been found to depend on the presence of a nearby AG dinucleotide to undergo the first step of splicing in mammals¹⁷. Our results show that even the earliest events in 3'-splice-site recognition are affected by the proximity between the poly(Y) tract and the AG dinucleotide. Furthermore, they show that the underlying molecular interactions also operate in RNAs with strong poly(Y) tracts highly enriched in U bases, and that these interactions can have a crucial role in splicing regulation, illustrating how the study of regulatory processes can illuminate basic mechanisms of gene expression. □

Methods

Constructs

pGEM-*msl-2*, pRm-*msl-2* and pRm-SXL were as described previously⁶, as was pAdML²⁰. All other clones were generated by PCR-based site-directed mutagenesis and confirmed by sequencing. In pm(5'U,PY)A, the stretches of 11 and 16 T bases corresponding to the SXL binding sites in *msl-2* RNA were introduced five nucleotides downstream of the 5' splice site and at the poly(Y) tract of the AdML intron, respectively. pm(PY + 3)A was prepared by replacing positions 107–119 in the AdML intron²⁰ by positions 103–131 in the *msl-2* intron¹. pβ(3)m was generated by replacing positions 119–131 in the *msl-2* intron by the human β-globin sequence 5'-ACTGGGCATGTGG-3'. pA(3)m was obtained by replacing positions 119–131 in the *msl-2* intron by positions 116–119 in the AdML intron. pshort(3)m was obtained by mutating position 122 of *msl-2* intron to G. pRm-A(3)m was generated by recloning the insert of pA(3)m into pRmHa-3 (ref. 6).

Splicing assays and RNA analysis

Transcription *in vitro*, splicing, spliceosome assembly and RNA analysis were as described^{6,7}.

Extracts and purified proteins

Nuclear extracts were prepared from HeLa cells as described²¹. RNase-H-mediated inactivation of U1 snRNP was performed by incubating 50 μl of extract with 500 pmol of an oligodeoxynucleotide complementary to the first 15 nucleotides of U1 snRNA in the presence of 1.1 mM ATP, 5.6 mM creatine phosphate, 2.2 mM MgCl₂, 40 U RNasin and 3 U RNase H at 37 °C for 15 min and at 30 °C for 45 min. Recombinant purified SXL and U2AF⁶⁵ were prepared as described^{8,13}. Recombinant purified U2AF³⁵ was purified from baculovirus-infected cells as described⁹.

Site-specifically labelled pre-mRNAs

These were obtained as described²² by using chemically synthesized 3' RNAs 5' end-labelled with [γ-³²P]ATP and T₄ polynucleotide kinase.

Crosslinking by ultraviolet light and immunoprecipitation

These were performed as described¹⁰ on 27-μl splicing mixtures by using 35 μl of anti-U2AF⁶⁵ hybridoma supernatant, 20 μl of anti-U2AF³⁵ (ref. 9) or control anti-β-importin antisera. The precipitates were washed with 500 mM NaCl (for U2AF⁶⁵) or 100 mM NaCl (for U2AF³⁵) buffers, and the bound proteins were fractionated on SDS–10% polyacrylamide gels.

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correction

Long-range electrostatic attraction between like-charge spheres in a charged pore

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In Fig. 3, an incorrect file was plotted for the data in the inset for the isolated spheres (square symbols). This is now plotted correctly, together with a more informative caption. This correction does not affect the conclusions of our paper. □

Figure 3 Potential along the midplane between two spheres at reduced surface–surface separation distance ($L = 6.0$): isolated spheres (square symbols) and spheres confined in a pore (circles). Zero distance corresponds to the line of centres of the spheres. On the right-hand side of the main graph, the pore wall is reached at $\Psi = 5.0$.

Long-range electrostatic attraction between like-charge spheres in a charged pore

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The existence of long-range attractive electrostatic forces between particles of like charge is one of the great current controversies of colloid science. The established theory (Derjaguin–Landau–Verwey–Overbeek; DLVO) of colloidal interactions predicts that an isolated pair of like-charged colloidal spheres in an electrolyte should experience a purely repulsive screened electrostatic (coulombic) interaction^{1,2}. Direct measurements of such interactions have shown quantitative agreement with DLVO theory^{3–5}. Recent experiments, however, provide evidence that the effective interparticle potential can have a long-range attractive component in more concentrated suspensions^{6,7} and for particles confined by charged glass walls^{3,5,8–10}. It is apparent that the long-range attraction in concentrated systems is due to multi-body interactions and may have a similar explanation to the attraction observed for otherwise confined colloids. Theoretical explanations have been proposed^{11–13} but remain the subject of controversy^{14,15}. Here we present a quantitative theoretical explanation of these attractive forces between confined colloidal particles, based on direct solutions of the nonlinear Poisson–Boltzmann equation for two like-charged spheres confined in a cylindrical charged pore. The calculations show that the attraction may be explained by the redistribution of the electric double layers of ions and counterions in solution around the spheres, owing to the presence of the wall; there is thus no need to revise the established concepts underlying theories of colloidal interactions.

