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Dynamic light scattering from power-law polydisperse fractals: Application of dynamic scaling to humic acid

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We report an investigation of dynamic light scattering (DLS) from humic acid, an organic colloidal fractal system in aqueous solution. The system is found to be power-law-polydisperse in size and the DLS spectra show the arithmetic and harmonic mean relaxation rates to be a fractional power of momentum transfer. This behavior is described by the dynamic scaling theory developed by Martin, Leyvraz, and Ackerson.

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The interest in the fractal morphology of many colloidal materials has stimulated many of the studies on the dynamics of such substances using dynamic light scattering (DLS) [1–4]. In principle, information on the size of a colloid fractal, its growth during an aggregation process, and structural changes in response to changes in solution conditions can be obtained by calculating the autocorrelation function of the temporal fluctuations for the light scattered from these objects [4]. In practice, however, size determination using the DLS can be an imprecise exercise that depends on many aspects of the system under investigation. In particular, it depends on the nature of the colloid's particle-size distribution.

Fractals are geometric representations of strongly disordered structures whose dimension cannot be described by the Euclidian dimensions of 1, 2, or 3 [5]. These noninteger dimensions are referred to as fractal dimensions (D_f). A fundamental tenet of fractal geometry is that the morphology of the material under investigation does not change even if the characterization scale used to examine the substance is varied. In addition, many properties of a fractal material have been observed to be scale-invariant. Fractal clusters produced by a percolation-type aggregation exhibit a polydisperse particle-size distribution that is described by a power law, a functional form that is intrinsically scale-invariant [6].

This power-law polydispersity makes the interpretation of DLS data on the basis of simple particle dynamics difficult. Martin has shown that in solutions of power-law-polydisperse fractal silica aggregates, the relaxation rates scale with the momentum transfer by noninteger exponents, an unusual phenomenon that cannot be explained using rigid-particle models with monodisperse or bell-shaped polydisperse size distributions [1]. Martin and Leyvraz [2] and Martin and Ackerson [7] (MLA) treated the dynamics of power-law-polydisperse rigid fractals (in which the internal structural dynamics of colloidal aggregates can be neglected) scale with the momentum transfer through a power law whose exponents may have noninteger values that are related to D_f and the polydispersity of the particle-size distribution.

Since polydispersity of the scattering objects induces a distribution $A(\Gamma)$ on their relaxation rates Γ, the field autocorrelation function $S(q,t)$ is a result of a continuous relaxation spectrum $S(q,t)=\int_0^\infty A(\Gamma)e^{-\Gamma t}d\Gamma$, with $S(q,0)=\int_0^\infty A(\Gamma)d\Gamma$ being the normalization factor for $A(\Gamma)$. From this an initial relaxation rate Γ_i can be defined as

$$\Gamma_i = -\left.\frac{d\ln S(q,t)}{dt}\right|_{t=0} = \frac{\int_0^\infty A(\Gamma)\Gamma\,d\Gamma}{\int_0^\infty A(\Gamma)d\Gamma} = \langle \Gamma \rangle , \tag{1}$$

which represents the mean relaxation rate under the distribution $A(\Gamma)$ and is referred to as the *arithmetic* mean. Numerically, Γ_i is obtained from the first cumulant in the conventional cumulant analysis. The *harmonic* mean relaxation rate Γ_a, which is defined as

$$\Gamma_a^{-1} = \frac{\int_0^\infty S(q,t)dt}{S(q,0)} = \frac{\int_0^\infty A(\Gamma)\frac{1}{\Gamma}d\Gamma}{\int_0^\infty A(\Gamma)d\Gamma} = \left\langle \frac{1}{\Gamma} \right\rangle , \tag{2}$$

is the inverse of average of $1/\Gamma$. It is obtained directly from the integration of $S(q,t)$.

