the chromosphere, exhibit a significantly larger broadening than the absorption profiles on the disk (2 to 3 km s$^{-1}$) (*2*, *13*).

The large horizontal velocities implied by these excess line widths are reminiscent of the almost adiabatically expanding cool gas overlying granules in the upper reaches of granular simulations (*14*). Our observations suggest that on the real sun the convective overshoot does not stop at the temperature minimum, as is tacitly assumed in practically all current granular simulations, but continues into the lower chromosphere. In addition, the horizontal supersonic velocities seen in recent numerical simulations of solar convection (*15*, *16*) are possibly common in the dark heart of the lower chromosphere. One interpretation of the observations is that the CO lines form mainly in the granule centers, upstream of the shock fronts located near the downflow lanes. Hence, although the CO limb emission is well reproduced by hydrostatic atmospheres, the influence of convective dynamics on the stratification of the cool gas should be carefully investigated.

This cold chromospheric component survives even in the presence of substantial acoustic energy deposition (except at locations where the heating is particularly intense, such as magnetic elements) because of a combination of CO radiative cooling (*17*) and adiabatic expansive cooling. Energy deposition does produce a hot thermal zone overlying the cool layers (*4*, *18*). The magnetic field, which produces a magnetic canopy with a base close to $Z_C$ (*19*), probably tends to stabilize the location of the steep rise of the temperature at the top of the heart of darkness of the solar chromosphere.

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# Void Structure in Colloidal Dispersions

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**The time evolution of void structures in highly purified polymer latex dispersions was studied with a confocal laser scanning microscope. In such dispersions, which were initially homogeneous, the voids grew with time when the dispersions were kept standing and formed more quickly in the internal material than in material close to the glass-dispersion interface. Void formation is thus not an artifact arising from the presence of the interface. A similar structural inhomogeneity, in apparently homogeneous systems, is discussed for simple ionic solutions, ionic polymer solutions, and Langmuir-Blodgett films.**

Dilute polyelectrolyte solutions give a single, broad peak in the small-angle x-ray scattering profile which is attributed to the formation of an ordered structure (*1*). Although this interpretation of the peak was substantiated by a theoretical calculation of the scattering function by Matsuoka *et al.* (*2*, *3*), we were left with the intriguing result that the Bragg spacing between macroions in the ordered structure ($2D_{\mathrm{exp}}$) (experimental uncertainty of order $\pm 10\%$) was much smaller than the theoretical average spacing ($2D_0$) expected from the overall macroion concentration. For example, a fractionated sodium polyacrylate with 1470 monomer units had a $2D_{\mathrm{exp}}$ value of 88 Å at a polymer concentration of 0.02 g/ml and 22°C, whereas the theoretical $2D_0$ was 222 Å. The same trend was observed for various ionic polymers, including highly charged globular proteins.

According to a simple stoichiometric consideration, the difference between the two spacings indicates that localized, non–space-filling ordered structures exist. The total sum of the volumes of these ordered structures must be 0.06 $[\approx(88/222)^3]$ of the solution volume (although the volume of the single localized structure is not known), leaving 94% of the solution volume occupied by disordered macroions or voids. The coexistence of the ordered structure and free macroions appears to be supported by observation of slow and fast diffusion modes by dynamic light scattering (*4*).

Independently, Hachisu *et al.* (*5*) successfully observed under microscope void structures in dispersions of ionic polymer latex particles. This observation was confirmed by two groups (*6*–*8*), which reported huge and stable voids in apparently homogeneous dispersions. Voids were stable over about 10 hours and were observed even in samples several months old (*7*). Thus, we decided that the void structure must be considered if the true nature of interparticle interactions is to be sought. To eliminate the effect of the glass-dispersion interface (wall effect) in the void formation, we (*9*) used a confocal laser scanning microscope, which allowed observation of particles at a greater distance from the interface than previous microscopes (for example, even at 700 µm in a latex concentration of 0.01% for polystyrene-based particles in a $D_2O$-$H_2O$ mixture). We found that huge, stable voids existed in the interior of the dispersion. Voids as large as 50 µm by 150 µm by 50 µm have been photographed (*10*).