The calculation of the interaction between two spheres close to a planar wall, which has been measured experimentally^{6,10}, requires a full three-dimensional solution of the governing equations. However, consideration of the case of like-charge spheres confined in a long, charged cylindrical pore simplifies the calculations by reducing the dimensions of the problem to two. Nevertheless, the calculations remain directly relevant to the experimental situation and have been carried out for conditions of sphere-radius/pore-radius (sphere-radius/sphere-wall separation) ratio, sphere surface potential, pore surface potential and Debye length comparable to those occurring experimentally^{6,10}. We have solved the nonlinear Poisson–Boltzmann equation using an adaptive finite-element method with error minimization¹⁶, and have then calculated the electrostatic forces acting on the spheres.

The normalized Poisson–Boltzmann equation for a two-dimensional electrostatic double layer in cylindrical coordinates may be written as

$$\frac{\partial^2 \Psi}{\partial R^2} + \frac{1}{R} \frac{\partial \Psi}{\partial R} + \frac{\partial^2 \Psi}{\partial Z^2} = -\sigma \quad (1)$$

where the non-dimensional space-charge density is written

$$\sigma = \frac{1}{2} \sum_i z_i C_i \exp(-z_i \Psi) \quad (2)$$

with $C_i = c_i/I$ being the relative concentration. Other variables are defined in Methods. The summation is taken over all ionic species present in the electrolyte. For a symmetric 1:1 electrolyte system, equation (2) reduces to $\sigma = \sinh \Psi$. The dimensionless parameters

and coordinates are defined in accordance with the usual practice in colloid science¹⁶, $R = \kappa r$; $Z = \kappa z$; $\Psi = e\psi/kT$ and

$$\kappa = \left(\frac{e^2 \sum_i z_i^2 c_i}{\epsilon kT} \right)^{1/2} = \left(\frac{2e^2 N_A I}{\epsilon kT} \right)^{1/2}$$

where κ is the Debye parameter and $1/\kappa$ provides a measure of the range of the electrostatic interactions.

Equation (1) is solved with appropriate boundary conditions for the geometry in question. The non-dimensional parameters of relevance are the reduced potential Ψ , the scaled particle radius κa , the sphere-radius to pore-radius ratio λ , and the scaled distance between sphere centres, D ($D = \kappa d$). The electrostatic force acting on the sphere can be obtained directly by integrating the stress tensor, over the sphere surface¹⁷

$$F_E = \int_s \left[\left(\Pi + \frac{1}{2} \epsilon E^2 \right) \mathbf{I} - \epsilon \mathbf{E} \mathbf{E} \right] \cdot \mathbf{n} ds$$

where $\mathbf{E} = -\nabla \psi$ is the electric field and $ds = a^2 \sin \theta d\theta d\phi$. Owing to symmetry, this becomes

$$F_E = \epsilon \pi (\kappa a)^2 \left(\frac{kT}{e} \right)^2 \int_0^\pi |\nabla \Psi|^2 \cos \theta \sin \theta d\theta$$

The results of the calculations are shown in Fig. 1, which indicates how the force varies with the sphere centre–centre distance for two cases: one where the spheres are isolated with radius $a = 0.325 \mu\text{m}$, $\kappa a = 1.185$ and a surface potential $\Psi_s = 3.0$ (top curve); and the corresponding case in which the spheres are confined within a charged pore of surface potential $\Psi_p = 5.0$ and size ratio $\lambda = 0.13$ (bottom curve). These conditions parallel those used in previous experimental work^{6,10} for interacting spheres close to a charged planar wall.