An essential feature of the dynamic scaling proposed in the MLA theory is that the two relaxation rates satisfy scaling relations

$$\Gamma_i = D_z q^2 f(qR_z) , \tag{3}$$

$$\Gamma_a = D_z q^2 h(qR_z) , \tag{4}$$

with the scaling function $f(x)\sim 1$, $h(x)\sim 1$ for $x \ll 1$ and $f(x)\sim x^{\alpha-2}$, $h(x)\sim x^{\beta-2}$ for $x \gg 1$. Here D_z is the z-averaged diffusion coefficient, and the z-averaged radius R_z is formally defined as $R_z^2 = Z^{-1}\int N(M)M^2R_M^2dM$

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and $Z \equiv \int N(M) M^2 dM$, and α and β can be nonintegers. In these expressions, $N(M)$ is the number distribution of the clusters having molecular weight M, $R_M \sim M^{1/D_f}$ is the radius of gyration of the clusters of molecular weight M, and D_f is the fractal dimension. The power-law polydispersity is seen in the form of $N(M) \sim M^{-\tau}$, where τ is the polydispersity exponent.

Martin presented the first experimental test of the MLA theory using fractal silica aggregates [1]. In this paper we describe an application of the MLA theory to the characterization of a naturally occurring colloid known as humic acid. Humic acid is an extremely heterogeneous mixture of polyelectrolytic organic molecules formed by the profound alteration of organic matter in natural environments [8,9]. Unlike most other substances, the fundamental chemical characteristic of humic acid is not a discrete chemical structure but, instead, an essentially continuous distribution of molecular and structural properties [10]. The molecular weight distribution of humic acid determined by flow field-flow fractionation [11] or size-exclusion chromatography [12] clearly shows a polydisperse size distribution that typically displays an asymptotic, high-mass tail. This description suggests a power-law polydispersity and the likelihood that these materials are fractal. And, in fact, small-angle x-ray scattering (SAXS) measurements have shown a power-law scattering intensity $I(q) \sim q^{\mu}$ [13], confirming a fractal nature of humic acid. And, as we report here, DLS measurements show noninteger power-law exponents in relaxation rates.

The humic acid used in this study was extracted from a peat using a traditional alkaline extraction procedure [14]. The extracted humic acid was then filtered through a 0.22 μm prefilter. To attempt to meet the criterium that $qR_z \gg 1$, as we discuss below, the humic acid was size-fractionated using several ultrafiltrations in series to remove those small aggregates. The fraction retained by the first membrane, which had a molecular weight cutoff of $> 50\,000$ daltons, was used in this study. The sample was diluted with reagent water, and solutions with various neutral electrolyte concentrations (NaCl) were prepared. The pH of the solutions were adjusted with NaOH or HCl and were above the isoelectric point. Dynamic light scattering measurements were performed using an ALV-5000/E 256 channel multi-τ digital correlator (ALV, Germany) operating at $\lambda = 514.5$ nm produced by an argon ion laser.

In the MLA theory, we expect that $\Gamma_i \sim q^{\alpha}$ and $\Gamma_a \sim q^{\beta}$ in the regime $qR_z \gg 1$, where q is the momentum transfer defined as $q = (4\pi n/\lambda)\sin(\theta/2)$ (n is the refractive index of the scattering medium, λ is the incident light wavelength, and θ is the scattering angle). For rigid scatterers the exponents α and β are related to both D_f and τ as follows:

$$\alpha = \begin{cases} 2\,, & \tau < 2 - \dfrac{1}{D_f}\,, \\ 3 - D_f(2-\tau)\,, & 2 - \dfrac{1}{D_f} < \tau < 2\,, \\ 3\,, & 2 < \tau < 3\,, \end{cases} \tag{5a}$$

$$\beta = \begin{cases} 2\,, & \tau < 2\,, \\ 2 + D_f(2-\tau)\,, & 2 < \tau < 2 + \dfrac{1}{D_f}\,, \\ 3\,, & 2 + \dfrac{1}{D_f} < \tau < 3\,. \end{cases} \tag{5b}$$

