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Normal modes of weak colloidal gels

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(Received 4 February 2017; revised manuscript received 12 December 2017; published 12 January 2018)

The normal modes and relaxation rates of weak colloidal gels are investigated in calculations using different models of the hydrodynamic interactions between suspended particles. The relaxation spectrum is computed for freely draining, Rotne-Prager-Yamakawa, and accelerated Stokesian dynamics approximations of the hydrodynamic mobility in a normal mode analysis of a harmonic network representing several colloidal gels. We find that the density of states and spatial structure of the normal modes are fundamentally altered by long-range hydrodynamic coupling among the particles. Short-ranged coupling due to hydrodynamic lubrication affects only the relaxation rates of short-wavelength modes. Hydrodynamic models accounting for long-ranged coupling exhibit a microscopic relaxation rate for each normal mode, \( \lambda \) that scales as \( l^{-2} \), where \( l \) is the spatial correlation length of the normal mode. For the freely draining approximation, which neglects long-ranged coupling, the microscopic relaxation rate scales as \( l^{-\gamma} \), where \( \gamma \) varies between three and two with increasing particle volume fraction. A simple phenomenological model of the internal elastic response to normal mode fluctuations is developed, which shows that long-ranged hydrodynamic interactions play a central role in the viscoelasticity of the gel network. Dynamic simulations of hard spheres that gel in response to short-ranged depletion attractions are used to test the applicability of the density of states predictions. For particle concentrations up to 30% by volume, the power law decay of the relaxation modulus in simulations accounting for long-ranged hydrodynamic interactions agrees with predictions generated by the density of states of the corresponding harmonic networks as well as experimental measurements. For higher volume fractions, excluded volume interactions dominate the stress response, and the prediction from the harmonic network density of states fails. Analogous to the Zimm model in polymer physics, our results indicate that long-ranged hydrodynamic interactions play a crucial role in determining the microscopic dynamics and macroscopic properties of weak colloidal gels.

DOI: 10.1103/PhysRevE.97.012608

1. INTRODUCTION

Normal mode analysis provides a framework for understanding linear excitations of complex systems. The normal modes are those degrees of freedom which, for small perturbations away from equilibrium, do not interact with each other. Each mode oscillates or relaxes independently of the others with its own characteristic frequency or relaxation rate. The distribution of normal mode frequencies or rates, known as the density of states (DOS), is central in the investigation of condensed matter, because it allows one to calculate the specific heat, thermal conductivity, and other thermal and mechanical properties [1]. Normal mode analysis is also a basis for predicting liquid-state dynamics [2], biomolecular relaxation [3], the jamming transition of granular materials [4], and the phonon density of colloidal crystals and glasses [5,6].

Developed frameworks aim to connect the spectrum of relaxation rates in a soft material to its macroscopic rheological properties [7,8]. For example, the normal modes of soft materials and their associated DOS may be directly related to their linear viscoelastic response [9]. While significant effort has been devoted to the investigation of the DOS of dense glasses and other disordered colloidal solids [10,11], much less is known for the case of colloidal gels [12]. The rheological and structural properties of these gels make them highly desirable for numerous and diverse applications ranging from thermal insulators, LEDs, catalytic electrodes in fuel cells [13,14], and drug delivery implants [15] to common dairy products and cosmetics [16]. Colloidal gels form as a result of kinetic arrest of attractive colloidal dispersions. While the kinetic pathway is dependent on the volume fraction and strength and range of interaction [17], these state parameters are not sufficient to fully characterize the final nonequilibrium state and its properties. Because control of aggregation of gels is critical to many applications, there is a drive for developing computational models with better predictive capabilities.

Recent work has used simulations of microstructural dynamics and relaxation to predict mechanical properties of gels [18–22]. Such work neglects the role of hydrodynamic coupling of the suspended particles. While for atomic systems the phonon dispersion curve is entirely determined by particle mass and interparticle potentials, due to the relevant length scales in colloidal systems, dissipative interactions mediated by the suspending fluid must be considered [23,24]. Many-bodied hydrodynamic interactions are long-ranged and are therefore usually neglected in large systems. However, recent work has shown that neglecting long-ranged dissipative coupling in discrete element modeling of gelling systems leads to predictions of structure and dynamics that are at
odds with experimental observations [25,26]. Because the modes of relaxation are modulated by the hydrodynamic interactions between particles, the fluid mechanics within a gel must be central to its linear viscoelastic response when deformed macroscopically. Several experiments [5,27] have found that models neglecting hydrodynamic coupling fail to reproduce measured dynamics and friction coefficients. To date, no computational model has been used to investigate the role of hydrodynamic interactions in the mechanical response of arrested colloidal gels, and there is thus a need for a hydrodynamic theory to explain the observed relaxation modes [23,28]. Notably, Hurd et al. [29] developed a systematic transport theory for normal modes in a harmonic lattice of colloidal particles immersed in a viscous medium and obtained predictions of the relaxation spectrum for dilute colloidal crystals. For amorphous, space-spanning configurations, such as colloidal gels, no analytical models have been constructed.

