe particle may locally affect the polymerization kinetics and lead to a positionally dependent F-actin density near the probe spheres that is independent of equilibrium effects such as the steric interaction between the actin rods and the probes. We do not consider this situation is detail, but later in this article we do explore the consequences of polymer depletion near the surface of the bead in equilibrium. In this example the steric interaction of the polymers with the probe particle produces regions surrounding the beads with a softer shear modulus than the bulk. Recently Crocker *et al.*[7] have proposed a modification of the standard microrheological technique that can remove the effect of the perturbed pockets by studying the *inter*–particle position correlations of rather distant probe spheres. This claim can be reexpressed in terms of the two–particle response function or compliance tensor, $\alpha_{ij}^{(n,m)}$, defined by

$$r_i^{(n)}(\omega) = \alpha_{ij}^{(n,m)}(\mathbf{r}^{(m)} - \mathbf{r}^{(n)}, \omega) F_j^{(m)}(\omega), \qquad (2)$$

where $\mathbf{r}^{(n)}(\omega)$ is the displacement of the nth sphere and $\mathbf{F}^{(m)}$ is the external force applied to the mth sphere. The claim is that when the spheres (of radius a) are separated by a distance r, $r \gg a$, $\alpha_{ij}^{(n,m)}(\mathbf{r}, \omega)$ for $n \neq m$ depends upon only the bulk properties of the material.

In this paper we demonstrate the validity of the Crocker hypothesis by solving the elastic problem of two spheres embedded in an inhomogeneous elastic medium. We calculate the mutual response function of these beads, $\alpha_{ij}^{(1,2)}$ and show, in the limit mentioned above, that this response function measures the bulk rheological properties of the medium independently of the rheological properties of the regions immediately surrounding the two beads.

The remainder of the paper is organized as follows. In section II we identify an analogy between the viscoelastic problem that we posed and the physics of embedded conductors in an inhomogeneous dielectric. We use this analogy in combination with well-known results for the mutual capacitance of two spheres to elucidate the more complex viscoelastic problem. This heuristic analogy guides our approach to the full viscoelastic problem which is studied in section III. We approach the full prob-

lem in stages by first considering a rheologically homogeneous material in section III A and then by studying, in section III B a simple model of a rheologically inhomogeneous material consisting of the bulk medium and "pockets" of rheologically perturbed material surrounding each probe sphere as depicted in figure 1. We show, in the limit that the radii of these anomalous pockets are small compared to the separation of the probe spheres, that the inter–particle response function can be obtained with a minimum of computational effort through the use of a global property of the stress tensor. Most importantly, the leading term in the inter–particle response function is determined solely by the properties of the bulk medium. Following up this result we turn to the more computationally complex problem of finding the *single* particle response function in this composite medium. This is accomplished in section III C. This result will be shown to depend on the rheological properties of both the bulk material and the perturbed material in the pockets. It is interesting to note that the combination of the results of sections III B and III C suggest that one can experimentally determine the material properties of both the bulk and perturbed media through a combination of single–particle and two–particle microrheology experiments.

Motivated by this realization we study in section III D a more physical model of the probe particle in a soft, complex medium. We now assume that the rheological properties of the medium vary continuously with the distance from the probe sphere. Our previous algebraic solution to the two material problem (bulk and perturbed pocket material) now has to be generalized to a integral technique. As an example, we apply this technique to a polymer solution with concentration slightly above $c^\star$ in order to study the effect of polymer depletion near the probe sphere. This problem is revelent to recent experiments on DNA solutions[12]. Finally, we summarize
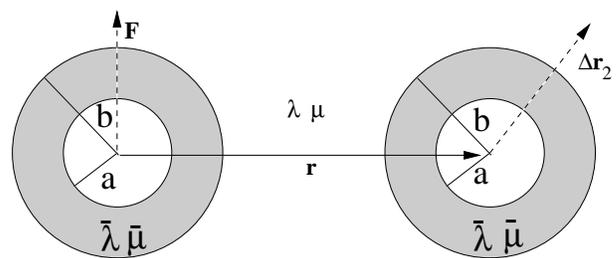

FIG. 1: Diagram of the simplest inhomogeneous elastic medium consistent with the assumed rotational symmetry of the problem. Each rigid sphere of radius a is surrounded by a spherical pocket with radius b, $b > a$ of material with elastic constants: $\bar{\lambda}, \bar{\mu}$. The bulk material has elastic constants: λ, μ. A force $\mathbf{F}$ is applied to sphere 1 (on the left). We seek the resulting displacement of sphere 2 (on the right), $\Delta \mathbf{r}_2$. In the following we will assume that the separation of the two spheres, r is large compared to b; the picture is not drawn to scale.

TABLE I: Correspondence between the electrostatics and viscoelastics

Electrostatics	Viscoelastics
potential $\phi(\mathbf{x})$	displacement $u_i(\mathbf{x})$
charge density $\rho(\mathbf{x})$	force density $f_i(\mathbf{x})$
dielectric tensor $\epsilon_{ij}(\mathbf{x},\omega)$	elastic tensor $K_{ijkl}(\mathbf{x},\omega)$

these results and conclude in section IV.

II. THE ELECTROSTATIC ANALOGY

To keep our treatment as simple as possible, we will assume that our viscoelastic medium is characterized by a local relation between the stress σ_{ij} and the strain u_{ij} described by a local, frequency–dependent, but possibly spatially varying elastic constant tensor $K_{ijkl}(\mathbf{x},\omega)$. The analysis we present here will have to be modified if the local stress–strain relation does not hold as is argued to be the case in systems of experimentaly interest such as actin networks[11]. Under our assumptions, the equation of force balance in a linear viscoelastic medium can be written as

$$-\partial_j \left[(K_{ijkl}(\mathbf{x},\omega)\partial_k u_l\right] = f_i(\mathbf{x},\omega), \qquad (3)$$

where $u_l(\mathbf{x},\omega)$ is the local displacement variable and $f_i(\mathbf{x},\omega)$ is a local force density at $\mathbf{x}$. We compare the above expression to the Gauss's law in an inhomogeneous dielectric medium:

$$-\partial_j \left[\epsilon_{jk}(\mathbf{x},\omega)\partial_k \phi(\mathbf{x},\omega)\right] = 4\pi\rho(\mathbf{x},\omega), \qquad (4)$$

where $\epsilon_{jk}(\mathbf{x},\omega)$ is the local frequency–dependent dielectric constant tensor, $\rho(\mathbf{x},\omega)$ is the frequency–dependent charge density and $\phi(\mathbf{x},\omega)$ is the electric potential at $\mathbf{x}$. In Eq. (4) we have assumed, as we have done with the elastic constant tensor, that the dielectric tensor is local. We consider the above electromagnetic problem at low enough frequencies so that that we may ignore the transverse electric fields.

Comparing Eqs. (3) and (4), we note that the following correspondence table (see table I) may be drawn: The charge density in Eq. (4) is the scalar analog of the vector source, $f_i(\mathbf{x},\omega)$ in Eq. (3). Similarly the electric potential, $\phi(\mathbf{x},\omega)$ in Eq. (4) is analogous to vector displacement field, $\mathbf{u}(\mathbf{x},\omega)$ in Eq. (3), and the position–dependent dielectric tensor, $\epsilon_{ij}(\mathbf{x},\omega)$, has as its analog in Eq. (3) the elastic constant tensor, $K_{ijkl}(\mathbf{x},\omega)$.

Finally, we note that the rigidity of objects embedded in the inhomogeneous viscoelastic medium requires that the displacement field, $\mathbf{u}$, be constant on their surfaces. Therefore, in order to maintain the analogy between the viscoelastic problem and the electrostatic problem, we study collections of embedded conducting objects so that the electric potential is constant on their surfaces.

Recall that the goal of our calculation is to determine the compliance tensor introduced in Eq. (2). This response function relates a set of forces applied to rigid objects embedded in an (in general inhomogeneous) dielectric to the displacements of those objects. In order to discuss this calculation in terms of the simpler electrostatic problem, we need to consider the electrostatic quantity that is analogous to the compliance tensor. This quantity is the inverse capacitance tensor of a collection of conducting objects embedded in an inhomogeneous dielectric. Since the electrostatic problem is a simpler, scalar version of the viscoelastic problem, we begin an with analysis of the that system. Afterward, insights drawn from the electrostatic problem should lead to complimentary results in the elastic problem, which remains the actual problem of interest.

