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1. Hoffman, J. I. E. & Kaplan, S. *J. Am. Coll. Cardiol.* **39,** 1890–1900 (2002).
2. Pashmforoush, M. *et al. Cell* **117,** 373–386 (2004).
3. Bodmer, R. *Development* **118,** 719–729 (1993).
4. Lyons, I. *et al. Genes Dev.* **9,** 1654–1666 (1995).
5. Schott, J. J. *et al. Science* **281,** 108–111 (1998).
6. Basson, C. T. *et al. Nature Genet.* **15,** 30–35 (1997).
7. Bruneau, B. G. *et al. Cell* **106,** 709–721 (2001).
8. Garg, V. *et al. Nature* **424,** 443–447 (2003).
9. Srivastava, D. *Annu. Rev. Physiol.* **63,** 451–470 (2001).

Metrology

Electrifying effects in colloids

Patrick Warren

The electric field generated in the sedimentation or centrifugation of charged colloidal particles could be exploited to determine the charge and the mass of macromolecules in a single experiment.

It might be thought that the last word on sedimentation or centrifugation had been said long ago. But over the past decade there have been persistent indications from experiment[1], theory[2] and simulations[3] of an unusual phenomenon in the sedimentation equilibrium of suspensions of charged colloidal particles when the ionic strength is low. Colloids are small particles, typically less than one micrometre in size, that have many technological applications as well as relevance to fundamental science. On page 857 of this issue, Raşa and Philipse[4] present convincing evidence that a macroscopic electric field, generated when the charged colloid is centrifuged to equilibrium, is behind the strange effect.

In 1926, Jean Baptiste Perrin was awarded the Nobel Prize in Physics "for his work on the discontinuous structure of matter, and especially for his discovery of sedimentation equilibrium"[5]. What Perrin had discovered was that the same law that governs the rarefaction of Earth's atmosphere with height — its barometric profile — also governs the distribution of suspended colloid particles undergoing brownian motion. At the time, Perrin's measurements of the barometric profile in a painstakingly prepared gamboge (gum resin) suspension gave an independent determination of Avogadro's number, thus contributing to the establishment of the atomistic hypothesis as experimental fact. In centrifugation — which is now well established as a means of determining molecular mass — the modest effects of Earth's gravity are replaced by a strong radial centripetal acceleration, as a sample is whirled around at high speed in a specialist device.

Piazza *et al.*[1] found that, for charged colloidal particles at reduced ionic strength, the barometric profile is inflated, as though the particles weigh less than they should do. Biben and Hansen[2] have since suggested, using density functional theory, that the sample column behaves like a condenser, in the sense that imbalanced charges accumulate at the top and bottom. The resulting electric field spans the whole column and acts to lift the colloid particles up against the force of gravity.

So, what is going on? A simple explanation, first discovered by van Roij[6], relates the phenomenon to a now-classic piece of physical chemistry. In 1911, Frederick Donnan considered the equilibrium across a semi-permeable membrane separating a salt solution from a suspension of charged colloidal particles or macromolecules[7]. The membrane is permeable to the small ions of the salt but impermeable to the colloids. Naively, one might expect that the small ions would distribute themselves so as to have the same concentration on both sides of the membrane. However, Donnan discovered that this is not the case. Rather, the ions become redistributed; for example, ions with the same charge as the colloids tend to be expelled from the colloid-containing compartment — the Donnan common-ion effect (Fig. 1). The effects arise from a microscopic charge imbalance that builds up in the vicinity of the membrane, creating a potential difference between the compartments, now known as the Donnan potential.

Raşa and Philipse[4] have made a connection between the Donnan membrane problem and the sedimentation profile of charged colloids. The macroscopic electric field in the sedimentation case can be attributed to a gradient in the Donnan potential, corresponding to the gradient in the concentration of colloidal particles (Fig. 1). The full problem has to be solved self-consistently, to obtain the coupled density and electric-field profiles — which is exactly what Raşa and Philipse have done.

Their calculations show that a careful analysis of the density profile for a dilute suspension of charged colloids or macromolecules could allow both the molecular mass and the charge of the sedimenting species to be determined. What remains to be demonstrated is that the phenomenon can be measured not just for colloidal particles but also for macromolecules. In this respect, globular proteins such as lysozyme might be good candidates. If it works, the approach offers an interesting alternative to electrophoretic methods for characterizing proteins. ■

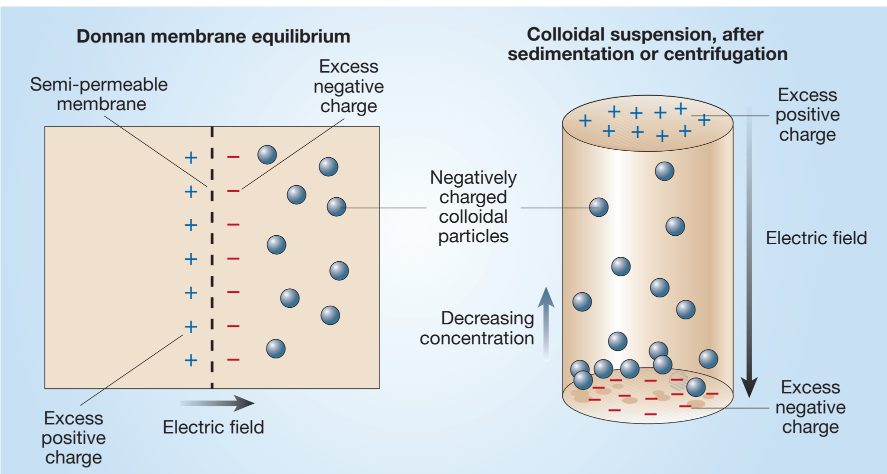

Figure 1 **The Donnan membrane equilibrium and sedimentation of a charged colloidal suspension. In a Donnan equilibrium, the charge imbalance in the vicinity of a semi-permeable membrane gives rise to an electric field, with a jump in the electrostatic potential typically occurring over a length of less than a micrometre[8]. Similarly, if a colloidal suspension has a gradient of concentration (such as is produced in sedimentation or centrifugation), then a macroscopic electric field is generated by the charge imbalance appearing at the top and bottom of the sample column. The presence of this field has observable consequences for the density profile of negatively charged colloidal particles, as has been confirmed experimentally by Raşa and Philipse[4].**

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1. Piazza, R., Bellini, T. & Degiorgio, V. *Phys. Rev. Lett.* **71,** 4267–4270 (1993).
2. Biben, T. & Hansen, J.-P. *J. Phys. Condens. Matter* **6,** A345–A349 (1994).
3. Hynninen, A.-P., van Roij, R. & Dijkstra, M. *Europhys. Lett.* **65,** 719–725 (2004).
4. Raşa, M. & Philipse, A. P. *Nature* **429,** 857–860 (2004).
5. *Nobel Lectures on Physics 1922–1941* (World Scientific, Singapore, 1998).
6. van Roij, R. *J. Phys. Condens. Matter* **15,** S3569–S3580 (2003).
7. Donnan, F. G. *Z. Elektrochem.* **17,** 572–581 (1911).
8. Sear, R. P. & Warren, P. B. *J. Chem. Phys.* **117,** 8074–8079 (2002).