In this work we report for the first time how hydrodynamic forces in gels built from colloidal spheres affect the normal modes of relaxation and thus their macroscopic mechanical properties. We compute and compare the normal mode structure and density of states for relaxation rates in colloidal gels of varying concentration using several different approximations of the hydrodynamic interactions among the colloids. We present a clear case for long-ranged hydrodynamic interactions playing an essential role in the macroscopic stress relaxation of colloidal gels. In the models developed for the normal modes, the gels are treated as networks of hydrodynamically interacting elements connected via Hookean springs. Thus, the normal modes computed are derived solely from fluctuations and relaxation of this harmonic network structure. The analysis neglects the contribution of excluded volume interactions between the elements to the relaxation process, which are expected to be relevant in highly localized normal modes and at high volume fractions. Also neglected are the breakage and formation of bonds in the network, which contribute to long-time aging and restructuring as well as relaxation of tensioned network elements [30]. We test the validity of the harmonic network approximation by comparing the computed relaxation spectrum with stress relaxation in dynamic simulations of step shear strain in the same gels.

This article is organized as follows: In Sec. II we first present the normal mode analysis of the overdamped momentum balance on colloidal scale particles and investigate the role of both lubrication and long-ranged hydrodynamic interactions, including higher hydrodynamic moments, in the relaxation of gelled structures. Section III examines the role of hydrodynamic interactions in setting the characteristic length scale dependence of the normal modes and presents a dispersion relation for colloidal networks. In Sec. IV we demonstrate agreement between the asymptotic scaling of the predicted relaxation modulus with that obtained from dynamic simulations and experiments following a step strain at low and moderate concentrations for particles interacting via more realistic hard sphere and depletion potentials. We end with remarks on the consequences of our findings for developing accurate computational tools capable of predicting the mechanical properties of amorphous materials.

II. NORMAL MODE ANALYSIS

We have recently developed methods for rapid calculation of hydrodynamic interactions in suspensions of monodisperse spheres with controlled accuracy for system sizes up to $10^6$ particles [25,31,32]. Using these methods, we generate representative gel configurations by conducting Brownian dynamics simulations with hydrodynamic interactions for $N = 10^2–10^4$ spherical particles of radius $a$ with thermal energy $k_B T$ in a solvent of viscosity $\eta$ for up to $10^4$ bare diffusion times: $\tau_D = 6\pi \eta a^3 / k_B T$. A short-range attraction between the particles, mimicking the polymer induced depletion attraction in experimental systems [33–35], given by the Asakura-Oosawa form, is used to drive aggregation [36]. The range of the attractive interaction is set to $0.1a$, and its strength, proportional to the polymer concentration, is $-10k_B T$ at contact. The Heyes-Melrose potential-free algorithm ensures hard-sphere repulsion at contact [37]. For each of the three volume fractions studied, $\phi = 15\%, 30\%$, and $45\%$, we generate five independent configurations [25]. At the end of each simulation the sample is gelled, with all particles belonging to a percolating cluster. The static structure factor and representative snapshots of the particle configurations are shown in Fig. 1.

We use particle positions from the terminal states of these simulations to determine the distribution of microscopic relaxation rates and the spatial structure of the normal modes as follows. Evolution of the particle positions, $\mathbf{x}(t) \in \mathbb{R}^{3N}$, is dictated by the overdamped momentum balance: $\ddot{\mathbf{x}} = -\mathbf{M}(\mathbf{U} - \mathbf{F}_B)$, where $\mathbf{M} \in \mathbb{R}^{3N \times 3N}$ is the hydrodynamic mobility tensor, $\mathbf{U}$ is the interparticle potential, and $\mathbf{F}_B$ is the Brownian force satisfying the fluctuation-dissipation theorem [38]. The kinetically arrested gel state is close to mechanical equilibrium, and the interparticle interactions in this state
can be approximated as nearly harmonic. Denoting particle fluctuations about the arrested state, \( x_{\text{eq}} \), as \( \delta (t) = x(t) - x_{\text{eq}} \), the time evolution of an average fluctuation is to leading order: 
\[
\delta = -\left( k/(6\pi \eta a) \right) \hat{M} \hat{R} \delta.
\]
The tensor \( \hat{M} \) is the hydrodynamic mobility in the \( x_{\text{eq}} \) configuration scaled on the Stokes drag of an individual particle, \( 6\pi \eta a \). The quantity \( \hat{H} \) is the Hessian of \( U \) in the \( x_{\text{eq}} \) configuration scaled on the characteristic bond stiffness, \( k \). This harmonic network model represents the gel as a network of springs connecting bonded particles in the configuration \( x_{\text{eq}} \).

The perturbation may be decomposed into normal modes, \( v_i \), \( i = 1, 2, \ldots, N \), with respective scalar weights \( C_i \), for which 
\[
\delta(t) = \sum_{i=1}^{3N} C_i v_i e^{-\lambda_i t}.
\]

Equation (1) describes the displacements of every particle in a normal mode, denoted \( v_i \), and the corresponding relaxation rate, \( \lambda_i \), of that same mode. The relaxation rates of the normal modes are made dimensionless on the relaxation rate of a single particle pulled by a harmonic spring, \( \lambda_0 = k/(6\pi \eta a) \). The quantity, \( \hat{R} = \hat{M}^{-1} \), is called the hydrodynamic resistance tensor, which is simply the inverse of the hydrodynamic mobility and maps the velocities of the suspended particles onto the set hydrodynamic forces resisting that motion.