We study a particularly simple realization of the so far arbitrary inhomogeneous dielectric medium. The simple model is meant to begin the study of the "pocket model" discussed in the introduction (See figure 1.) from within the electrostatic analogy. We consider that the inhomogeneous dielectric is made up of two materials. The bulk material has dielectric constant $\epsilon_{ij}(\mathbf{x}) = \delta_{ij}\epsilon$. However in concentric pockets around the conducting spheres (of radius a) there are spherical shells of material ($a < r < b$) with a different dielectric constant: $\epsilon_{ij}(\mathbf{x}) = \delta_{ij}\bar{\epsilon}$. Hereafter we assume that the dielectric tensor is diagonal and suppress its tensorial indices.

To support the notion that the off-diagonal elements of the compliance tensor, $\alpha_{ij}^{(n,m)}$, $n \neq m$, in the elastic problem depend only on the bulk values of the elastic constants and not on their values in the anomalous shells around the rigid spheres, we will calculate the off–diagonal component of the inverse capacitance tensor, $C_{nm}^{-1}, n \neq m$, for this system of two spheres and check that it does not depend on the values of the dielectric constant ($\bar{\epsilon}$) near either of the conducting spheres.

To compute the mutual capacitance of two conducting spheres one generally employs the method of images to iteratively fix the boundary conditions ($\phi = $ const) on each sphere in turn. This procedure leads to a convergent series for the capacitance tensor of two conducting spheres[9]. We apply a similar technique. To obtain just the component of the two by two inverse capacitance matrix that we seek we will study the problem where one sphere (say $n = 1$) has a unit charge on it and the other sphere (say $m = 2$) is charge neutral. The matrix element in question (C_{12}^{-1}) is then simply the potential of sphere two. Furthermore, since we intend to show that this component of the inverse capacitance tensor is independent of the value of the inner dielectric constant ($\bar{\epsilon}$) only in the limit that the sphere–sphere separation (L) is large compared to the both the sphere and cavity radii, we may truncate the series generated by the method of reflections at the first term. The higher–order reflections will contribute corrections to our result that are smaller by factors of a/L or b/L. We will return to the issue

of higher order corrections in b/L due to subdominant terms in the elastic displacement field and higher order reflections.

At the lowest order reflection we may ignore sphere two while we discuss the free and polarization charge distribution on sphere one and its surrounding cavity. That distribution is equivalent to a unit charge at the center of sphere one and two shells of bound, polarization charge. One shell is at the interface of the sphere and the inner dielectric ($r = a$) and the second shell is at the interface of the inner and outer dielectric ($r = b$). These two polarization charge densities, σ_{inner} and σ_{outer} respectively, are both spherically symmetric, and due to the neutrality of the dielectric layer, $a < r < b$, we have the relation

$$\oint d\Omega a^2 \sigma_{\text{inner}} + \oint d\Omega b^2 \sigma_{\text{outer}} = 0. \tag{5}$$

Thus, at distances $r > b$, including the position of sphere two and its surrounding pocket, the electric field due to this charge distribution is simply that of a unit charge at the center of the sphere one.

We now consider the potential of sphere two in this electric field. Because the spheres are conductors, the potential of sphere two is the same as the potential at its center. That potential is due to the linear superposition of the potential of a unit charge a distance L away (at the center of sphere one) and that of two spherical shells of polarization charge centered on sphere two. One shell is at the interface between sphere two and the medium with dielectric constant $\bar{\epsilon}$ while second shell is at the interface between that dielectric material and the bulk dielectric (with dielectric constant ϵ). These surface charge distributions, unlike those of sphere one, are not spherically symmetric. However, the surface integrals of the two polarization charge densities over the two surfaces vanish independently of each other. Thus the net effect on the potential at the center of sphere two due to each shell of polarization charge density is zero. The potential at the center of sphere two is then solely due to the distant charge on sphere one; we find that the potential of sphere two is simply $1/(4\pi\epsilon L)$. To lowest order in reflections we have shown that

$$C_{12}^{-1} = \frac{1}{4\pi\epsilon L} + \cdots \tag{6}$$

where the additional terms (not shown) come from higher order reflections. These higher order reflections will generically depend on both a, b and $\bar{\epsilon}$. A more detailed discussion of this derivation in addition to a discussion of the form of the higher order reflections is given in appendix A.

It is worth while at this stage to point out that to the same level of approximation (lowest order reflections) the potential on sphere one due to a unit charge on sphere one does, in fact, depend on the properties of the inner, dielectric layer. The potential on sphere one given by the diagonal element of the inverse capacitance matrix is

$$C_{11}^{-1} = \frac{4\pi a b \bar{\epsilon}}{b + a \left(\frac{\bar{\epsilon}}{\epsilon} - 1\right)} + \cdots . \tag{7}$$

Once again, the additional terms not shown come from higher order reflections.

Based on this simple analysis it seems reasonable to explore the elastic problem in more detail to determine if this basic result holds in the actual problem of rheological interest.

III.   THE VISCOELASTIC PROBLEM

A   The homogeneous medium

We begin the study of the viscoelastic problem by considering the displacement field produced by the displacement of a rigid spherical particle embedded in a homogeneous, elastic medium. A sphere of radius a is displaced by $\epsilon \hat{z}$. We now calculate the resulting displacement field.

Local force balance in the medium demands that the displacement field obey the partial differential equation

$$0 = \mu \nabla^2 \mathbf{u} + (\mu + \lambda) \nabla \nabla \cdot \mathbf{u} \tag{8}$$

where μ and λ are the two Lamè constants characterizing the isotropic, elastic medium. Eq. (8) is supplemented by boundary conditions at the surface of the sphere and at infinity:

$$\mathbf{u}(|\mathbf{x}| = a) = \epsilon \hat{z} \tag{9}$$
$$\lim_{|\mathbf{x}| \longrightarrow \infty} \mathbf{u}(\mathbf{x}) = 0. \tag{10}$$

Our solution of this problem is aided by two basic points: (i) the solution must be azimuthally symmetric, and (ii) the solution must be linear in $\epsilon \hat{z}$. With their aid, we immediately write the most general possible form of the displacement field

$$\mathbf{u}(\mathbf{x}) = \sum_n A_n \frac{\hat{r} \cos \theta}{r^n} + \sum_m B_m \frac{\hat{z}}{r^m}. \tag{11}$$

We have chosen these two sets of terms since they constitute the only solution of Eq. (8) that are azimuthally symmetric. As we will see, A_n and B_n are proportional to ϵ so that $\mathbf{u}$ satisfies the requirement of linearity in ϵ. We now put our ansatz, Eq. (11), into the partial differential equation, Eq. (8). Writing the radial ($\hat{r}$) and polar ($\hat{\theta}$) components of that expression separately we find:

$$\mathcal{M}(n, \zeta) \cdot \begin{pmatrix} A_n \\ B_n \end{pmatrix} = 0 \tag{12}$$

where the 2×2 matrix $\mathcal{M}(n, \zeta)$. depends on the Lamé constants only through the dimensionless ratio, $\zeta =$

$(\mu + \lambda)/\mu$. This matrix is given by:

$$\begin{pmatrix} [(1+\zeta)(n-2)(n+1)-2] & [(1+\zeta)n(n+1)-2n] \\ (1+\zeta)(n-2)-n & (1+\zeta)n-n^2 \end{pmatrix}. \tag{13}$$

A necessary and sufficient condition for Eq. (12) to be satisfied for nontrivial values of A_n, B_n is that $\det \mathcal{M}(n,\zeta) = 0$. There are four such solutions: $n = -2, 0, 1, 3$. By finding the eigenvectors associated with these eigenvalues we may write the most general solution of Eq. (8) consistent with the two conditions discussed above,

$$\mathbf{u}(\mathbf{x}) = \frac{aC_1}{r}\left[\gamma_1 \hat{r}\cos\theta + \hat{z}\right] + \frac{a^3 C_2}{r^3}\left[3\hat{r}\cos\theta - \hat{z}\right]$$
$$+ C_3\hat{z} + \frac{C_4 r^2}{a^2}\left[\gamma_2 \hat{r}\cos\theta - \hat{z}\right] \tag{14}$$

where the constants C_m are determined from boundary conditions and the two dimensionless constants

$$\gamma_1 = \frac{1}{3 - 4\sigma} \tag{15}$$

$$\gamma_2 = 2\left(\frac{2 - 3\sigma}{3 - 2\sigma}\right) \tag{16}$$

are functions of the Poisson ratio:

$$\sigma = \frac{1}{2}\frac{\lambda}{\mu + \lambda}. \tag{17}$$

Since the Poisson ratio can vary between -1 and $1/2$[4], $1/7 < \gamma_1 < 1$ and $1/2 < \gamma_2 < 2$. In the incompressible limit $(\lambda \longrightarrow \infty)$ $\sigma \longrightarrow 1/2$, $\gamma_1 \longrightarrow 1$, and $\gamma_2 \longrightarrow 1/2$. Since we are considering complex, frequency–dependent bulk and shear moduli, $\sigma = \sigma(\omega)$ depends on frequency and is in general complex.