The implication of the existence of such large and stable voids has recently been discussed (*10*). The voids testify to the presence of an attractive interaction between the colloidal particles. Here we describe a preliminary study of how the void structures in latex dispersions changed with time and depth from the top of the dispersion. The confocal laser scanning microscope (Carl Zeiss, Oberkochen, Germany) had a ×100 oil-immersion objective and a 5-mW Ar laser. We used styrene-based latex (N1000; diameter, 0.96 µm; charge density, 12.4 µC/cm$^2$; Sekisui Chemical, Osaka). The density was matched by selecting a $D_2O$-$H_2O$ mixture. The dispersion temperature was kept constant with a thermostatted air bath. As described previously (*11*), latex dispersions were extensively washed with an Amicon Model 202 and a Diaflo XM300 with Milli-Q reagent-grade water. The dispersions were put into a container with highly purified ion exchange resins. The containers were allowed to stand or were rotated to facilitate rapid ion exchange until the resin particles started to

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become suspended in the dispersions. Then, the dispersions were transferred into a (cylindrical) Pyrex cell (height, 1 cm; diameter, 2 cm) together with Bio-Rad ion exchange beads [AG501-X8(D)], which had been washed with a mixture of $D_2O$ and freshly obtained Milli-Q water. The whole mixture was vigorously shaken and placed on the microscope platform. The homogeneity of the particle distribution was confirmed by observation. After the dispersions had been left standing for 24 hours, void formation was observed. The void-containing dispersions were again shaken, particle distribution was randomized (Fig. 1), and the dispersions were again allowed to stand on the microscope platform (this was defined as time $t = 0$). Thereafter, scanning micrographs were taken of particles that were sufficiently distant from the resin particles (>0.5 cm).

A series of pictures taken at various times and distances (Fig. 2), showing cross-sectional views of particle distribution, reveals some interesting features. Comparison of pictures at a fixed distance *d* from the glass-dispersion interface and at three different times (Fig. 2, second row at $d = 10$ μm and, though less clearly, first row at $d = 0$) shows that the particle distribution changed with time from homogeneous to inhomogeneous, that is, the voids grew with time. This observation suggests that the voids were not induced by a third substance on the uncleaned glass surface. If the void is an artifact, stable voids ought to have been visible from the beginning of observation.

When the particle distributions are compared at a fixed time and at different distances (Fig. 2, columns), it is clear that the voids are formed more quickly internally than very close to the interface. That is, the void size increases with increasing *d*. This observation also excludes the possibility that voids originate from impurities because the effect of impurities should decrease, hence the void size should decrease, with increasing distance from the interface.

Adsorption of particles by oppositely charged resin particles can be thought of as a possible cause of void formation under these experimental conditions. However, if this were the case, the overall concentration of particles would definitely be lowered. Consequently, this hypothesis cannot account for "localized" diminution of particle concentration, namely void formation.

Previously (*5–8*), with small particles (diameter, 0.3 to 0.5 μm), void structures were seen to coexist with ordered structures. However, here and in recent studies (*9, 10*), void structures coexisted with disordered particles. Because the purification of the dispersion was always carried out to the same extent in our work (*6, 8–10*), it is unlikely that the observed discrepancy is a result of different levels of ionic impurity. One plausible explanation is that the particles used in these recent papers were fairly large (about 1 μm in diameter). Because of the relatively low diffusibility of such large particles, ordered structures could not form within the observation period. However, a detailed discussion must await a systematic study of the relation between particle size and crystallization rate.

It is of interest to consider the possible presence of void structures in other ionic systems. Void structures were never suspected to exist in colloidal dispersions before the

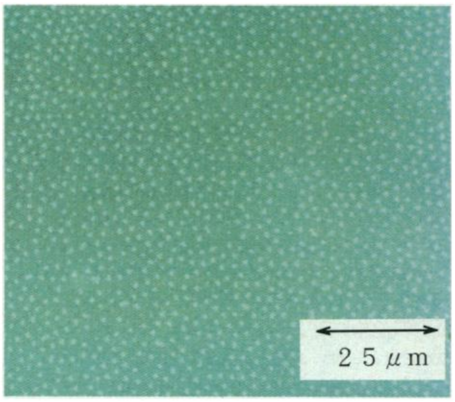

**Fig. 1.** Confocal laser scanning micrographic image of random particle distribution. Latex, N1000 (diameter, 0.96 μm; charge density, 12.4 μC/cm$^2$); latex concentration, 2%; dispersant, $D_2O$-$H_2O$. The latex particles are seen as white dots. The image shows the particle distribution in a horizontal focus plane.