These eigenvectors form a complete set of independent relaxation modes with structure given by particles in the positions \( x_{\text{eq}} \) and interparticle interactions modeled as Hookean springs of stiffness \( k \). The hydrodynamic resistance, \( \hat{R} \), and the Hessian of the interactions, \( \hat{H} \), are the linear operators on which this generalized eigenvalue problem is posed. In the analysis of glassy and crystalline colloidal packings, many researchers have performed an analogous decomposition with harmonic springs between contacting particles [11, 12, 39], but with the additional approximation, \( \hat{R} \rightarrow \hat{I} \), and the identity, \( \lambda_i = \omega_i^2 \). Here \( \hat{I} \) is the identity tensor and \( \omega_i \) is thought of as a characteristic frequency of normal mode vibration in a mass-spring network having the same Hessian, \( \hat{H} \). The normal modes computed in this approximation are referred to as the normal modes of a “shadow” system behaving like an underdamped oscillator [40]. There are appealing analogies to molecular and atomic dynamics model, which accurately represents both classes of hydrodynamic interaction but has only been used to simulate up to \( O(10^4) \) particles; the Rotne-Prager-Yamakawa model, which accounts for only long-ranged far-field hydrodynamic interactions but can be extended to simulate up to \( O(10^6) \) particles; and the freely draining model, in which all hydrodynamic interactions are neglected and the particles interact as in the shadow system.

### A. The role of hydrodynamic lubrication

The resistance tensor, \( \hat{R} \), can be approximated quite accurately and efficiently for any particle configuration using the accelerated Stokesian dynamics (ASD) method [43, 44]. ASD has been used to compute transport properties in suspensions of hard spheres with volume fractions up to random close packing and produces reasonable agreement with experimental measurements [45]. In this framework, \( \hat{R} \) is a superposition of a far-field contribution due to long-ranged hydrodynamic interactions evaluated from a multipole expansion and a near-field component accounting for pairwise lubrication forces: 
\[
\hat{R} = \hat{R}_{\text{FF}} + \hat{R}_{\text{NF}}.
\]

The near-field component is dominated by squeezing flows between pairs of nearly touching particles generated by motion along their line of centers. As a consequence, the block of \( \hat{R}_{\text{NF}} \) corresponding to interactions between bonded particles \( i \) and \( j \) is approximately proportional to the dyad \( r_{ij} r_{ij} \), where \( r_{ij} \) points between the centers of \( i \) and \( j \). For centrosymmetric interparticle interactions \( U \) the block of the Hessian of \( U \) corresponding to bonded particles \( i \) and \( j \) is proportional to the same dyad.

Therefore, we postulate that for all particles in the gel, \( \hat{R}_{\text{NF}} \) is approximately congruent to the Hessian of the interaction potential [41]. If this postulate holds, we can make the following simplifying assumption: 
\[
\hat{R}_{\text{NF}} \approx \alpha \hat{H},
\]

such that 
\[
\hat{R} = \hat{R}_{\text{FF}} + \alpha \hat{H}.
\]
The parameter \( \alpha \) can be understood as the relaxation time for a spring connecting nearly touching particles, whose relaxation is modulated by the squeeze flow between the particles. The hydrodynamic drag in that scenario scales as the inverse of \( \xi \), where \( \xi = r_{eq} - 2a \) is the equilibrium separation between neighboring particle surfaces. When the time scale \( \alpha \) is made dimensionless on \( 6\pi \eta a k / \), it can be written in the simple form: 
\[
\alpha = a / \xi.
\]

Particles that are closer together relax more slowly in response to the spring due to the squeeze flow between their surfaces.

Substituting the postulated form, \( \hat{R} = \hat{R}_{\text{FF}} + \alpha \hat{H} \), into (1) yields a new eigenvalue problem: 
\[
\lambda_{\text{FF}} \hat{R}_{\text{FF}} v_i = \hat{H} v_i,
\]

where \( \lambda_{\text{FF}} \) is the relaxation rate for a spring connecting nearly touching particles, and \( \hat{H} \) is the Hessian of the interaction potential.
having the same eigenvectors as (1) and new eigenvalues that are related to the eigenvalues of (1) by

$$\lambda_i = \frac{\lambda_{FF,i}}{1 + \alpha \lambda_{FF,i}}. \quad (3)$$

Equation (2) is a generalized eigenvalue problem whose solution are normal modes for a harmonic network with an approximation of the hydrodynamic resistance given by \( \hat{R} = \hat{R}_{FF} \). That is, (2) describes the normal modes when only far-field hydrodynamic coupling among the particles is considered. Therefore, if the postulated congruence of the near-field hydrodynamic interactions and the Hessian holds, the effect of hydrodynamic lubrication is simply to reduce the relaxation rates of the true normal modes, \( \lambda_i \), relative to \( \lambda_{FF,i} \). Additionally, hydrodynamic lubrication does not change the spatial structure of the modes, as the same \( \mathbf{v}_i \) appear in both (1) and (2). The characteristic time scale \( \alpha \) relates the relaxation spectrum of models for \( \hat{R} \) neglecting hydrodynamic lubrication, \( \hat{R} \approx \hat{R}_{FF} \), to those including it, \( \hat{R} = \hat{R}_{FF} + \hat{R}_{NF} \).