Examining the solution we see that the first term on the RHS of Eq. (14) decays only as $1/r$ away from the rigid sphere. The second term is a dipole field. The third term is simply a constant shift of the entire medium which is clearly a solution, but cannot contribute to the stress tensor. The fourth term grows as r^2 as one moves away from the sphere. In order to satisfy the boundary conditions at infinity for the problem under consideration we must set $C_3 = C_4 = 0$. The remaining two constants are determined by the boundary conditions at the surface of the rigid sphere. We find

$$\mathbf{u}(\mathbf{x}) = \frac{\epsilon}{2}\left[3\frac{a}{r}\left(\eta_1\hat{r}\cos\theta + \eta_2\hat{z}\right) - \eta_1\frac{a^3}{r^3}\left(3\hat{r}\cos\theta - \hat{z}\right)\right] \tag{18}$$

where $\eta_1 = 1/(5 - 6\sigma)$ and $\eta_2 = (3 - 4\sigma)/(5 - 6\sigma)$. We note that in the incompressible limit, the displacement field around the displaced sphere takes the form of what would be the perturbation of the velocity field of an incompressible fluid produced by the same sphere inserted in a uniform flow in the $\hat{z}$ direction (at low Reynolds number).

Since we wish to calculate the response of the sphere to an applied force we need to determine the force applied to the sphere that resulted in the imposed displacement of $\hat{z}\epsilon$. To do this we calculate the restoring force of the medium on the sphere. The external force $\mathbf{F}$ is the negative of the force the medium exerts on the sphere. We can calculate the latter force, which by symmetry must point in the $\hat{z}$–direction by integrating the stress tensor over the surface of the sphere to obtain

$$F_z = -\oint a^2 d\Omega\left[\sigma_{rr}\cos\theta - \sigma_{r\theta}\sin\theta\right], \tag{19}$$

From this result we obtain the response function[10]

$$\alpha(\omega) = \frac{\partial\epsilon}{\partial F_z} = \frac{1}{6\pi a\mu(\omega)}\left[1 + \frac{\sigma(\omega) - 1/2}{2\left(\sigma(\omega) - 1\right)}\right]. \tag{20}$$

We note that in the incompressible limit, $\sigma(\omega) \longrightarrow 1/2$, we recover the form of the Stokes mobility of the sphere in an incompressible fluid. The only difference between that result and Eq. (20) in the incompressible limit is the substitution of the shear modulus, $\mu(\omega)$, for $i\omega\eta$.

B The inhomogeneous medium: the results for distant particles

Having solved the single–sphere problem, we are in a position to extend the analysis to the two–sphere response function in a spatially inhomogeneous elastic medium. As in the analogous electrostatic problem, we approach this problem via the method of reflections. To compute the response function to lowest order, we simply need to calculate the displacement field at the location of the second sphere due to a force applied to the first sphere. Once again, we model the inhomogeneous elastic medium by the simple, anomalous pocket discussed in our study of the analogous electrostatic problem. We assume that the spheres are surrounded by a spherical pocket of material (of radius b) with elastic properties characterized by the Lamé coefficients, $\bar{\lambda}, \bar{\mu}$. See figure 1. The bulk material, far from the rigid spheres has Lamé constants: λ, μ.

Using Eq. (14) we write down solutions to the force balance equations that apply in the inner, anomalous region, and the outer bulk material respectively,

$$\mathbf{u}^{\mathrm{i}}(\mathbf{x}) = \frac{aC_1^{\mathrm{i}}}{r}\left[\bar{\gamma}_1\hat{r}\cos\theta + \hat{z}\right] + \frac{a^3 C_2^{\mathrm{i}}}{r^3}\left[3\hat{r}\cos\theta - \hat{z}\right] +$$
$$+ C_3^{\mathrm{i}}\hat{z} + \frac{C_4^{\mathrm{i}}r^2}{a^2}\left[\bar{\gamma}_2\hat{r}\cos\theta - \hat{z}\right] \tag{21}$$

$$\mathbf{u}^{\mathrm{o}}(\mathbf{x}) = \frac{bC_1^{\mathrm{o}}}{r}\left[\gamma_1\hat{r}\cos\theta + \hat{z}\right] + \frac{b^3 C_2^{\mathrm{o}}}{r^3}\left[3\hat{r}\cos\theta - \hat{z}\right]. \tag{22}$$

In the above equation, $\bar{\gamma}_{1,2}$ are identical to the γ's defined in Eqs. (15)–(16) with the Poisson ratio equal to that of the inner material. Using the boundary condition at infinity, Eq. (10), we have set $C_{3,4}^{\mathrm{o}} = 0$. We

are left with six remaining constants that are determined by two boundary conditions at the surface of the sphere [see Eq. (9)] and four boundary conditions at the interface of the two different elastic media, $|\mathbf{x}| = b$. These four conditions enforce the continuity of the displacement field: $\mathbf{u}^i(|\mathbf{x}| = b) = \mathbf{u}^o(|\mathbf{x}| = b)$ and stress tensor: $\sigma_{rj}^i(|\mathbf{x}| = b) = \sigma_{rj}^0(|\mathbf{x}| = b), j = r, \theta$ at that interface. These conditions are sufficient to determine the six remaining constants.

Recall that we wish to show that the long–range part of the interparticle response function measures the bulk material properties of the medium independently of the local modification of the material's elastic properties by the rigid spheres. In order to do this we first concentrate on the part of the displacement field $\mathbf{u}^o(\mathbf{x})$ that varies as $1/r$. We will independently solve for the coefficient of this term. Such a solution allows a good approximation to the displacement field in the far–field regime and will test the ideas discovered via the electrostatic analogy.

To calculate the coefficients $C_1^{o,i}$ we employ a global constraint on the stress tensor: the integral of the flux of the stress tensor, $\sigma_{ij} dS_j$, over any closed surface (with local outward normal parallel to dS_j) enclosing the rigid sphere, which applies a force $\mathbf{F}$ to the elastic medium, must be equal and opposite to that applied force. The integral of the stress tensor over such a surface is $-\mathbf{F}$. Thus we may write this condition, for a particular spherical surface of radius r, with $r > a$ in the following form:

$$F_z = - \oint r^2 d\Omega \, \sigma_{rz}^{i,o}, \qquad (23)$$

where choice of the appropriate form of the stress tensor, σ_{rz}^i or σ_{rz}^o, is determined by magnitude of r, i.e. whether the surface of integration is contained in the inner region or in the bulk material. In the above equation we have taken the force on the sphere to be in the $\hat{z}$–direction and the integral is over all solid angles. Counting powers of r in the stress tensor and noting that $\sigma \sim \nabla\mathbf{u}$, we find that only the part of the stress tensor coming from the term in $\mathbf{u}$ proportional to C_1^o can contribute to the result. This term, which depends on the radial distance from the sphere as $1/r^2$ is the only one that will lead to an r–independent result on the RHS of Eq. (23). Since the LHS of this equation is clearly r–independent, the other contributions to the stress tensor coming from C_n, $n > 1$ must all vanish under the angular integration.

