Brief Reports

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Experimental determination of the random-parking limit in two dimensions

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The two-dimensional random-parking limit is the area fraction of a plane covered by circles when the circles are added sequentially in a random way, without overlap, until no further circles can be added. As yet, no analytical solution exists for this limit. Several computer simulations and one experimental study have been carried out in the past, with results varying from 50% to 62% for the parking limit. In our work, we carry out an experimental determination of this parking limit, utilizing a spherical colloid that sticks irreversibly to a flat substrate. The experimental value obtained is 0.55 ± 0.01, which agrees with two of the most recent, computer-generated values.

The random, incommensurate, irreversible adsorption of atomic units at interfaces is a phenomenon basic to many areas of physics, chemistry, and biology. The arrangement and fractional coverage at full saturation are related to what is known as the two-dimensional (2D) random-"parking" problem. This problem involves the random placement of equal size circles on a surface such that none overlap. At the 2D random-parking limit, expressed as an area fraction, there is no uncovered space large enough to fit another circle.

At present, no analytical solution exists for this 2D parking limit; however, several computer simulations have been carried out. Finegold and Donnell[1] found a limit of 0.5027, while Tanemura[2] as well as Feder[3] report a value of 0.547.

Feder and Giaever[4] attempted to measure experimentally the random-parking limit, using the adsorption of protein molecules from an aqueous solution onto a carbon film. Electron microscopy revealed a maximum coverage of 0.78 molecules per $(10\ \text{nm})^2$. The diameters of the adsorbed proteins were measured to be 10.1 ± 0.8 nm. Using these values, we calculate that the projected area coverage is 0.625 ± 0.100. This mean value varied considerably from their own computer-simulated value of 0.547. Thus, either the true parking limit is higher than the computer-generated values, or else the experimental error was too large. Discrepancies can be due to several sources. Protein molecules might, for example, become flattened upon drying as a result of capillary forces. If so, the area coverage may have become higher during drying. A 7% change in the projected diameter, for example, is sufficient to vary the calculated coverage between 0.547 and 0.625. Also, as suggested by Feder and Giaever, the protein molecules do not adsorb irreversibly and could have diffused along the surface to some extent, allowing more efficient packing and space for a larger number of molecules.

In this present study, we attempt to overcome experimental problems by meeting the following criteria as closely as possible: (1) the depositing units are spherical and uniform so that their projected areas are uniform circles; (2) the spheres are rigid enough to resist permanent distortion by the strong capillary forces acting during the final stages of drying in the sample preparation; (3) the spheres are irreversibly bonded to the surface so that diffusion does not occur and, later, none are removed during rinsing; (4) the spheres do not bond to each other so that clustering does not occur before deposition and so that second layer particles do not form during deposition; (5) the spheres approach the surface in a random fashion so that a biased structure does not develop.

Latex colloids satisfy the criteria of being uniform, spherical, and rigid. These are available in different sizes. We choose for this study polystyrene lattices of 2.95-μm diameter because they can be readily seen in an optical microscope (supplied by Seragen Diagnostics, Inc.).

Irreversible bonding of latex spheres to a flat surface was achieved by a multistep procedure utilizing a cationic polyacrylamide (a high molecular weight polyelectrolyte). These polymers are well-known flocculants in waste water treatment that bond colloidal particles together in suspensions by adsorbing and forming molecular bridges between particles. The adsorption of these polymers at solid/liquid interfaces is irreversible under normal conditions. Our procedure consisted of preparing a dilute solution of a cationic polyacrylamide in water and immersing a glass slide into this solution for approximately 10 min. Thereafter, the slide is removed and rinsed thoroughly in running distilled water, which removes all excess solution. The slide is then dried, leaving an invisible molecular layer of the polymer on the surface. This coated slide is then immersed horizontally for 1 h at the bottom of a beaker containing a 10% aqueous suspension of latex particles. In this step, the polyacrylamide on the slide is not desorbed; therefore it does not adsorb onto the latex particles in the suspension. As latex spheres deposit on the surface, they are bonded to it by the floccu-

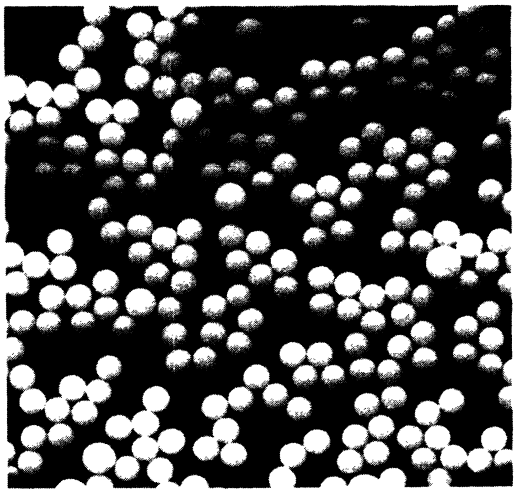

FIG. 1. Configuration of latex spheres deposited on a surface, illustrating the clumping that results during drying.