To determine if the normal modes from Eqs. (1) and (2) are in fact related as postulated, we compare the normal modes from different hydrodynamic models. We use gels formed from 500 particles and compute \( \hat{R} \) using ASD and \( \hat{R}_{FF} \) using the inverse of the Rotne-Prager-Yamakawa (RPY) mobility tensor, which treats the particles as renormalized Stokeslets. The RPY tensor is the leading order far-field contribution to a multipole expansion describing the hydrodynamic flows generated by spherical particles [46]. First, the normal modes of (2), the eigenpairs \( \{\lambda_{FF,i}, \mathbf{v}_{FF,i}\} \), are calculated. Then the value \( \alpha_i \) that best satisfies (1) using the eigenpair \( \{\lambda_{FF,i}/(1 + \alpha_i \lambda_{FF,i}), \mathbf{v}_{FF,i}\} \) is determined by minimizing the objective function:

$$f(\alpha_i) = \left\| \frac{\lambda_{FF,i}}{1 + \alpha_i \lambda_{FF,i}} \hat{R} \mathbf{v}_{FF,i} - \hat{H} \mathbf{v}_{FF,i} \right\|_2. \quad (4)$$

\( f(\alpha_i) \) is the norm of the difference between the left- and right-hand sides of (1) after substituting \( \lambda_i = \lambda_{FF,i}/(1 + \alpha_i \lambda_{FF,i}) \) and \( \mathbf{v}_i = \mathbf{v}_{FF,i} \). When the objective function is normalized, a normal mode is considered normalized, the far-field part, \( \mathbf{v}_{FF,i} \), with associated relaxation rate \( \lambda_{FF,i}/(1 + \alpha_i \lambda_{FF,i}) \), best represents a normal mode of the full hydrodynamic problem. For each normal mode, a different value of \( \alpha_i \) might minimize \( f(\alpha_i) \). The postulate formed by replacing \( \hat{R}_{NF} \) with \( \alpha \hat{H} \) asserted that a single time constant \( \alpha \) could be used to remap all the eigenvalues between problems. For consistency with the postulate, we expect to find nearly constant optimal values for \( \alpha_i \) across different modes.

We plot the optimal value of \( \alpha_i \) as a function of \( \lambda_{FF,i} \) in Fig. 2 and depict \( f(\alpha_i)/||\hat{H} \mathbf{v}_{FF,i}||_2 \), which is a measure of the normalized error of this approximation for each mode. The optimal value of \( \alpha_i \) is nearly independent of \( \lambda_{FF,i} \) at a fixed volume fraction. That is, for a given particle volume fraction, the same constant \( \alpha = \alpha \) can be employed to make nearly any normal mode of the far-field problem consistent with the full hydrodynamic one. As \( \phi \) increases, so does \( \alpha \), which may be interpreted as the effective equilibrium separation between particles, \( \xi \), decreasing slightly at higher volume fractions. Direct computation of the average surface to surface separation between bonded particles yields values matching with \( a/\alpha \) at each volume fraction as would be expected. The time constant \( \alpha \) inferred this way represents a sort of speed limit on the relaxation processes within the gels. From (3), when \( \lambda_{FF,i} \gg \alpha^{-1} \), we find \( \lambda_i \approx \alpha^{-1} \), such that no modes of the full hydrodynamic problem relax faster than the rate \( \alpha^{-1} \).

These results suggest that for virtually all the modes computed the approximation \( \hat{R}_{NF} = \alpha \hat{H} \) holds. A normal mode analysis employing the RPY model enables prediction of the normal modes of the full hydrodynamic problem. This can be understood by recognizing that slowly relaxing normal modes involve collective motion of the particle network and are unaffected by the localized squeezing flows accounted for in the near-field part of the hydrodynamic resistance tensor. The far-field model alone is able to capture the structure and relaxation rate of the slow modes quite accurately. The normalized error in approximating a full hydrodynamic normal mode with a far-field mode is smaller than 5% for modes with dimensionless relaxation rates, \( \lambda_{FF,i} \), smaller than 1. Larger normalized errors are found for modes with \( \lambda_{FF,i} > 1 \). As we will show, these fast modes involve localized rather than collective motion for which we might expect the details of the near contact hydrodynamic interactions to play a significant role. As a consequence, the eigenvectors in this part of the relaxation spectrum computed using the ASD and RPY models are expected to differ.

To examine the effect of system size on our approximation we compute \( \hat{R} \) and \( \hat{R}_{FF} \) for \( N = 100, 250, 500, \) and 5000 at a fixed volume fraction \( \phi = 15\% \) and determine \( \alpha \) and the corresponding approximation error, as shown in Fig. 3. Both the proportion of fast modes and the error in \( f(\alpha_i) \) over the spectrum shrink with increasing \( N \). The value of the best fit \( \alpha_i \) appears to grow systematically with the system size, \( N \), but it is important to recognize that the structure of the gel also depends on \( N \). For \( \phi = 0.15 \), the correlation length of the gel formed via arrested phase separation is on the order of 10 particle radii (see Fig. 1). Consequently, for the smallest system size in Fig. 3, the scale of the simulation box is on the order of the correlation length of the gel. Thus the gel structure and the nearest neighbor separation are changing with \( N \) and would not be expected to give the same values of \( \alpha_i \) with different \( N \). Instead, Fig. 3 simply indicates that the far-field approximation improves its ability to describe the normal modes of the full hydrodynamic
problem with increasing system size, and that the effects of hydrodynamic lubrication influence only a small fraction of fast relaxation modes. Thus, the proposed renormalization may become exact in the limit $N \to \infty$. The values of $N$ that can be accessed with ASD simulations currently are limited. However, we have shown that the eigenpairs $\{\lambda_{FF,i},v_{FF,i}\}$ represent the relaxation spectrum of the full hydrodynamic problem well. Therefore, we switch now to understanding the collective modes of relaxation utilizing only the RPY mobility as a far-field approximation for the normal modes that can be extended to much larger system sizes.

