

behavior was seen for SERS of the internal heterocycle modes for the  $\text{Ru}(\text{NH}_3)(\text{py})^{3+/2+}$  couple (py = pyridine) at gold in 0.1 M KCl [cf. the behavior of  $\text{Os}(\text{III})/(\text{II})$  nitrogen heterocycles<sup>4</sup>].

**(c) Small Organic Adsorbates.** In view of the suitability of gold electrodes for oxidizing small organic molecules<sup>20</sup> we have initiated SERS studies of such systems. One objective is to elucidate heterogeneous reaction mechanisms by detection of vibrational bands for adsorbed reactants, intermediates, and products. Figure 3 shows a SERS spectrum at gold obtained for an ethylene-saturated 1 M  $\text{H}_2\text{SO}_4$  solution. The bands around 1545 and 1278  $\text{cm}^{-1}$  correspond to the  $\text{C}=\text{C}$  stretch and  $\text{CH}_2$  scissors modes, respectively; these are shifted substantially from the gas-phase values of 1623 and 1342  $\text{cm}^{-1}$ .<sup>21</sup> The spectra are stable over the range -400 to 500 mV, the Raman frequencies remaining constant within 5  $\text{cm}^{-1}$ . At more positive potentials ethylene oxidation commences; a SERS study of the electrooxidation mechanism will be reported elsewhere.<sup>22</sup> Such spectra could not be obtained at silver,

probably due to the weaker adsorption of ethylene anticipated at this surface compared to that at gold.

**Conclusions.** Generally speaking, the SERS bands for all these adsorbates, as well as a variety of others recently studied in our laboratory, exhibit comparable or higher intensities along with substantially greater stability at gold than at silver when using 647.1-nm irradiation. Given that a number of these adsorbates, such as halides or pseudohalides, are typically present at amounts approaching a monolayer at both surfaces, this indicates that the Raman surface-enhancement factor tends to be larger at gold than at silver under these conditions. Besides the obvious ramifications regarding the details of the SERS effect itself, the results reveal an unexpected and hitherto unexplored opportunity to utilize SERS to gain molecular structural information for a wide variety of reactive electrochemical systems.

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## Visible Evidence for Interparticle Attraction in Polymer Latex Dispersions

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Highly charged latex solutions were studied by the ultramicroscopic method with the aid of a movie device. At a relatively low latex concentration, a localized (i.e., non-space-filling) ordered structure was observed to coexist with a disordered region. This is possible only when the net interparticle interaction is attraction. The trajectories of the particles were determined: the amplitude of the vibrational motion of the particles in the ordered region was about  $10^3$  Å of the average interparticle spacing ( $10^4$  Å) whereas the average displacement of the particles in the disordered region was about  $10^4$  Å for 1 s.

Dilute dispersions of spherical particles are known to form ordered structures when they are electrically charged and monodisperse and the level of foreign salt is low.<sup>1</sup> Direct evidence was obtained for polymer latex particles by Hachisu et al. by taking pictures with an ultramicroscope.<sup>2</sup> Applying this technique, we found that the interparticle center-to-center distance measured directly ( $2D_{\text{exp}}$ ) on the micrographs was smaller (by a factor of 2 at low concentrations) than the average value calculated from the latex concentration with the assumption of a uniform simple cubic distribution ( $2D_0$ ) for highly charged

particles.<sup>3</sup> Independent X-ray scattering measurements on synthetic macroion solution showed a diffraction peak in the low-angle region (the scattering vector being 0.05–0.1  $\text{\AA}^{-1}$ ), whose position gave the relation  $2D_{\text{exp}} < 2D_0$ , similar to the results obtained for latex dispersion.<sup>4–6</sup> This inequality relation suggests the existence of the two-state structure in solutions, which consists of ordered regions

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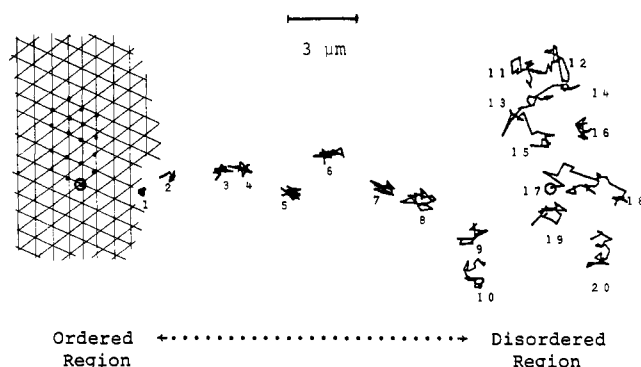
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**Figure 1.** Two-state structure and the trajectory of the particles in 1 s. Latex SS-37, number of charges per particle  $1.76 \times 10^5$ , diameter 4500 Å, concentration 2.0 vol %, film speed 24 frames/s, exposure 1/67 s. The  $2D_{\text{exp}}$  in the ordered region was found to be  $10^4$  Å from the present figure, whereas  $2D_0$  was  $1.5 \times 10^4$  Å. Thus the total volume of the ordered regions amounts to  $1/3.4 = [(10^4)/(1.5 \times 10^4)]^3$  of the total solution volume. The trajectories of 38 particles are determined by following the centers of the particles as a function of time using 24 consecutive still pictures of the 16-mm movie film. Of 38 particles 18 are in the ordered region and 12 are in the disordered one. It should be noted that these numbers do not represent the actual number densities of the particles in the respective regions.