Figure 1 is a representative log-log plot of the relaxation rates vs q found for various neutral electrolyte concentrations. From the slopes of these curves we obtain values of α and β that are 2.5 and 2.1, respectively. In a rigid fractal system with moderate polydispersity, the relationship $2 - D_f^{-1} < \tau < 2$ will apply, and according to Eq. (5a), α will be a fraction number between 2 and 3 ($2 < \alpha < 3$). The value of α is related to D_f and τ via $\alpha = 3 - D_f(2-\tau)$. Thus, the α value obtained here (≈ 2.5) indicates that the humic acid is only weakly polydisperse ($\tau < 2$). Under this condition ($\tau < 2$), D_f can be directly calculated from the slope of SAXS data (Fig. 2) without making corrections for polydispersity effects [2]. Using the value of D_f ($\cong 2.1$), obtained from the SAXS data, and $\alpha \cong 2.5$, obtained from Fig. 1, we determined $\tau \cong 1.76$ [Eq. (5a)]. We note that without the dynamic measurements reported here from which τ was calculated, the humic acid D_f could not have been determined directly from the static SAXS measurement. For a more polydisperse system, where $2 < \tau < 3$ and $\alpha = 3$, corrections for polydispersity effects in SAXS measurements would have to be made [2].

In addition, the values $\tau < 2$ and $\beta = 2$ would be expected for the relaxations of rigid particles . Realizing that we may have been observing scattering from an internal mode regime under $qR_z \gg 1$ (i.e., the probing scale q^{-1} on which the diffusion is probed is smaller than R_z), we could argue that the fractional value of α may be due to the internal mode effects. However, Martin has demonstrated experimentally that for flexible objects such as polymer coils, α would be equal to β and has an integer

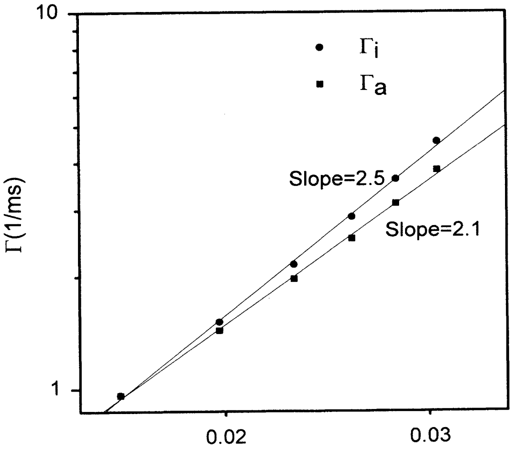

FIG. 1. Representative plot of Γ_i and Γ_a vs q. The sample concentration was 0.5 g/l and electrolyte concentration was 0 M. Light scattering was performed at room temperature.

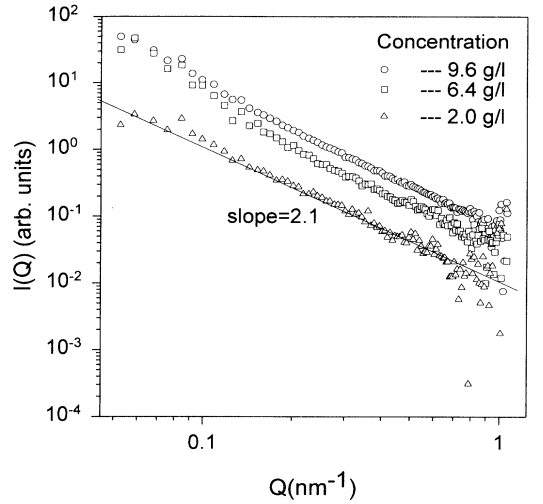

FIG. 2. SAXS characterization of humic acid sample used in this study. Electrolyte concentration was 0 M. $I(Q)$ is the scattering intensity and Q is the scattering vector in SAXS measurement.

value of 3, an exponent typically noted for the internal modes of linear polymer chains [1,3]. It is clear from our data that $\alpha \neq \beta$ and that $\beta \approx 2$, indicating that the polydispersity dominates. In other words, the internal mode scattering is not a significant factor in accounting for the scattering behavior observed here. The fact that the β value we obtained ($\beta \approx 2.1$) is slightly larger than 2 may be due to the asymptotic effects; i.e., qR_z is not sufficiently greater than 1 [1,2]. This effect has also been demonstrated by Martin on the basis of computer simulations [1]. The simulation results demonstrated that β asymptotically approaches the limiting value 2 slowly as qR_z becomes very large. This effect would mean that the polydispersity exponent $\tau = 1.76$ that we obtained would represent the lower limit of the true τ value [1].