B. The role of long-ranged hydrodynamic interactions

To understand how long-ranged hydrodynamic coupling affects relaxation in colloidal gels, we make a comparison of normal modes obtained from the freely draining approximation (FD), where $\hat{R} = I$ with those obtained from the RPY tensor using $10^4$ particles. We characterize the distribution of slow modes responsible for macroscopic viscoelasticity via calculation of the relaxational density of states. For both FD and RPY we solve (1) to determine the normal modes of the five different particle configurations for each value of $\phi$. This generates an extensive set of the relaxation rates and eigenvectors associated with the models at different volume fractions. At a $\phi$, the set contains a total of 150,000 relaxation rates and eigenvectors from which we compute the DOS and other representative measures for the relaxation process.

In Fig. 4 we plot the DOS obtained for each volume fraction with the FD and RPY models. The DOS as a function of relaxation rate, $P(\lambda)$, highlights the significant effect of long-ranged hydrodynamic interactions on the normal mode response in weak colloidal gels. For the FD model, we find an overabundance of slow modes. The DOS scales as $\lambda^{-1/2}$, where $\beta \approx -1/2$ for $\phi = 15\%$. In contrast, for the RPY spectrum, the occurrence of slow and fast relaxation modes is equally probable, and $\beta = 0$ for all $\phi$. Long-ranged hydrodynamic interactions through the suspending medium enhance collective large-scale relaxation dynamics, and consequently the fraction of fast modes increases relative to slow modes when compared to the FD approximation. With increasing $\phi$, differences between the two hydrodynamic models diminish, and $\beta$ approaches zero as the fraction of slow modes decreases for the FD model. These different DOS are analogous to observations from polymer physics. A dilute solution of ideal polymer chains obeying the Zimm model, which treats the hydrodynamic interactions in the same way as the RPY model, has $P(\lambda) \sim \lambda^{-1/3}$. In contrast, when hydrodynamic coupling is neglected as in the Rouse model (FD), $P(\lambda) \sim \lambda^{-1/2}$ [38]. Long-ranged hydrodynamic interactions tend to flatten the distribution of relaxation rates as collective motion through fluid mechanical coupling accelerates stress relaxation in soft materials.

It is important to note that there is no way of knowing in advance how the distribution of relaxation rates should scale without performing a normal mode analysis. In the case of dilute polymer solutions, exact solution of the normal modes in the Zimm model is not possible and a preaveraging approximation is applied to the Oseen tensor to yield the analytical result $P(\lambda) \sim \lambda^{-1/3}$. This approximation has been tested via direct calculation of the normal modes and confirmed by experiment [38]. In much that same spirit, we have used a normal mode analysis of colloidal gels for increasing particle concentrations in the harmonic network limit to understand the role of different hydrodynamic interactions in determining the distribution of relaxation rates. We find distinct roles for lubrication and long-ranged hydrodynamic interactions and significant departures from the freely draining approximation with this direct numerical simulation of the relaxation spectrum for the harmonic network model. Neglected from this analysis are relaxation modes due to excluded volume interactions and the breakage and reformation of colloidal bonds. Both may play an additional role in the relaxation spectrum, and comparison of experiments with this baseline calculation should be used to validate the calculation.

The DOS computed from (1) is intimately related to stress relaxation in the gels. To confirm that the solutions to (1) were computed accurately, we perform dynamic simulations of the stress relaxation in colloidal gels following a step-strain deformation. The interactions among the particles in the gel configurations are modeled precisely as in the harmonic network model. Each pair of bonded colloids is connected with
a permanent Hookean spring having rest length $2a$, and non-bonded particles interact only hydrodynamically. The gels are subjected to a step shear strain of $1\%$ during which all particles undergo affine motion. Then the particles are allowed to relax back to equilibrium. The virial contribution to shear stress is subjected to a step shear strain of $1\%$ during which all particles undergo affine motion. Then the particles are allowed to relax back to equilibrium. The virial contribution to shear stress is

To characterize the structure of the normal modes we compute the collectivity index $[3]$,

$$
\kappa_i = \frac{1}{N} \exp \left[ - \sum_{j=1}^{N} \mu_i \left| v_j^{(i)} \right|^2 \log \left( \mu_i \left| v_j^{(i)} \right|^2 \right) \right],
$$

where $\mu_i$ is the normalization constant, $\mu_i = \sum_j \left| v_j^{(i)} \right|^2$, and $v_j^{(i)}$ is a vector assigned to particle $j$ reflecting its contribution to the normal mode $i$. The collectivity index measures the extent to which particles participate in each mode. A mode that excites a larger number of particles in the gel has a higher collectivity index. With increasing volume fraction the degree of participation increases due to increased rigidity of the gel. In Fig. 6 we plot the likelihood of observing a mode with collectivity index $\kappa_i$ for all gels and both hydrodynamic models under study.

We find that the normal modes are more likely to have higher collectivity in the RPY model. Long-ranged hydrodynamic interactions lead to coupling and excitation of a larger fraction of the particles. As the volume fraction increases, differences between the two hydrodynamic models diminish. For $\phi = 0.45$, crowding leads to hydrodynamic screening, and $P(\kappa_i)$ is similar for both the FD and RPY models. The small $\kappa_i$ tail of the distributions corresponds to fast modes, $\lambda > 1$, for which relaxation is faster than the bare particle rate $\lambda_0$, and the normal modes are localized to only a few particles. The probability density of $\kappa_i$ is similar for both models in these tail regions.