From the global stress constraint [Eq. (23)] and our solution for the displacement field we determine the coefficient C_1^o to be

$$C_1^o = \frac{1}{8\pi a\mu} \left[\frac{\lambda + 3\mu}{\lambda + 2\mu} \right]. \qquad (24)$$

The analogous coefficient in the inner region, C_1^i, is given by the same expression, however, the Lamé coefficients take the values of the inner region: $\bar{\mu}, \bar{\lambda}$. We may use the above result to eliminate one variable from the set of six that must be determined to completely solve the

present elastic problem. Before we continue this program, however, it is useful to calculate the far-field part of the viscoelastic, interparticle response function. We have already seen, from the electrostatic analogy, that only the dominant long-range part of the sphere–sphere interaction is expected to be free of the influence of the anomalous pockets. We seek, therefore, to demonstrate, in a manner analogous to the problem of the inverse capacitance of two conducting spheres in an inhomogeneous dielectric, that the *inter*–particle response function is independent of the rheological properties of the local pockets surrounding the particles in the visco–elastic problem.

To do this we again use the lowest–order term in the series solution of the two–sphere problem that is generated by the method of reflections. This lowest–order term simply gives the displacement of sphere 2 in response to an applied force on sphere 1 as the value of the displacement field at the location of sphere 2 due to the displacement of sphere 1, where that displacement field is calculated without regard to the boundary conditions on sphere 2 or its surrounding shell of perturbed material. Thus the solution of the far-field part of the single–sphere problem is precisely the result that we need. The corrections to this result coming from higher–order reflections will be smaller than the previously calculated part by a non-zero power of b/r, where $\mathbf{r}$ is the separation vector between the two spheres. These corrections are discussed in appendix A. Ignoring higher–order corrections coming from both higher order reflections and the dipolar part of the far-field $\mathbf{u}$, we find

$$\alpha_{ij}^{(21)} = \alpha_{||}(r)\hat{r}_i\hat{r}_j + \alpha_\perp(r)\left(\delta_{ij} - \hat{r}_i\hat{r}_j\right), \qquad (25)$$

where the response along the line of centers is given by

$$\alpha_{||}(r) = \frac{1}{4\pi r\mu(\omega)}, \qquad (26)$$

and the response perpendicular to the line of centers is

$$\alpha_\perp(r) = \frac{1}{8\pi r\mu(\omega)} \left[\frac{\lambda(\omega) + 3\mu(\omega)}{\lambda(\omega) + 2\mu(\omega)} \right]. \qquad (27)$$

We have explicitly written the frequency dependence of the Lamé to emphasize the applicability of this calculation to the complete viscoelastic problem. We note, however, that by neglecting inertial terms (which has been justified previously in the single–sphere case at frequencies of experimental interest[6]), we are here imposing a more stringent requirement. The above result assumes that two spheres are close enough that there is no significant phase shift between the oscillation of the two spheres at the probing frequency, ν i.e. $|\mathbf{r}| \ll c/\nu$, where c is the speed of sound in the medium. Even for soft materials with relatively high compressibility, it is possible to have the necessary separation of length scales, $b \ll r \ll c/\nu$ for Eq. (25)– (27) to hold at all experimentally accessible frequencies.

Finally it is interesting to observe that in the incompressible limit, $\lambda(\omega) \longrightarrow \infty$, the ratio of the response

along the line of centers to that perpendicular to the line of centers is $2:1$. The experimental determination of the deviation of this ratio from $2:1$ measures the compressibility of the material at the frequency of observation.

C Single particle response in the composite medium

It is interesting to compare the above results for the interparticle response function in the composite (two-shell) medium with the single–particle response in the same medium. From the electrostatic analogy we expect to find that the single–particle response function depends on the elastic properties of both types of materials making up the composite medium. Below we will show this to be the case. That calculation also demonstrates that the comparision of the single particle response to the two–particle response functions allows one to determine the material properties of both materials making up the composite medium. This result shows, at least within the simplified pocket model of the inhomogeneous medium, that measurements of the probe particle autocorrelations combined with two–point measurements of distant particles completely characterize the bulk material and perturbation zone surrounding the probe. In a later section we will revisit this result and show that even in a more physical model, in which the material properties of the medium vary continuously with distance from the probe, it is still possible to extract information about the perturbed region (as well as the bulk properties) from a combination of one- and two–point correlation measurements.

In order to solve for the single–particle response function, we must continue along the lines of the previous section and solve for the complete deformation field in the two–shell medium surrounding a particle. As above we put a force $\mathbf{F} = F\hat{z}$ on the particle and determine the deformation field. From the value of that field at the surface of the probe sphere ($|r| = a$) we calculate the displacement of the probe and thus the response function in question. Returning to Eqns. (21),(22) we note that there are now only four undetermined coefficients: From Eq. (24) we already know C_1^{o}, C_1^{i} in terms of the applied force $\mathbf{F}$. We now continue with the simple but tedious task of matching boundary conditions at the interface of the two elastic media and at the surface of the sphere as discussed in the previous section.

At the surface of the sphere we find that:

$$C_1^{\mathrm{i}} - C_2^{\mathrm{i}} + C_3^{\mathrm{i}} - C_4^{\mathrm{i}} = \epsilon \tag{28}$$

$$\bar{\gamma}_1 C_1^{\mathrm{i}} + 3C_2^{\mathrm{i}} + \bar{\gamma}_2 C_4^{\mathrm{i}} = 0, \tag{29}$$

where ϵ is the displacement of the sphere in the $\hat{z}$ direction. The above set of equations actually contributes only one relation among the remaining four unknown coefficients since Eq. (28) only exchanges one of these

unknowns for the, as yet, undetermined sphere displacement. It is this quantity, however, that we need to determine the response function.

From the continuity of the displacement field, $\mathbf{u}$, at the interface of the two elastic media ($r = b$) we find two more relations:

$$C_1^{\mathrm{o}} - C_2^{\mathrm{o}} = \beta C_1^{\mathrm{i}} - \beta^3 C_2^{\mathrm{i}} + C_3^{\mathrm{i}} - \beta^{-2} C_4^{\mathrm{i}} \tag{30}$$

$$\gamma_1 C_1^{\mathrm{o}} + 3C_2^{\mathrm{o}} = \beta\bar{\gamma}_1 C_1^{\mathrm{i}} + 3\beta^3 C_2^{\mathrm{i}} + \beta^{-2}\bar{\gamma}_2 C_4^{\mathrm{i}}, \tag{31}$$

where $\beta = b/a$.

For the remaining relation needed to specify all four undetermined coefficients, we require the continuity of one component of the stress tensor across the interface of the two media ($r = b$). We choose to consider $\sigma_{r\theta} = \mu\left[\partial_\theta u_r/r + \partial_r u_\theta - u_\theta/r\right]$. This yields the condition:

$$\mu\left[C_1^{\mathrm{o}}\left(1 - \gamma_1\right) - 6C_2^{\mathrm{o}}\right] = \bar{\mu}\left[\beta\left(1 - \bar{\gamma}_1\right)C_1^{\mathrm{i}} + \right.$$
$$\left. -6\beta^3 C_2^{\mathrm{i}} + \beta^{-2}\left(2 - \bar{\gamma}_2\right)C_4^{\mathrm{i}}\right] \tag{32}$$

We now have four equations to determine the unknown coefficients: $C_{2,3,4}^{\mathrm{i}}, C_2^{\mathrm{o}}$ and another equation to eliminate one of these four coefficients in favor of the quantity that we seek – the displacement of the sphere, ϵ. The response function for the single sphere in the two–shell medium is then given by

$$\frac{\epsilon}{F} = \alpha_{ij}^{(1,1)} = \frac{1}{6\pi\mu a}Z(\bar{\gamma}_1, \bar{\gamma}_2, \beta)\delta_{ij}. \tag{33}$$