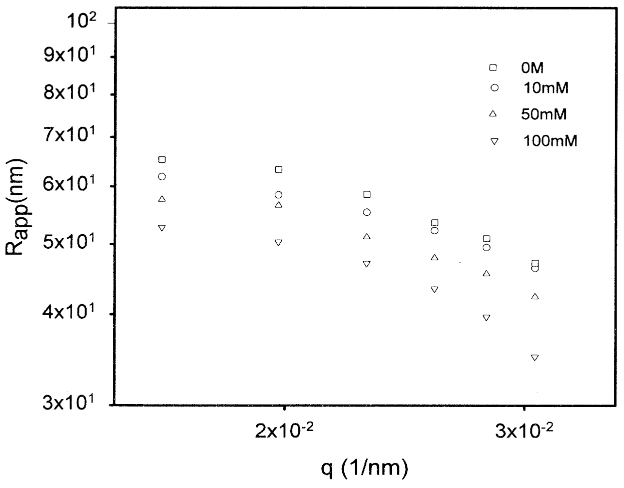

FIG. 3. Plot of apparent radius $R_{\text{app}} = (KT/6\pi\eta)(q^2/\Gamma_i)$ vs q in a log-log scale for electrolyte concentrations from 0 M to 100 mM.

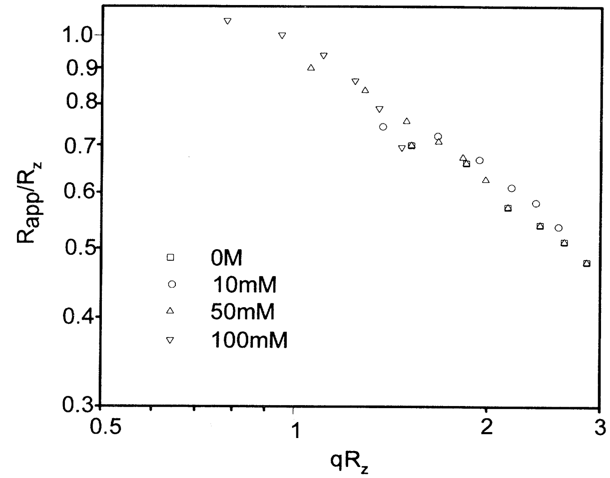

FIG. 4. Master curve for R_{app}/R_z as a function of qR_z after collapsing the data in Fig. 3.

Another important quantity that is of interest and can be obtained from the MLA theory is R_z. Equation 3 allows the scaling relationship $R_{\text{app}} = R_z F(qR_z)$ to be derived, where R_{app}, the apparent radius, is defined as $R_{\text{app}} \equiv (KT/6\pi\eta)(q^2/\Gamma_i)$, based on the Einstein-Stokes relation $D_z = KT/6\pi\eta R_z$. Here KT is the thermal energy and η is the solvent viscosity. This relationship indicates that the quantity R_{app}/R_z is an universal function of qR_z. Thus, the data obtained for R_{app} at different q and different R_z (which is controlled by the electrolyte concentration) should collapse to a master curve in a plot of R_{app}/R_z vs qR_z. Figure 3 is a plot of R_{app} vs q at different electrolyte concentrations. By shifting the curves in the log-log scale, we found R_z's for each electrolyte concentration that do indeed collapse the data to a master curve $R_{\text{app}}/R_z = F(qR_z)$ (Fig. 4). This result is clearly consistent with the MLA theory. Plotting R_z vs

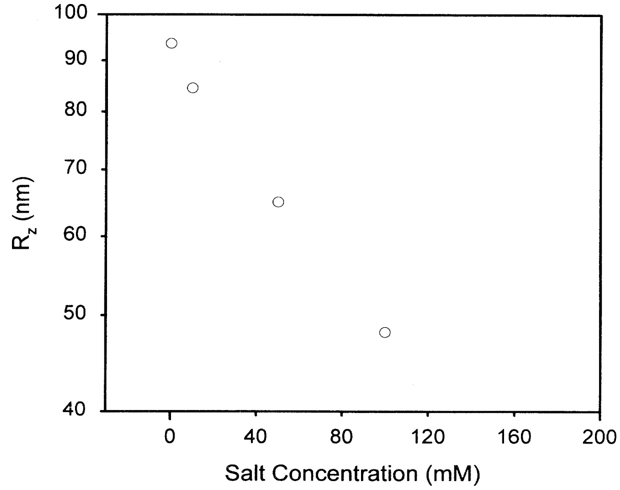

FIG. 5. Plot of z-averaged radius R_z vs electrolyte concentration.