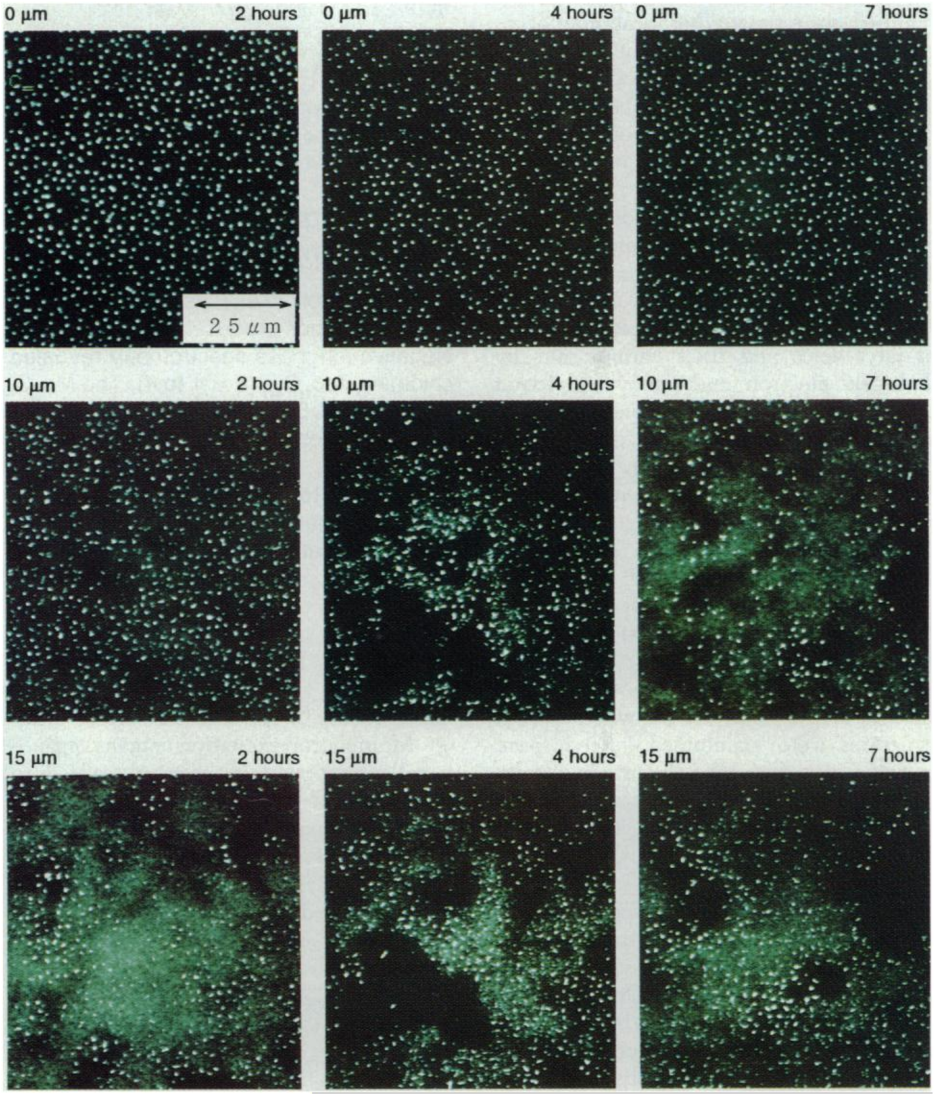

**Fig. 2.** Void structures as seen by confocal laser scanning microscope at various times and distances from the glass-dispersion interface. The experimental conditions are the same as in Fig. 1. Direct micrographs were image-processed by an image data analyzer SEM-IPS (Carl Zeiss, Oberkochen, Germany) to obtain stronger contrast. Photographing conditions were adjusted between pictures so as to attain better contrast between particles and background. This caused distortions (for example, in the particle size) in the final images. The scale given applies to all nine pictures.