The response function has been written as the product of the single particle response in an incompressible bulk material with shear modulus μ and a correction factor, $Z(\bar{\gamma}_1, \bar{\gamma}_2, \beta)$, which depends on the ratio of the radius of the anomalous pocket to the radius of the sphere, $\beta = b/a$, and *all* of the elastic constants. The correction factor in terms of the constants $\gamma_{1,2}$ [defined in Eqns. (15), (16)] is given by:

$$Z(\bar{\gamma}_1, \bar{\gamma}_2, \beta) = \frac{z_1}{z_2} \tag{34}$$

where

$$z_1 = 6\beta^5\left(\bar{\gamma}_1 + \bar{\gamma}_2\right)\bar{p}\kappa(\kappa - 1) + \tag{35}$$
$$(\bar{\gamma}_1 + 3)\bar{p}\kappa(\bar{\gamma}_2 - 2 - 2\bar{\gamma}_2\kappa) + 2\beta^6\bar{\gamma}_2(\kappa - 1)\times$$
$$\times\left(p(\gamma_1 + 3) - \kappa\bar{p}(\bar{\gamma}_1 + 3)\right) + \beta\left((\gamma_1 + 3)(\bar{\gamma}_2 - 2)p + \right.$$
$$-(3 + 5\bar{\gamma}_2 + \gamma_1(3 + \bar{\gamma}_2))p\kappa + \bar{p}\kappa(9 - 4\bar{\gamma}_2 - \bar{\gamma}_1 +$$
$$6(\bar{\gamma}_1 + \bar{\gamma}_2)\kappa) + \beta^3(\bar{\gamma}_2 - 3)\kappa$$
$$\times\left((-p(\bar{\gamma}_1 + 1)\bar{p}(1 + \bar{\gamma}_1(4\kappa - 3)))\right)$$

and

$$z_2 = 4\left(\bar{\gamma}_2\left[1 + 2\beta^5(\kappa - 1) - 2\kappa\right]\right), \tag{36}$$

with $\kappa = \mu/\bar{\mu}$ and

$$p = \frac{\lambda + 3\mu}{\lambda + 2\mu}; \tag{37}$$

there is a corresponding term $\bar{p}$ which applies to the material of the inner region.

It may be checked that the above expression [Eqs. (33) – (36)], reduces to the simpler result for the single particle response function in a homogeneous medium, Eq. (20), when the elastic properties of the two shells are equated. As expected the full result is a complicated function of both the elastic constants of the inner, perturbed shell of the material, and the range of the perturbation: b.

Both because of the complexity of the above result and because many applications of the these techniques apply to systems that are essentially incompressible (polymeric solutions and melts fall into this category) it is worthwhile to also record a simpler version of the response function that obtains when both the perturbed and the bulk material may be considered to be incompressible. In that limit we find that the correction factor takes the form:

$$\frac{4\beta^6\kappa'^2 - 10\beta^3\kappa' + 9\beta^5\kappa'\kappa - 2\kappa\kappa'' - 3\beta(2 + \kappa - 3\kappa^2)}{2\left[\kappa'' - 2\beta^5\kappa'\right]}$$

(38)

where $\kappa' = \kappa - 1$ and $\kappa'' = 3 + 2\kappa$.

We end this section of the paper by noting that the above calculations not only give the complete result for the single–particle response function in the two material composite medium but they also determine the next–to–leading order corrections for the interparticle response function of two spheres in the same composite medium. We discuss this point further in Appendix A. Here we record the coefficient of the dipolar term in the displacement field. Based on arguments presented in Appendix A, it can be shown that this dipolar term gives the next–to–leading order correction in the two–particle response function for distant particles. The dipolar coefficient of the displacement field in the bulk medium (C_2^o) has been completely determined already in the course of our solution of the single–particle response function presented above. We have found that in the case where both media are incompressible it takes the form

$$C_2^\mathrm{o} = -\frac{F}{8\pi b\mu}\frac{(1-\kappa)(3+2\beta^5) + 5\beta^2\kappa}{3(3+2\kappa) + 6\beta^5(1-\kappa)}.$$

(39)

As expected on more general grounds, this next–to–leading order correction depends on all the elastic constants and the ratio of pocket radius to the sphere radius.

D Differential Shell Method

A more physical model of the anomalous region surrounding the probe particle allows for the rheological properties of the medium to vary *continuously* with distance from the probe. In order to perform quantitive fits to the single particle response function measured in a complex fluid via microrheology, it is necessary to fit the data to a continuous model of the anomalous zone. As we will see, this fit requires a theoretical model of the variation of the complex material's rheological behavior as a function of distance from the sphere. In this section, we first present a general set of equations describing the variation of the four displacement–field coefficients with distance for a given functional form of the variation of the shear modulus with distance from the probe: $\mu = \mu(|\mathbf{r}|)$. As an illustration of this method we then apply our procedure to the case of a polymer solution at concentrations near $c^\star$, the overlap concentration.

Having solved the two–shell model above, we can now generalize this technique to many shells. To compute the displacement field in the continuous variation limit, we divide the material into spherical shells of infinitesmal thickness, Δr, centered on the probe particle. Within each spherical shell we may take the Lamè coefficients to be constant. Now we can determine a relation between the set of displacement field coefficients in the nth shell ($\{C_i^n\}, i = 1, \ldots, 4$) to those of the $n^{\mathrm{n}+1}$ shell ($\{C_i^{\mathrm{n}+1}\}, i = 1, \ldots, 4$) by using the same set of boundary conditions at the interface of the two shells as have been applied above. See figure 2. Taking the thickness of the shells to zero we determine derivatives of the displacement field coefficients with respect to r. These linear differential equations can be integrated to give the variation of the displacement field coefficients, and thereby determine the form of the stain field. The single–particle response function follows naturally. For the two–particle response function, we assume that there still exists the large separation of length scales between the distance separating the two probe particles and the distance over which there is an appreciable variation of the elastic constants (the size of the anomalous zone). The two–particle response function, which does not depend on properties of the anomalous zone, therefore, still applies. Below we derive the differential equations for the displacement field coefficients for the case where the material is everywhere incompressible ($\lambda(r) = \infty$ for all r).

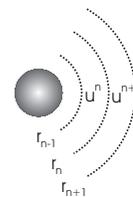Matching the displacement field at the interface $|\mathbf{r}| =$

FIG. 2: Differential shell method: Using stress and displacement continuity at the interface of the nth and $(n+1)^\mathrm{th}$ shells we determine the coefficients of displacement field $\mathbf{u}^{n+1}$ in terms of the coefficients in of the displacement field $\mathbf{u}^n$. Later, taking the thickness of the shells to zero: $\Delta r = r_{n+1} - r_n \longrightarrow 0$ we arrive at a set of differential equations governing the variation of the displacement field coefficients – the Cs.

r_n we find two equations. The first coming from matching the radial components of the field is:

$$\frac{2a}{r_n}\Delta C_1 + \frac{2a^3}{r_n^3}\Delta C_2 + \Delta C_3 - \frac{1}{2}\left(\frac{r_n}{a}\right)^2 \Delta C_4 = 0 \quad (40)$$

where $\Delta C_i = C_i^{n+1} - C_i^n$. Taking the limit of thin shells *i.e.*

$$\Delta C_i = \Delta r \left.\frac{dC_i}{dr}\right|_{r=r_n} = \Delta r\, \dot{C}_i, \quad (41)$$

we arrive at the differential equation

$$\frac{2a}{r}\dot{C}_1 + \frac{2a^3}{r^3}\dot{C}_2 + \dot{C}_3 - \frac{1}{2}\left(\frac{r}{a}\right)^2 \dot{C}_4 = 0 \quad (42)$$

Using a similar procedure to match the u_θ parts of the displacement field we find the differential equation:

$$\dot{C}_3 = -\frac{a}{r}\dot{C}_1 + \left(\frac{a}{r}\right)^3 \dot{C}_2 + \left(\frac{r}{a}\right)^2 \dot{C}_4. \quad (43)$$

The remaining two equations come from matching the σ_{rr} and $\sigma_{r\theta}$ components of the stress tensor. We recall from section III C [see the discussion following Eqns. (28)(29)], however, that only one more equation is needed to determine the coefficients since we already know the functional form of C_1,

$$C_1 = \frac{1}{8\pi a\mu(\omega)}, \quad (44)$$

from the same global property of the stress tensor applied in the two–particle problem. We again choose to enforce the continuity of $\sigma_{r\theta}$, which, in the thin shell limit, yields

$$6\frac{a^3}{r^4}\dot{C}_2 - \frac{3}{2}\frac{r}{a^2}\dot{C}_4 + \frac{\dot{\mu}}{\mu}\left[6\frac{a^3}{r^4}C_2 - \frac{3}{2}\frac{r}{a^2}C_4\right] = 0 \quad (45)$$