In using the RPY approximation for long-ranged hydrodynamic interactions, higher order moments in the hydrodynamic scattering series were neglected [41]. However, the hydrodynamic torque, stresslet, or higher order traction moments in the colloidal gel also may also affect the relaxation dynamics. The algorithm used to rapidly compute RPY interactions also allows for explicit accounting of higher order multipoles of the hydrodynamic traction on the particle surfaces [32]. Figure 7 compares the density of states obtained from the RPY model with a hydrodynamic model that accounts for next higher order multipoles: the torque and stresslet, which is denoted the Force-Torque-Stresslet (FTS) model. Here, the mobility used in the normal mode analysis is $\hat{M} = \hat{M}_{UF} \sim \hat{M}_{US} \hat{M}_{ES} \hat{M}_{EF}$, where the individual mobilities are blocks of the grand hydrodynamic mobility matrix and linearly couple force to velocity (UF), stresslet to velocity (US), stresslet to strain (ES), and force to strain (EF) on particles, respectively [43]. The DOS at each $\phi$ matches very well those computed via the RPY model, indicating that the relaxation rate and collective dynamics of the gel are largely unaffected by higher order moments of the traction.

III. DISPERSION RELATION FOR RELAXATION MODES

We compute the correlation length of each normal mode through a quantity used in the analysis of flow structures in

$\phi$  FD  RPY

15%  $\bullet$  $\circ$

30%  $\Delta$  $\triangle$

45%  $\square$  $\blacksquare$

$P(\kappa)$

0  0.3  0.4  0.5  0.6  0.7

FIG. 6. The probability density for the collectivity index of all gels, modes, and both models under study shows that the normal modes are more likely to have a higher participation in the RPY model.

FIG. 5. The relaxation modulus $G(t)$ of the gels modeled as a permanent network of particles connected with Hookean springs in response to a step strain of $1\%$ using the FD and RPY hydrodynamic models agrees with the computed DOS. Measurements were averaged over 100 realizations for each data set to reduce thermal noise.
The results indicate that the collective relaxation dynamics are not qualitatively affected by the higher moments of the force density. In turbulent flow, the Karhunen-Loève decomposition [47]:

$$S_{\nu}(q) = \lambda_i \mu_i \sum_{j,k=1}^{N} v^{(j)} \cdot v^{(k)} \exp[i q \cdot (x^{(k)}_{eq} - x^{(j)}_{eq})],$$

with $x^{(j)}_{eq}$ the position of particle $j$ in the $x_{eq}$ configuration. For a normal mode $i$, the set of $v^{(j)}$ forms a field:

$$v_i(x) = \sum_{j} v^{(j)}(x - x^{(j)}_{eq}).$$

The Karhunen-Loève decomposition is proportional to the Fourier transformation of the autocorrelation of that vector field:

$$\tilde{v}_i(q) = \mathcal{F}[v_i(x)] = \sum_{j} v^{(j)} \exp(i q \cdot x^{(j)}),$$

such that $S_{\nu}(q) \sim \tilde{v}_i(q) \cdot \tilde{v}_i(-q)$. $S_{\nu}(q)$ is analogous to the static structure factor of the gel and characterizes spatial organization of a normal mode, $i$. However, unlike the static structure factor the correlation is weighted by the amount that each particle participates collectively in the normal mode through the dot product $v^{(j)} \cdot v^{(k)}$. A peak in $S_{\nu}(q)$ reflects the spatial correlation length of the normal mode just as a peak in the static structure factor reflects the spatial correlation length of the underlying gel structure. The association between the correlation length of normal modes and their relaxation rate forms a dispersion relation for the gel that describes how the correlation length of normal modes and their relaxation length of the underlying gel structure. The association between the spatial correlation length of the normal mode just as a continuous, multivariate distribution $P(\lambda, q)$, extending the density of states $P(\lambda)$. A scatter plot (not shown) of the sampled relaxation rates and wave vectors indicates that the dispersion relation follows a power law. To quantify the dispersion relation in an ensemble averaged sense, we construct a sample mean of $S_{\nu}(q)$ over sets of modes having relaxation rates $\lambda_i$ that fall within finite logarithmically spaced, finite width bins. The set of computed normal modes possesses enough samples that all the bins contain at least 10 modes. For the modes within a bin of width $\Delta \lambda$, an average

$$S_{\nu}(q) = \sum_{i \in S} S_{\nu}(q) \sum_{i \in S} 1$$

with $S = \{i : |\lambda_i - \lambda| \leq \Delta \lambda\}$ is computed. The peak in $S_{\nu}(q)$ for each bin as well as the peaks associated with each individual sample within that bin are identified. The average relaxation rate in a bin, $\lambda$, and the peak wave vector of the corresponding $S_{\nu}(q)$, denoted $q$, are the pair of coordinates describing the dispersion relations of the gels.