Curve a in Fig. 1 shows that a purely repulsive interaction occurs at all distances for the isolated spheres. This is the interaction used in DLVO theory. Curve b shows that the situation is different for confined spheres of identical surface potential and with identical solution conditions. In this case, the repulsive force at shorter

Figure 1 Electrostatic force (F_E) as a function of the sphere centre–centre distance (d) for two cases. **a**, Case where the spheres are isolated with $a = 0.325 \mu\text{m}$, $\kappa a = 1.185$ and a surface potential $\Psi_s = 3.0$. **b**, The corresponding case where the spheres are confined within a charged pore of surface potential $\Psi_p = 5.0$ and size ratio $\lambda = 0.13$. These conditions parallel those in previous experimental work^{6,10} for interacting spheres close to a charged planar wall.

sphere–sphere separation distances is essentially the same as that for the isolated spheres. However, as the separation increases, so the repulsive force becomes less than that for the isolated spheres. Eventually, at even greater distances, the force changes sign, that is it becomes attractive. At very large distances, the force approaches zero. The attractive minimum is similar in form to those previously reported experimentally^{6,10}. The magnitude of the attractive interaction potential corresponding to the force–distance curve in Fig. 1 is about an order of magnitude greater than the experimental value^{6,10} for a planar surface due to the different geometry in the calculations (cylindrical) and possibly some uncertainty in the experimental surface potential. It is, however, of the order expected for interactions in concentrated colloidal dispersions²⁰, for which the cylindrical geometry is a useful analogy. It should be noted that the attractive minimum arises naturally when proper account is taken of the presence of the wall in the calculations. It is not necessary to introduce any further assumptions, and the explanation is based on established colloid theory.

The attractive force arises as a result of a redistribution of the static electrical double layers around the spheres caused by the presence of the wall. This is apparent in Fig. 2, where isopotential lines are shown for the problem considered. Each part of the figure shows a half-section which, because of symmetry, is sufficient to describe the physical reality. (Numerical computation also makes use of the plane of symmetry between the spheres.) Figure 2a shows the calculated potential distribution for the isolated spheres; Fig. 2b shows the calculated potential distribution for the spheres confined in a pore. Comparison shows that in the latter case the potential distribution is disturbed both between the spheres and on opposing sides of the spheres. It is this modified distribution that results in a net attractive force due to the presence of the pore wall. This modified distribution is shown quantitatively in Fig. 3, which shows the potential along the midplane between the spheres for the two cases. In the absence of the wall, the potential along this plane is low at all distances. However, the presence of the wall induces a significant potential between the spheres (Fig. 3, inset).

Our calculations confirm speculation that the attraction between confined spheres may result from the electrostatic influence of the confining plates⁸. Further, the case of two interacting spheres in a tube could be taken as a very first approximation to multiparticle interactions in concentrated systems. The attractive minima calcu-

lated here could therefore provide the basis of an explanation for phase separation and the formation of ordered structures in some concentrated colloidal systems^{6,7}. On this basis, curve b of Fig. 1 also shows that the repulsive force between particles in concentrated systems is expected to be less than that for isolated pairs of spheres, even for separations at which no attractive force exists, as has been found experimentally. The assessment provided here is in agreement with previous qualitative explanations of phase separation¹⁸. Other workers have also shown theoretically that a purely repulsive screened-Coulomb (DLVO) interaction between charged colloidal spheres is compatible with phase separation at low ionic strength¹⁹. It is not necessary to introduce a new description of interaction, such as a Sogami–Ise potential, as has been suggested²⁰. Indeed, the Sogami–Ise approach^{11,12} indicates a long-range attractive potential even for a pair of isolated spheres, which we do not find.

Our calculations indicate that further experimental and theoretical investigations of these phenomena could be very rewarding, for long-range attraction may have an important influence on the properties of colloids of industrial significance. Our results also show that the existence of such attraction does not in itself lead to a requirement to reformulate the basis of existing theories of colloidal systems. □

Methods

Variables. a , particle radius (m); c_i , concentration of ion species i (kmol m⁻³); C_i , relative concentration of ion species (c_i/I); d , centre–centre separation distance (m); D , reduced centre–centre distance; e , electronic charge (1.602 × 10⁻¹⁹ C); E , electric field (V m⁻¹); F_E , electrostatic force (N); I , ionic strength of the electrolyte, in kmol m⁻³ ($= (\sum z_i^2 c_i)/2$); $\mathbf{I}$, unit tensor; k , Boltzmann constant (1.381 × 10⁻²³ J K⁻¹); $\mathbf{n}$, outward normal; N_A , Avogadro's number (6.022 × 10²⁶ kmol⁻¹); r , radial coordinate (m); R , dimensionless coordinates ($R = \kappa r$); s , particle surface area (m²); T , absolute temperature (K); z , axial coordinate (m); Z , dimensionless coordinates ($Z = \kappa z$); z_i , charge number of ion species (i); ϵ , permittivity of the electrolyte ($= \epsilon_0 \epsilon_r$), in F m⁻¹; ϵ_0 , permittivity of vacuum (8.854 × 10⁻¹² in F m⁻¹); ϵ_r , relative permittivity (dielectric constant); κ , Debye parameter (m⁻¹); θ , angle subtended at a centre of circle by an arc (rad); λ , sphere–radius/pore–radius ratio; Π , difference in local osmotic pressure (N m⁻²); σ , non-dimensional space charge density; ϕ , azimuth angle in a plane normal to the axis (rad); ψ , electric potential (V); Ψ , reduced potential; Ψ_s , reduced potential at sphere surface; Ψ_p , reduced potential at pore wall.