We now find two differential equations for the variables C_2 and C_4 by eliminating C_3 in Eq. (40) using Eq. (42). Furthermore we use our solution for C_1 to write the set of differential equations in the following form [after undimensionalizing]:

$$B_2'(x) + \frac{x^5}{6}B_4'(x) = -\frac{x^2}{3}\frac{d}{dx}\left(\frac{\mu_0}{\mu(x)}\right) \quad (46)$$

$$B_2'(x) - \frac{x^5}{4}B_4'(x) = -\frac{d}{dx}\left(\ln\frac{\mu}{\mu_0}\right) \times \quad (47)$$
$$\left[B_2(x) - \frac{x^5}{4}B_4(x)\right]$$

where $x = r/a$, $\cdot'$ indicates a derivative with respect to x, μ_0 is a modulus scale, $x = r/a$, and

$$B_i = \frac{8\pi a\mu_0 C_i}{F}, \quad (48)$$

where F is the magnitude of the force applied to the sphere. We find it simpler, once again, to study the response function by fixing a known force on the sphere and computing its displacement, ϵ.

Eqs. (46),(47) can be integrated from the surface of the probe sphere, $x = 1$. Having a set of two first order differential equations we require two boundary conditions to determine a unique solution.

There are two boundary conditions coming from the specification of the displacement field at the surface of the sphere. In general, this vectorial equation specifies two independent relations, however, since the magnitude of the sphere's displacement is, as yet, unknown, we obtain only one boundary condition for Eqs. (46) and (47):

$$B_2(1) + \frac{1}{6}B_4(1) = -\frac{\mu_0}{3\mu(x=1)}. \quad (49)$$

The second equation

$$\frac{\mu_0}{\mu(x=1)} - B_2(1) + B_3(1) - B_4(1) = 8\pi\mu_0 a\frac{\epsilon}{F}. \quad (50)$$

coming from the boundary condition at the sphere expresses teh magnitude of the sphere's displacement ϵ, in terms of the B–amplitudes. We still need another boundary condition to specify a unique solution of Eqns. (46) and (47). The second boundary condition is that B_4, the coefficient of the quadratically growing term in the general solution of the displacement field with azimuthal symmetry, must vanish in the large r limit. Thus

$$\lim_{x\longrightarrow\infty} B_4(x) = 0. \quad (51)$$

Similarly, we know that there should be no constant term in the displacement at large distances from the sphere so $\lim_{x\longrightarrow\infty} B_3(x) = 0$. This boundary condition in combination with Eq. (43) allows the determination of B_3 at the surface of the sphere in terms of an integral over the (uniquely determined) functions B_2 and B_4:

$$B_3(1) = -\int_1^\infty \left\{-\frac{1}{z}\frac{d}{dz}\left(\frac{\mu_0}{\mu(z)}\right) + \frac{1}{z^3}B_2'(z) + z^2 B_4'(z)\right\} dz \quad (52)$$

The solution is effected by choosing $B_4(x=1)$ [using Eq. (49) to determine $B_2(x=1)$] and then integrating the differential equations from $x=1$ to infinity. $B_4(x=1)$ is chosen so that this function goes to zero at large x. Given this solution for B_2 and B_4 one can integrate Eq. (52) to determine $B_3(1)$. Finally, with the full set of initial values of $B_2, B_3,$ and B_4 one can evaluate the response function using Eq. (50).

We further organize this calculation by defining the effective shear modulus of the medium to be that value of the shear modulus needed to write the response function in the form that it would have taken in an incompressible, *homogeneous* material. In other words, we define μ_{eff} by

$$\frac{\epsilon}{F} = \alpha = \frac{1}{6\pi a\mu_{\mathrm{eff}}}. \quad (53)$$

Here the vectorial indicies have been suppressed since, by rotational symmetry, $\alpha_{ij}^{(1,1)} \sim \delta_{ij}$ for an isolated sphere.

With this definition we write the effective response function in terms of the initial values of $B_2, B_3,$ and B_4 and the modulus scale as

$$\frac{\mu_{\text{eff}}}{\mu_0} = \frac{4}{3} \left[\frac{\mu_0}{\mu(1)} - B_2(1) + B_3(1) - B_4(1) \right]^{-1}. \quad (54)$$

We note that in the homogeneous medium: $B_3 = B_4 = 0$ and $\mu_0/\mu(1) = 1$. In addition, we find that $B_2 = -1/3$ so that $\mu_{\text{eff}} = \mu_0$ as required for consistency.

As an example of the differential shell method we consider the case of a semi-dilute polymer solution – see appendix B. To apply the methods of one–point microrheology to this case, one would measure the fluctuating position of a probe particle in the liquid (due to Brownian diffusion) and compute from the position autocorrelations the diffusivity of that probe. Using the Stokes–Einstein relation one could then extract a measurement of the viscosity. However, such a measurement should be an underestimate since the probe sphere produces a spherical pocket of polymer–depleted solution surrounding it (see Appendix B for details). The local polymer concentration will approach its bulk value essentially exponentially with distance from the sphere with a "healing length" controlled by the polymer correlation length in the solution. This polymer–depleted shell of fluid has a lower viscosity than that of the bulk. We take a continuous polymer concentration profile suggested by self-consistent calculations[14, 16] and numerically integrate the differential equations for the case that the polymer correlation length is 30% of the sphere radius and the bulk solution visocity is four times the value of that of the solvent. The variation of the coefficients $B_1, \ldots, B_4$ with distance from the probe sphere are shown in figure 3.

Using Eq. (54) we find that indeed the *single* particle measurements suggest that the viscosity is smaller than it's bulk value. For this particular case the effect is small – the viscosity measurement coming from one–point microrheology is about 73% of the actual bulk value. If the depletion zone were larger compared to the sphere radius, the effect of the anomalously small value of the solution viscosity in the depletion zone would be more significant.

IV. SUMMARY

In this paper we have studied the single–particle and two–particle response functions in an inhomogeneous viscoelastic medium. These response functions must be known in order to use microrheological measurements as a probe of the material properties of soft materials. We restricted our analysis to the type of inhomogeneity that is caused by the introduction of the probe particles themselves. We have assumed that the rheological anomaly in the material relaxes to the unperturbed, bulk value as some function of radial distance from the probe particles. To make a model system that has the simplest possible

inhomogeneity of this form we have considered not only the "pocket model" (consisting of a spherical cavity surrounding each probe particle with perturbed viscoelastic properties), but also a more physical model in which the material's rheological properties vary continuously with distance from the probe sphere. We have also shown that the combination of one–point techniques (which measure a combination of the properties of the unperturbed, bulk material and the rheological anomalous material immediately surrounding the probe sphere) and two–point techniques (which measures the bulk rheological properties) allows the experimentalist to probe details of the probe–particle, medium interaction.

APPENDIX A: CORRECTIONS FOR CLOSER PARTICLES: HIGHER ORDER REFLECTIONS AND SUBDOMINANT TERMS IN THE STRAIN FIELD

There are two classes of corrections to the result of section III B for the interparticle response function of two distant spheres. These corrections produce terms that are higher order in a/R where R is the (large) separation of the two probe spheres. In general, these corrections depend on all the elastic constants of the composite
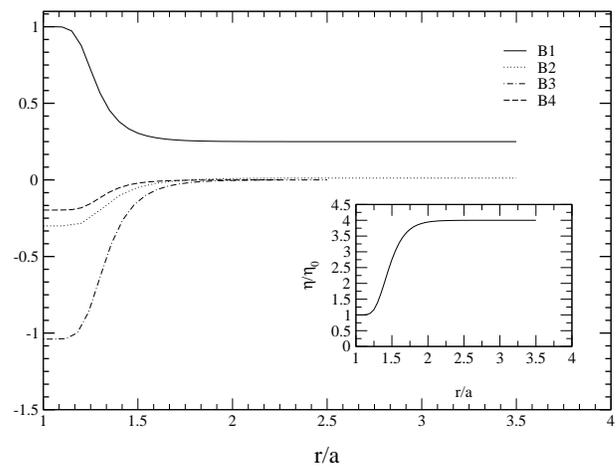

FIG. 3: The variation of the dimensionless displacement field coeffecients computed numerically. The characteristic length scale for the variation of the polymer concentration (thus the solution viscosity) is 0.30 in the dimensionless units r/a. The inset shows the variation of the fluid viscosity with distance from the sphere.

relative importance of these terms in order to determine how distant two probe particles must be in order for their correlated fluctuations to be governed primarily by the bulk elastic constants.