of a higher solute density and less dense disordered regions. For latex solutions, this structure was photographed directly.<sup>2,3</sup> However, the micrographs published were not clear enough to discern the structure clearly: in the case of Hachisu et al., the particles in disordered regions were smeared out, whereas we used a more sensitive film with a shorter exposure time and failed to reproduce the dynamic movement of the particles in disordered regions. In the present paper we obtain a clear picture showing the "solid-gas" (instead of "solid-liquid")-like partitions of the particles and describe the movement of the particles by reproducing their trajectory.

Figure 1 was obtained for a highly charged monodisperse copoly(styrene-styrenesulfonate) latex particle (SS-37, electron charge per particle,  $1.76 \times 10^5$ ; diameter,  $4500 \pm 100$  Å), which were synthesized and purified extensively as described earlier.<sup>3</sup> It should be noted that Figure 1 shows the particles in a horizontal, not perpendicular, plane, as described earlier.<sup>2</sup> The circles denote the particles and the straight, broken lines represent the trajectories of the centers of the particles. Even though the latex concentration is relatively high, the two-state structure is clearly observed. In the left-hand side is a "solid"-like hexagonal array with high density, which coexists with a much less dense "gas"-like disordered region (right-hand side). Between the two regions, there appears to exist a "liquid"-like boundary region.

Obviously, such a solid-gas-like two-state structure is the most direct evidence of the interparticle attraction. As already pointed out<sup>7-9</sup> and theoretically elucidated,<sup>10</sup> the

attraction (between similarly charged entities), which is brought into existence by counterions present between the particles, is balanced with repulsive forces between the particles, creating a "secondary" minimum. If the attraction does not exist, or if only repulsive interaction is operating, the localized ordered array as shown in Figure 1 is impossible. *Condensed systems with free boundary or surface cannot exist without attractive interaction.* Contrarily, if only the attraction is important, in other words, if the repulsion does not exist, then the particles would coagulate. The fact that the ordering in the localized space does exist in dilute solution, as demonstrated in Figure 1, might indicate the incorrectness of the widespread analysis assuming the interparticle repulsion exclusively since the ordered structure must cover the entire solution if it was formed by the repulsion only. Similarly it seems that the interpretation<sup>11</sup> of the latex ordering in terms of the Alder transition<sup>12</sup> would not be valid, either.

In the ordered solid-like region in Figure 1, the particles show oscillatory motion around the equilibrium point as described separately,<sup>13</sup> but its amplitude is too small to show in the scale of Figure 1. In the disordered gas-like region, random motion is obvious. The average displacement ( $\bar{x}$ ) for 12 particles is  $7.5 \times 10^3$  Å in 1 s, whereas Einstein's theory on Brownian motion<sup>14</sup> gives a value of  $1.5 \times 10^4$  Å. In the intermediate liquid-like region, the average value of  $\bar{x}$  is  $3.1 \times 10^3$  Å, showing long-ranged influence of the particle charges in the ordered region.

From Figure 1, furthermore, a spectrum of translational diffusion coefficient ( $D$ ) may be expected. Very small (practically zero)  $D$  may be ascribed to the particles in the ordered region, and  $D$  having a normal magnitude corresponds to the random motion. Depending on the experimental conditions,  $D$ 's having discrete values might be experimentally found. In this respect, recent reports on dynamic light scattering and dispersion, in that at least two diffusion coefficients were observed for macroions, are highly interesting.<sup>15-17</sup> For example, at a poly-L-lysine concentration of 0.84 mg/cm<sup>3</sup> and a sodium bromide concentration of  $7.41 \times 10^{-4}$  mol/L, the fast and slow relaxation modes gave  $D$  values of  $1.1 \times 10^{-6}$  and  $8.8 \times 10^{-9}$  cm<sup>2</sup>/s.<sup>17</sup> A full account of the work, with more accurate analysis for a large number of particles, will follow soon.

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