electrolyte concentration (Fig. 5), we see that R_z decreases as the electrolyte concentration increases. This is consistent with humic acid being viewed as a polyelectrolyte. As charge screening effects increase with increasing electrolyte concentration, electrostatic repulsion between the individual units forming humic acid aggregates is reduced, causing the aggregates to shrink and resulting in a smaller R_z. Thus, the MLA theory qualitatively describes the physical behavior of the system.

Finally, we address two interesting results from this study. First, the power-law mass distribution in real systems must have an upper mass limit M_ξ. This mass cutoff may produce a stretched exponential tail after the initial decay in correlation functions that results from the diffusive motions of the exponentially rare lager aggregates, as elaborated by Martin [1]. However, the sample fractionation employed here ensures that $qR_z \gg 1$ (R_z is proportional to the largest aggregate size). Thus, the observation that q^{-1} was smaller than R_z suggests that we were not observing diffusive motions of these large aggregates as a whole. Hence, the correlation functions that we obtained all conformed to a single exponential without longtime tails. Second, the fractal dimension $D_f \approx 2.1$ and polydispersity exponent $\tau \approx 1.76$ determined for this humic acid are typical of the values found for the fractals produced in the reaction-limited colloidal aggregation (RLCA) [4]. The RLCA is a slow process in which clusters must overcome the repulsive energy barriers between colloids before they stick together to form large aggregates. In light of the polyelectrolyte nature of humic acid, this is an appealing direction for further investigations into the aggregation behavior of this environmentally important colloid. It is also in contrast to the reports that conclude that a diffusion-limited particle-cluster aggregation model should be used to describe the formation of fractal colloids in humic acid [14].

In summary we have studied fractal dynamics of humic acid colloids. Our data and their interpretation are entirely consistent with the MLA theory and provide additional experimental support for its application to power-law-polydisperse colloids.

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[1] J. E. Martin, Phys. Rev. A **36**, 3415 (1987).
[2] J. E. Martin and F. Leyvraz, Phys. Rev. A **34**, 2346 (1986).
[3] *Dynamic Light Scattering-Applications of Photon Correlation Spectroscopy,* edited by R. Pecora (Plenum, New York, 1985).
[4] M. Y. Lin *et al.*, in *Fractals in the Nature Sciences,* edited by M. Fleischmann *et al.* (Princeton University Press, Princeton, NJ, 1989), p. 71.
[5] B. Mandelbrot, in *Fractals in the Nature Sciences* (Ref. [4]), p. 3.
[6] M. Adam and M. Delsanti, Contemp. Phys. **30**, 203 (1989).
[7] J. E. Martin and B. J. Ackerson, Phys. Rev. A **31**, 1180 (1985).
[8] M. H. B. Hayes *et al.*, *Humic Substance II. In Search of Structure,* edited by M. H. B. Hayes *et al.* (Wiley-Interscience, Chichester, England, 1989), pp. 689–733.
[9] F. J. Stevenson, *Humus Chemistry: Genesis, Composition, Reactions* (Wiley, New York, 1982).
[10] P. MacCarthy and J. A. Rice, *Scientists on Gaia,* edited by S. Schneider and P. J. Boston (MIT Press, Cambridge, MA, 1991), pp. 339–345.
[11] R. Beckett, Environ. Sci. Technol. **21**, 289 (1987).
[12] J. A. Rice and J. S. Lin, Environ. Sci. Technol. **27**, 413 (1993), and references therein.
[13] J. A. Rice, Ph.D. thesis, Colorado School of Mines, 1987 (unpublished).
[14] N. Senesi *et al.*, *Humic Substances in the Global Environment and Implications on Human Health,* edited by N. Senesi and T. M. Miano (Elsevier, Amsterdam, 1994), pp. 115–120.