The two classes of corrections are due to either subdominant terms in the displacement field of sphere one at the level of the zeroth order reflection (in which we ignore the role of second sphere in determining its subsequent displacement) or corrections to the displacement field that result from higher order reflections (iteratively correcting the boundary conditions of **u** at the surface of each sphere–and–pocket). In this section we determine which of these effects first presents deviations to the far–field results presented earlier. We have already seen that subdominant corrections in the far–field **u** are of a dipolar form, decaying with distance as R^{-3}. These corrections also depend on the properties of the inner pockets. We now look at the corrections coming from higher order reflections.

Because the full elastic problem in the composite medium is quite complex, once again it is helpful return to the electrostatic analogy for guidance. As before we replace the rigid particle of radius a and its surrounding spherical pocket (of radius b) of anomalous material by its electrostatic analog: a conducting sphere of radius a surrounded by a region of radius b with dielectric coefficient $\bar{\epsilon}$. To simplify the formulae we set the bulk dielectric constant to unity. We consider first the potential at sphere two to lowest order. At this iteratation we may still replace (the charged) sphere one and its surrounding dielectric pocket by a point charge Q at the origin of that sphere. First we calculate the potential at the second (uncharged) sphere and then we determine the correction to that potential coming from higher order reflections. See figure 4 for a diagram of the electrostatic problem under consideration.

Using the azimuthal symmetry of the problem we can write the general form for the electrostatic potential, ϕ_{outer}, in the bulk material ($r > b$) by

$$\phi_{\text{outer}}(\mathbf{r}) = \frac{Q}{4\pi} \sum_{\ell=0}^{\infty} \frac{r_<^\ell}{r_>^\ell} P_\ell(\cos\theta) +$$
$$+ \frac{1}{4\pi\epsilon} \sum_{\ell=0}^{\infty} D_\ell r^{-(\ell+1)} P_\ell(\cos\theta), \quad (A1)$$

where $r_<$, $r_>$ are the minimum, maximum of r and R respectively. The functions $P_\ell(x)$ are the the standard Legendre polynomials. The first term represents the potential due to the point charge at $\mathbf{r} = \hat{z}R$ (we take the origin of the coordinate system to be at the center of the sphere.) and the second term gives the corrections to that potential field in the bulk due to polarization charges induced at the interface of the two dielectric media and on the conducting sphere. These corrections are given in terms of the yet unspecified coefficients D_ℓ. We can similarly write the expression for the potential in the
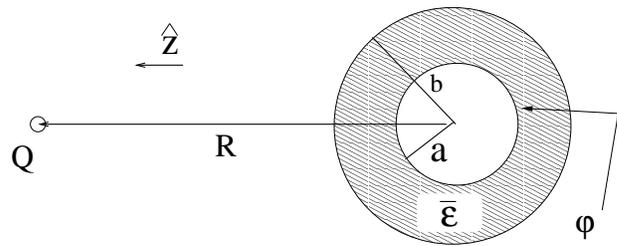

FIG. 4: Schematic diagram of the simpler electrostatic problem designed to test the importance of first order reflections upon the elastic response function. The first sphere, that is charged, can be replaced by a simple point charge to this order in the reflections. We focus on the response (potential) of the second sphere which sits in its pocket of material with dielectric $\bar{\epsilon}$. The bulk material has dielectric constant $\epsilon = 1$.

pocket ($a < r < b$),

$$\phi_{\text{inner}}(\mathbf{r}) = \sum_{\ell=0}^{\infty} \left[E_\ell r^\ell + F_\ell r^{-(\ell+1)} \right] P_\ell(\cos\theta), \quad (A2)$$

in terms of two sets of unknown coefficients, E_ℓ and F_ℓ.

We are trying to find the potential of the conducting sphere two ($|\mathbf{r}| = a$). Since the sphere is an equipotential surface, we find from Eq. (A2) that $E_\ell = F_\ell = 0$ for all $\ell \neq 0$. Furthermore, if we define ϕ_0 to be the as yet unknown potential of the sphere, we find that

$$E_0 + \frac{F_0}{a} = \phi_0 \quad (A3)$$

We now note that there are no free charges in the system other than the distant charge Q, so the surface integral of the electric displacement field over a sphere of radius r, $b < r < R$ must vanish. This condition forces $D_0 = 0$. From that result and the continuity of the radial component of the electric displacement vector at the interface of the two dielectric media ($r = b$) we determine that $F_0 = 0$ as well. Finally, from the continuity of tangential components of the electric field at the same interface, $\nabla(\phi_{\text{inner}} - \phi_{\text{outer}})|_{r=b} \times \hat{r} = 0$, we find that the remaining coefficient of interest, E_0 is given by: $E_0 = Q/(4\pi R)$ so from Eq. (A3) we arrive at the result

$$\phi_0 = \frac{Q}{4\pi\epsilon R}. \quad (A4)$$

This rather remarkable conclusion is that the presence of the anomalous dielectric pocket does not effect the result of the zeroth order reflection at all. We can physically understand this result along the lines presented in the text. We also note that the argument presented there can be extended to an arbitrary number of such dielectric shells; this suggests that the effect of *any* radially symmetric dielectric coefficient variation on the potential of the central conducting sphere always vanishes at the level of the zeroth reflection.

Next we consider the first correction to the potential on sphere two coming from higher order reflections. Since there is no free charge on either sphere two, or its surrounding dielectric, we know that the integral of the normal component of the electric displacement field over a surface just inside the dielectric shell (and just outside the surface of sphere two) vanishes:

$$\oint_{r=a+} D_r r^2 d\Omega = 0 \longrightarrow \oint_{r=a^+} E_r r^2 d\Omega = 0. \quad (A5)$$

The vanishing of the same integral of the normal component of the electric field follows from the fact that the dielectric constant in the material outside sphere two is assumed to be spherically symmetric. This assumption is clearly valid in the somewhat artifical two–shell model of the composite medium, but it should remain valid in a more physical model in which the dielectric constants vary continuously with distance from the probe particles, at least as long as the two particles are farther apart that a "healing length" over which the material recovers it bulk properties away from the probe particles.

We now study the polarization charge induced on the dielectric interfaces surrouding sphere two. It is clear that we can replace the dielectric shell around sphere two with two spherical surfaces of bound, polarization charge density (at $r = a$ and $r = b$). Our solution of the electrostatic problem defined in figure 4 shows that the bound polarization charge on the outer surface of the pocket surrounding sphere two (at the order of lowest reflections) is given by:

$$\sigma_{\text{outer}}(\theta) = Q \sum_{\ell=1}^{\infty} \frac{b^{\ell-1}}{R^{\ell+1}} \left(\frac{2\ell+1}{\Gamma_\ell + \ell + 1} \right) \left[\frac{1-\bar{\epsilon}}{\bar{\epsilon}} \right] P_\ell(\cos\theta) \quad (A6)$$

In the above equation, we have defined

$$\Gamma_\ell = \bar{\epsilon} \frac{\ell + (\ell+1)\left(\frac{a}{b}\right)^{2\ell+1}}{1 - \left(\frac{a}{b}\right)^{2\ell+1}} \quad (A7)$$

It is clear in the above result that if there is no dielectric discontinutiy at the edge of the pocket ($\bar{\epsilon} = 1$) this polarization charge density vanishes.