observation by Hachisu *et al.* (*5*). In simple ionic systems, the presence of void structures can be inferred at least qualitatively from extended x-ray absorption fine structure data, which showed that the average distance between $Zn^{2+}$ and $Br^-$ is 2.37 Å in 0.089 M $ZnBr_2$ aqueous solutions and 2.30 Å in 0.05 M solutions (*12*). These values are very close to the interionic distance observed in the crystalline state (2.40 Å). From these findings, it was claimed that "some local order, resembling that of the corresponding crystals, exists" in the aqueous solutions. The same conclusion was also reached for $NiBr_2$-ethyl acetate solutions (*13*) and aqueous $CuBr_2$ solutions (*14*). Comparing the reported interionic distances with the average interionic distance (22 and 19 Å for 0.05 and 0.089 M solutions, respectively) [$\approx(1000/3CN_A)^{1/3}$, where C is the molar concentration and $N_A$ is Avogadro's number], we estimate that local order occupies only a very small portion of the solution volume, implying that voids occupy most of the solution volume. It should be mentioned that local structures and also voids in simple ionic solutions, such as metal halides, have very short life-spans (*15*).

The following recent finding suggests that microscopic inhomogeneity in solute distribution is a general characteristic of ionic systems. Matsumoto *et al.* (*16, 17*) studied single Langmuir-Blodgett (LB) films of fatty acids and their barium salts by dark-field electron microscopy and found the coexistence of solid, liquid, and gas structures (being "hole" or "porous," according to their terminology). Amazingly, pictures of holes as large as 4 μm in diameter can be seen in the film [figure 9 of (*17*) for arachidic acid]: It does not seem unreasonable to imagine much larger holes in the solutions before they are cast into film. Atomic force microscopy (AFM) has revealed domain formation in "liquid-like" regions in LB films (*18*). Although it is not clear from the AFM images whether void structures were maintained in the space between the domains, this study clearly demonstrates structural inhomogeneities that could not be seen by conventional fluorescence microscopy.

Needless to say, relatively rapid Brownian agitation of small ionic species smears out the void structures so that their presence does not matter on the time scale of thermodynamic measurements. On the other hand, the long time scale of the motion of latex particles and their size enabled us to make real time microscopic observations of structural inhomogeneities, such as two-state structure and void formation in colloidal dispersions. Such structural inhomogeneities would seem to be important if the thermodynamic properties of the dispersions are to be thoroughly understood.

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# Synthesis and Characterization of Molybdenum Carbide Clusters $Mo_nC_{4n}$ ($n$ = 1 to 4)

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**Laser radiation (XeCl laser, 308-nanometer wavelength) focused into a cell containing $Mo(CO)_6$ vapor produced ultrafine particles in the extended waist of the laser beam. Negative ion mass spectrometry revealed molybdenum carbide cluster ions with a stoichiometry $Mo_nC_{4n}$ ($n$ = 1 to 4). The $Mo_nC_{4n}^-$ ($n$ = 2 to 4) ions are completely unreactive with $NH_3$, $H_2O$, and $O_2$, suggesting structures in which the molybdenum atoms are unavailable for coordination to additional ligands. Collision-induced dissociation studies of these anions show the loss of $MoC_4$ units as the main fragmentation pathway. This observation, together with the lack of addition reactions, provides a basis for structures in which a planar cluster of two, three, or four molybdenum atoms is surrounded by, and bonded to, carbon dimers.**

Mechanisms leading to the multiphoton excitation and ionization of organometallic molecules are of considerable current interest. Multiphoton excitation of many organometallic compounds in the gas phase leads to the copious formation of bare metal atoms and metal ions (*1*). Laser irradiation of organometallic vapors has found many applications in chemical vapor deposition (*2*).

Recent studies (*3, 4*) have reported the formation of ultrafine particles when gas-phase carbonyls of transition metals such as $Mo(CO)_6$, $Cr(CO)_6$, and $W(CO)_6$ were exposed to XeCl laser radiation. Scanning electron microscopy studies indicated that the particles are less than 1 μm in diameter. The composition and properties of these particles were not characterized. In this report, we present a detailed description of the identification and characterization of the bulk material formed by XeCl laser irradiation of $Mo(CO)_6$ in the gas phase. A class of molybdenum carbide clusters, $Mo_nC_{4n}$ ($n$ = 1 to 4), was observed. The stoichiometry and properties of these clusters were examined by laser desorption Fourier transform ion cyclotron resonance mass spectrometry (FTMS) and thermal desorption electron capture mass spectrometry. FTMS ion-trapping and manipulation techniques were also used to examine the collision-induced dissociation, ion-molecule reactions, and charge exchange reactions of

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