Figure 8 plots $\lambda$ as a function of $q$ for all the gels using both the FD and RPY approximations. We observe a power law trend, $\lambda \sim q^{\gamma}$, that depends qualitatively on the hydrodynamic model. For the RPY model, $\gamma \approx 2$. The scaling of relaxation rate with spatial correlation length is independent of $\phi$, much the same as with the density of states. In contrast, the FD modes exhibit significant dependence on volume fraction. For $\phi = 0.15$, we find $\gamma \approx 3$, while at higher volume fractions, $\gamma$ decreases. The dispersion relation for the FD model approaches that of the RPY model. These results indicate that normal modes correlated over a length scale, $l \sim q^{-1}$, always relax faster in the RPY model than in the FD model. The effect of the suspending solvent on a normal mode structure of these amorphous colloidal systems is substantial and suggests that fluctuations are excited across larger length scales because of the long-ranged hydrodynamic interactions among the particles.

Care must be taken to ensure that the peak wave vector determined from the ensemble average is representative of the underlying samples. The variation of the sampled wave vectors about the ensemble averaged value is characterized by computing $\epsilon_i = (q_i - q)/q$ for each of the modes. This is
The relative variation in the peak wave vector of each of the modes with respect to the value determined from the ensemble average. Figure 9 plots \( \epsilon_i \) as a function of the peak wave vector, \( q \), for 1000 samples at each volume fraction as well as a histogram of these normalized residuals. The residuals are normally distributed about the ensemble-averaged value suggesting that the underlying distribution of the sampled \( \lambda_i \) and \( q_i \) can be modeled as

\[
P(\lambda, q) \sim \exp\left\{-\frac{(q/q_\text{model}(\lambda) - 1)^2}{\sigma^2}\right\} P(\lambda),
\]

with \( q_\text{model}(\lambda) = c \lambda^{1/\nu} \) reflecting the inferred dispersion relation.

The relaxation rate can be thought of as the ratio of an effective elastic bond strength, \( k(l) \), and an effective viscous drag coefficient, \( \zeta(l) \), such that \( \lambda \sim k(l)/\zeta(l) \) [20]. The dispersion relation arises due to the variations with respect to \( l \) of the elasticity and drag coefficient characteristic of the relaxation of a normal mode having correlation length \( l \). The elastic response of a domain of size \( l \) is characterized by a spring constant \( k(l) \sim l^{-\nu} \), which is size dependent due to the tenuous nature of the bonds within the domain. With increasing \( l \), a smaller fraction of bonds connect the domain to the rest of the gel, which leads to softening and a decrease in \( k(l) \). \( \zeta \) is the elasticity exponent and is sensitive to the nature of the bonds and the resulting stiffness of the gel backbone [48]. In our study we consider only central forces between the particles, which leads to no bending rigidity and an exponent \( \zeta < 3 \) that will depend solely on the backbone structure at given \( \phi \) [49,50]. The viscous drag \( \zeta(l) \) experienced by the domain will depend on the hydrodynamic model chosen. We therefore expect differences between the dispersion relations for the two models. For the FD model, the drag on a domain of size \( l \) relaxing in a viscous

medium scales as \( l^{d_f} \), so that \( \lambda_{FD} \sim l^{-(d_f+\zeta)} \), where \( d_f \) is the fractal or Minkowski-Bouligand dimension of the gel [51]. For the RPY model, the drag is linear in \( l \) such that \( \lambda_{RPY} \sim l^{-1+\zeta} \). We cannot know the elasticity exponent of the gels a priori, however, from the observed dispersion relation of the RPY spectrum, \( \lambda \sim l^{-2} \), we conclude that the elasticity exponent \( \zeta \) of the gel \( \phi = 0.15 \) gels under study is approximately one. Employing the box-counting method we determine that \( d_f \) of the gels at \( \phi = 0.15 \) is 2.1, so that \( d_f + \zeta \approx 3.1 \) and yields the observed scaling exponent for the FD dispersion relation. Therefore, the observed dispersion relations of the FD and RPY models for 15% particles by volume are consistent with an elasticity exponent, \( \zeta \approx 1 \).

As \( \phi \) increases, hydrodynamic screening makes the effective drag coefficients for the two models similar, and the drag coefficient on the domains scales as roughly \( l^2 \). Additionally, the fraction of isostatic particles, those with six or more bonded neighbors, increases to more than 92% for \( \phi = 0.45 \). Consequently, the elasticity exponent, \( \zeta \), approaches zero because the number of dangling chains in the gel, which lead to softening over larger length scales, is greatly diminished in the rigidified microstructure. Therefore, the dispersion relations for both models at the highest volume fraction are similar: \( \lambda \sim l^{-2} \). Unexpectedly, while both the elasticity exponent and the drag coefficient for the normal modes are expected to change with volume fraction, the power law scaling of the dispersion relation for the RPY model remains the same regardless of particle packing fraction. We cannot yet explain how \( k(l) \) and \( \zeta(l) \) change independently with volume fraction in the RPY model, yet they produce virtually the same dispersion relation at each concentration studied.

IV. IMPLICATIONS FOR THE RHEOLOGY OF WEAK COLLOIDAL GELS

We have detailed the influence of hydrodynamic coupling on the relaxation dynamics of a colloidal gel in the linear response limit via normal mode analysis. However, these calculations rely on a key approximation: the conservative interparticle forces are treated as simple Hookean springs. This approximation enabled analytical progress but is not necessarily consistent with real colloidal interactions. Here we compare data from dynamic simulations employing hard-sphere and depletion interactions [26] and experimental results in which the same interaction potential has been measured [52].