We now compute the bound charge at the interface between the conducting sphere (two) and the inner dielectric. To distinguish the bound polarization charge from that free charge on the conductor, we need to calculate the difference in charge density at $r = a$ between the general case and the particular case of no anomalous dielectric, i.e. we determine: $\tilde{\sigma}(\theta) = \sigma_{\text{inner}}(\theta) - \sigma_{\text{inner}}(\theta)|_{\bar{\epsilon}=1}$ to be

$$\tilde{\sigma}(\theta) = Q \sum_{\ell=1}^{\infty} (2\ell+1) \frac{a^{\ell-1}}{R^{\ell+1}} \Xi_\ell P_\ell(\cos\theta), \quad (A8)$$

where Ξ_ℓ is given by

$$\Xi_\ell = \left\{ 1 - \frac{2\ell+1}{1 + \ell(\bar{\epsilon}+1) - (1-\bar{\epsilon})(\ell+1)\left(\frac{a}{b}\right)^{2\ell+1}} \right\}. \quad (A9)$$

Since we are interested in understanding the next-to-leading order correction to the result presented in this article for the mutual response function of distant spheres, we may approximate the three charge distributions in the large R limit as follows: From the shell of bound polarization charge at the outer interface surrounding sphere two ($r = b$) we get an effective dipole moment of

$$\mathbf{P}_{\text{outer}} = -\frac{3Q}{R^2}(\bar{\epsilon}-1)b^3 \frac{1 + 2\left(\frac{a}{b}\right)^3}{2 + \bar{\epsilon} + 2(\bar{\epsilon}-1)\left(\frac{a}{b}\right)^3} \hat{z}. \quad (A10)$$

From the shell of bound polarization charge on the inner interface of the dielectric shell ($r = a$) we get the effective dipole moment

$$\mathbf{P}_{\text{inner}} = \frac{3Q}{R^2} a^3 \left\{ 1 - \frac{3}{2 + \bar{\epsilon} + 2(\bar{\epsilon}-1)\left(\frac{a}{b}\right)^3} \right\} \hat{z}. \quad (A11)$$

Note for $\bar{\epsilon} > 1$ The dipole moment of the outer shell points away from the first sphere and the dipole moment of the inner shell is anti-parallel to the outer dipole moment. This shows that, back at the first sphere, the net effect of these two effective dipoles is reduced by their partial cancellation. Finally we include the effect of the polarization of the conducting sphere two. This is simply given by the standard answer from the first reflection term for two spheres. The surface charge distribution of the conducting sphere produces the same field as a pair of point charges of equal and opposite magnitude within the sphere: a charge of $-Qa/R$ displaced from the center of sphere two towards the center of sphere one by a distance of a^2/R and the opposite charge (to ensure the charge neutrality of sphere two) at center of sphere two. This charge distribution at large distances, produces another dipolar field with dipole moment: $P_{\text{sphere}} = -Qa^3/R^2\hat{z}$.

The potential in the vicinity of sphere one produced by the dipoles induced in the neighborhood of sphere two is thus the sum of three dipole potentials, each centered at the origin of sphere two. Since the electric potential and, hence the electric field, is linear in the dipole moments we can approximate the net electric field at sphere one as the field of a single dipole located at the center of sphere two having a net dipole moment of:

$$\mathbf{P}_{\text{net}} = \mathbf{P}_{\text{inner}} + \mathbf{P}_{\text{outer}} + \mathbf{P}_{\text{sphere}} \quad (A12)$$

Collecting our previous results we find that the net dipole is given by:

$$\mathbf{P}_{\text{net}} = -\hat{z} \frac{Qb^3}{R^2} \left[\rho^3 + \frac{\bar{\epsilon}-1}{2 + \bar{\epsilon} + 2(\bar{\epsilon}-1)\rho^3} \left(1 - \rho^3\right)\left(1 + 2\rho^3\right) \right], \quad (A13)$$

where $\rho = a/b$. The most significant point coming from the calculation is that we have confirmed that the polarizibility of the combination of the conducting sphere and dielectric shell does, in fact, depend on properties of that dielectric shell. Without performing any further detailed calculations, we may assume that the polarizibility of the conducting sphere plus dielectric pocket takes the form: $\alpha_p = \alpha_p(a/b, \bar{\epsilon})b^3$. The dipole moment induced on sphere one by the dipole moment on sphere two then has a magnitude of:

$$P_1 = \alpha_p(a/b, \bar{\epsilon})b^3 \times \frac{b^3}{R^5} P_{\text{net}}. \tag{A14}$$

In the above equation the first term in the product is the polarizibility of sphere one and the second term is the electric field at sphere one due to the polarization of sphere two. So the shift in the potential of sphere two due to the next order reflection must take the form:

$$\Delta\phi_2 \simeq P_1 \frac{\alpha_p(a/b, \bar{\epsilon})b^3}{R^2} = \frac{b^6 Q \alpha_p^2(a/b, \bar{\epsilon})}{R^7}. \tag{A15}$$

Based on the electrostatic analog to the viscoelastic response function, we see that the next–to-leading order term in the approximate solution for the potential of sphere two decays as the seventh power of the sphere–sphere separation. The detailed calculation of the polarization sphere two serves to confirm that all these higher order terms necessarily involve all the properties of the anomalous pockets. The principal point of this section remains that we can conclude that the subdominant term in the displacement field in the elastic problem, which decays only as R^{-3}, give the next-to-leading order correction for the interparticle response function.

APPENDIX B: THE VISCOSITY OF SEMI–DILUTE POLYMER SOLUTIONS NEAR THE PROBE

In the semi-dilute regime the polymer volume fraction, ϕ, lies in the range: $\phi^\star \ll \phi \ll 1$, where $\phi^\star$ is the volume fraction at which the individual coils overlap. Here we may approximate the relaxational dynamics of a single chain as the reptation of a string of blobs with mean radius equal to the polymer correlation length ξ and thus composed of

$$g = \left(\frac{\xi}{\ell}\right)^{5/3} \tag{B1}$$

monomers, where ℓ is the Kuhn length. A polymer of N monomers consists of N/g blobs, and its reptation time is

$$\tau_{\text{rep}} = \tau_{\text{Zimm}}(g) \left(\frac{N}{g}\right)^3 \tag{B2}$$

where $\tau_{\text{Zimm}} \sim \xi^2/D(\xi)$ where $D(\xi) \sim 1/\xi$, the diffusion constant of a sphere of diameter ξ. is the Zimm relaxation time of a blob. In the semi–dilute regime, ξ scales with polymer volume fraction as

$$\xi = \ell\phi^{-3/4}, \tag{B3}$$

which implies

$$g \sim \phi^{-5/4}. \tag{B4}$$

The reptation time thus scales with volume fraction as

$$\tau_{\text{rep}} \sim \phi^{3/2}. \tag{B5}$$

To find the contribution of τ_{rep} to the viscosity, we note that $\eta_{\text{P}} \sim G_0 \tau_{\text{rep}}$, where $G_0 \sim k_B T/\xi^3 \sim (k_B T/a^3)\phi^{9/4}$ is the plateau modulus of the semi–dilute solution. Thus

$$\eta_{\text{P}} = \eta_0 \phi^{15/4} \tag{B6}$$

where η_0 is a viscosity.

Finally, in order to discuss the variation of the effective solution viscosity near the surface of the probe sphere we need to understand the polymer concentration profile near an impenetreble obstruction. If we assume that the correlation length in the solution is much smaller than the radius of curvature of the probe sphere, we may approximate the polymer concentration profile surrounding the sphere by that of the profile near a flat, hard wall. This problem has been studied using self-consistent methods with ground state dominance[14, 15]. The solution for the concentration profile near a wall at $x = 0$ is

$$c(x) = c_0 \tanh^2\left(\frac{x}{\xi}\right), \tag{B7}$$

where c_0 is the bulk polymer concentration. The correlation length obtained from this calculation is known not to scale correctly with polymer concentration; we suppliment the above solution with the correct scaling form from Eq. (B3). We also point out that if ξ is compariable to the sphere radius, the detailed form of Eq. (B7) must be quantitively inexact. The qualitive results of this analyis still hold. In particular, even for a sphere size that is comparable to the correlation length, we expect that the recovery of the bulk viscosity occurs over the length scale ξ as one moves away from the sphere.

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[16] It should be pointed out that the self-consistent calculation is not quantitively correct. However, the existence of a mesoscopic length scale in the polymer solution which is on the the order of the bead size is clearly valid. Given this one length scale, the essentially expoenential dependence of the polymer concentration around the bead is at least reasonable. We do not include the effect of the curvature of the bead's surface in this calculation.