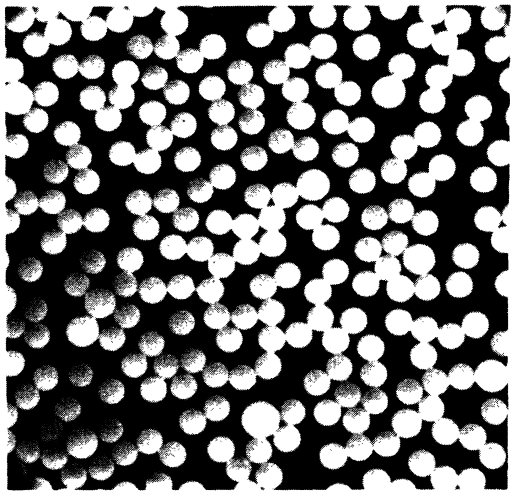

FIG. 2. Configuration of latex spheres at the random-parking limit, with clumping largely inhibited by the procedure described in the text.

lant molecules. Since the particles were orginally randomly distributed in the suspension, the deposition occurred randomly in the plane of the glass slide surface.

After the particles are deposited, the slide is removed and all excess material is rinsed away with running distilled water for about 15 sec until the surface appears clear. Particles that are deposited but are not in direct contact with the surface of the slide are readily removed during the rinsing operation because they were not bonded with the polymeric flocculant. After the excess water is shaken off, the slide is dried with a soft jet of air. The drying results in a white film caused by the enhanced light scattering when the liquid is removed from the particulate layer. Microscopic inspection of this layer reveals that only one layer of particles exists.

The drying stage (after particles are deposited and excess suspension is rinsed away) was observed at high magnification with an inverted optical microscope. What was seen was a clustering of the particles when the last traces of water were removed. At this point, the remaining water forms capillary bridges between particles and provides strong enough forces to draw nearby particles together, despite the resistance offered by the polymer bond. The resulting packing arrangement (Fig. 1) was clearly more clustered than the arrangements arrived at by the previous computer simulations.

To inhibit this clustering action, the procedure for producing the latex layer was modified at the point where the excess suspension is washed away. Instead of drying, the wet slide containing the layer is rinsed gently in acetone (which does not remove the particles) and then dipped in a dilute solution of amyl acetate in acetone for a few seconds; the excess is shaken off and the slide is allowed to dry. This treatment slightly softens the latex at its points of contact with the slide, causing them to stick. While a slight amount of clustering still occurred, the resulting structure (Fig. 2) is very similar to the computer simulations. The slight clustering on drying did open up a few areas that particles could fit, but it is believed that these did not exist before drying.

The projected area coverage of spheres on the glass slide are obtained from scanning-electron microscopy (SEM) micrographs (1600 magnification) at normal incidence. The photograph image was digitized, using a high-resolution TV camera. The area fraction covered by spheres is readily obtained from the data. Approximately 210–220 spheres were typically present in the photographs. There were no discernible differences in the values measured with the clustered and the cluster-inhibited samples, as expected, since only rearrangement occurs without the change in the number of particles.

Measurements were made on 25 micrographs (five views on five separately prepared samples). The area coverage was found to be $(55 \pm 1)\%$. This, then, is what we believe is the value for the random-parking limit. A concordance has thus been established between experiment and the most recent computer-simulated values of Tanemura[2] and of Feder and Giaever.[4]

[1]L. Finegold and J. Dunnel, Nature **278**, 443 (1979).
[2]M. Tanemura, Ann. Inst. Statist. Math. **31**, 351 (1979).
[3]J. Feder, J. Theor. Biol. **87**, 237 (1980).
[4]J. Feder and I. Giaever, J. Colloid Interface Sci. **78**, 144 (1980).

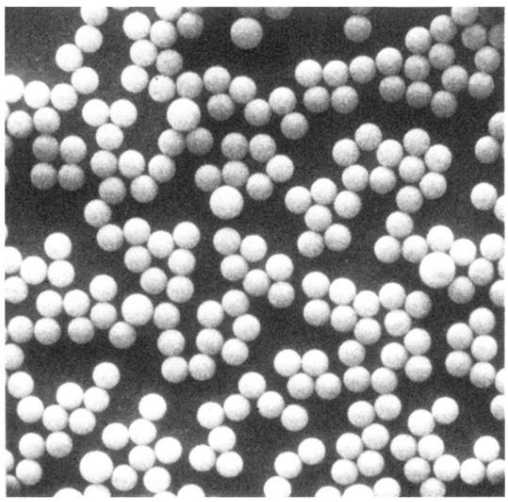

FIG. 1. Configuration of latex spheres deposited on a surface, illustrating the clumping that results during drying.

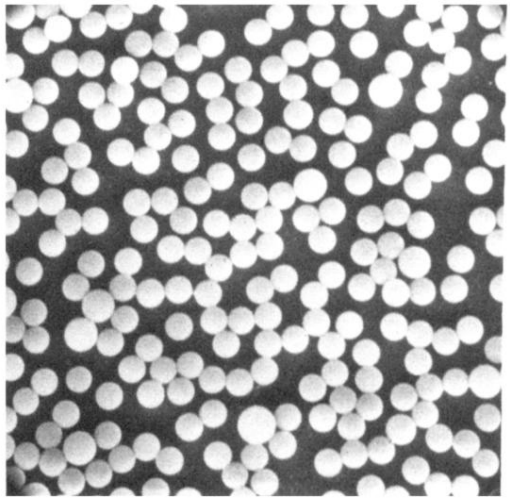

FIG. 2. Configuration of latex spheres at the random-parking limit, with clumping largely inhibited by the procedure described in the text.