Recall that the relaxation modulus is proportional to the Laplace transform of the DOS. Step strain simulations with the Hookean spring approximation were already used to validate the DOS calculations. However, the conclusions drawn from the computed DOS may not translate to stress relaxation in materials without idealized interaction potentials. In the harmonic network, nonbonded particles do not interact directly following a step strain. However, nonbonded hard spheres in a depletion gel will produce additional excluded volume interactions not reflected in the harmonic network. At the very least, the DOS and analysis of the structure of the normal modes suggest that the relaxation modulus at long times should decay significantly faster in simulations employing the RPY model when compared to simulations
using the FD model. In Fig. 10 we plot the previously published step-strain response for an experimentally studied depletion gel [52] and the calculated relaxation modulus, $G(t)$, from dynamic simulations using both the FD and RPY models. The simulated gels are built from hard spheres interacting with a $-10k_BT$ depletion attraction of range 0.1$a$, which is the same interaction potential used to generate the gel structures used in the normal mode analysis.

At short times, the stress decay in the simulations reflects fast relaxation modes due to hard core repulsion of the particles [25,37]. These decay modes are absent in the DOS computed from the harmonic network approximation. For longer lag times, these interactions influence stress relaxation and there are clear differences between the hydrodynamic models employed. For $\phi = 0.15$, the FD model gives $G(t)$ with a power-law scaling $t^{-1/2}$, while the RPY model exhibits significantly faster relaxation, as $t^{-1}$. For both hydrodynamic models, $G(t)$ displays the asymptotic scaling predicted by (5) using the DOS of the harmonic networks. Additionally, the scaling of the RPY model at long times is in excellent agreement with the measured relaxation modulus in the experiment, demonstrating that long-ranged hydrodynamic interactions play an essential role in macroscopic stress relaxation of gels. At short lag times, however, simulation and experimental results diverge. This is expected because the step-strain simulations neglect hydrodynamic lubrication, which alters the relaxation of localized, fast modes.

For $\phi = 0.30$, the stress relaxation of the RPY model at long times appears to match the predictions of the DOS analysis. However, the FD model does not exhibit the faster stress relaxation anticipated from the DOS. For $\phi = 0.45$, both the FD and RPY models deviate from the DOS predictions at long times. These persistent differences may stem from the relaxation of deformed local packings via the hard core excluded volume interactions. We find that at high volume fractions, these entropic interactions are the biggest part of the virial contribution to the shear stress. Yet the interactions are not reflected directly in the DOS computed via the harmonic network model. It makes some sense that the performance of the harmonic network model would become worse with increasing particle volume fraction since excluded volume interactions are explicitly neglected. We had expected that at long times the predictions of stress relaxation from the DOS would ultimately emerge. However, we are currently unable to carry out longer lag time simulations and still compute an ensemble average of the shear stress accurately in simulations with $O(10^4)$ particles. Resolving this discrepancy in the decay of $G(t)$ at high volume fractions and long lag times is left for future work.

At low volume fractions, where caging is not a dominant physical mode, the DOS computed from the harmonic network approximation with the RPY hydrodynamic model accurately describes stress relaxation in a gel built from hard spheres and driven to aggregate by a depletion attraction. At high volume fractions, the harmonic network approximation fails. However, softer repulsive interactions between nearly touching colloids will result in an interparticle potential whose mechanical equilibrium is better represented by a Hookean spring. Such interactions are easily engineered through use of polymer brush layers or surfactants attached to the surface of suspended particles to act as steric stabilization against van der Waals attractions or particle sintering. The DOS derived from the harmonic network approximation may yield even better predictions of the rheology of such materials.

V. CONCLUSION

We have computed the normal modes of weak colloidal gels with different approximations for the hydrodynamic interactions between the constituent particles. Our results show that the dynamics of a gel are a sensitive function of the hydrodynamic model. Long-ranged hydrodynamic interactions enhance the rate of stress relaxation in a strained gel and play a crucial role in determining the macroscopic properties of weak colloidal gels. Hydrodynamic lubrication merely modulates fast, localized relaxation modes. With increasing volume fraction, hydrodynamic screening occurs, the majority of particles are multiply bonded, and the gel dynamics are less sensitive to the hydrodynamic model. We have confirmed the normal mode predictions at low and moderate particle concentrations by performing stress relaxation simulations of the same gels. We also successfully compared our results to experimental observations without the harmonic network approximation. A computational model neglecting hydrodynamic interactions will yield erroneous estimates of $G(t)$ or the complex modulus.
among other related viscoelastic and mechanical properties in this concentration regime. Future work will incorporate noncentral forces between bonded particles, which could affect the modes of relaxation and dynamics of strong gels.

The normal mode analysis conducted here examines the gel at one particular instant in time. Our methodology explicitly computes the relaxation time spectrum for hydrodynamically interacting colloids when supplied solely with a particle configuration and an estimate of the interparticle potential. In the case of athermal systems, such as granular media, foams, and suspensions of large colloidal particles, recent advances in experimental techniques now allow tracking of the real space dynamics of individual particles and reconstruction of overall particle configurations with limited resolution [12,23,40].

Ensembles of these gel structures can be analyzed, and the DOS from each, along with those of nearby points in time, can be merged to yield a complete description of the relaxation spectrum. Such results could be utilized to understand the affect of aging and ripening as well as processing due to flow on both gel structure and viscoelasticity in a robust manner.

ACKNOWLEDGMENTS

The authors acknowledge helpful conversations with Prof. Eric Furst and Jan Vermant, and funding provided by the ACS Petroleum Research Fund (Grant No. 56719-DNI9) and the Institute for Soldier Nanotechnology at MIT.