Figure 2 Calculated isopotential lines for the problem considered. A half-section of the physical geometry is shown, with the line of symmetry lying at the bottom. **a**, Isolated spheres; **b**, spheres confined in a pore. The pore wall is at the top.

Figure 3 Potential along the midplane between two spheres: isolated spheres (square symbols) and spheres confined in a pore (circles). Zero distance corresponds to the line of centres of the spheres. On the right-hand side of the main graph, the pore wall is reached at $\Psi = 5.0$.

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Non-volatile holographic storage in doubly doped lithium niobate crystals

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Photorefractive materials are being widely investigated for applications in holographic data storage¹. Inhomogeneous illumination of these materials with an optical interference pattern redistributes charge, builds up internal electric fields and so changes the refractive index. Subsequent homogeneous illumination results in light diffraction and reconstructs the information encoded in the original interference pattern. A range of inorganic and organic photorefractive materials are known², in which thousands of holograms of high fidelity can be efficiently stored, reconstructed and erased. But there remains a problem with volatility: the read-out process usually erases the stored information and amplifies the scattered light. Several techniques for ‘fixing’ holograms have been developed^{3–6}, but they have practical disadvantages and only laboratory demonstrators have been built^{7–10}. Here we describe a resolution to the problem of volatility that should lead to the realization of a more practical system. We use crystals of lithium niobate—available both in large size and with excellent homogeneity—that have been doped with two different deep electron traps (iron and manganese). Illumination of the crystals with incoherent ultraviolet light during the record-

Figure 1 Band diagram of LiNbO₃ doped with iron (a) and doubly doped with iron and manganese (b). CB, conduction band; VB, valence band. Manganese has a deeper energy level than iron. Both elements occur in two different valence states. Electrons are excited into the conduction band from Fe²⁺ either by visible light or by ultraviolet light, or from Mn²⁺ by ultraviolet light only. Conduction-band electrons can recombine with Fe³⁺ or with Mn³⁺.

ing process permits the storage of data (a red-light interference pattern) that can be subsequently read, in the absence of ultraviolet light, without erasure. Our crystals show up to 32 per cent diffraction efficiency, rapid optical erasure of the stored data is possible using ultraviolet light, and light scattering is effectively prevented.

Build-up of space-charge fields in photorefractive materials requires redistribution of charge. Transition-metal ions can occur in inorganic crystals in different valence states: for example, iron is present in LiNbO₃ as Fe²⁺ and Fe³⁺ (ref. 11). The energy level of such a centre is located in the gap between valence and conduction band; Fig. 1a illustrates this. Iron is a deep centre, and hence thermal excitations are negligible. Light, however, excites electrons from Fe²⁺, the electrons migrate in the conduction band and finally they are trapped somewhere else by Fe³⁺ sites. The dominant charge driving force in LiNbO₃ is the bulk photovoltaic effect, which causes the excited electrons to migrate in a preferred direction. Drift and diffusion can also contribute to the movement of the charge carriers. Reconstruction of stored information, which requires homogeneous illumination with light of the recording wavelength, causes uniform electron excitation. As a result, the charge pattern is ‘washed out’ and the hologram becomes erased.

One approach to obtaining non-volatile storage is to copy the space-charge pattern into a pattern of immobile ions³ (‘thermal fixing’). Ions become mobile if the crystals are heated; they migrate to compensate the space-charge field and after cooling they become immobile again. The resulting ion pattern cannot be erased by light. Alternatively, the recorded space-charge field can be copied into ferroelectric domains⁴ (‘electrical fixing’). This is accomplished through application of external electric fields, which switch ferroelectric domains in the regions where the external and internal fields add up. The domain pattern is also stable against further illumination. Unfortunately, heating or application of large external fields is not practical and rapid refreshing of the memory is not possible. Two-step recording⁵ is an all-optical approach for non-volatile storage: recording light of low photon energy and sensitizing light

Long-range electrostatic attraction between like-charge spheres in a charged pore

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The normalized Poisson–Boltzmann equation for a two-dimensional electrostatic double layer in cylindrical coordinates may be written as

$$\frac{\partial^2 \Psi}{\partial R^2} + \frac{1}{R} \frac{\partial \Psi}{\partial R} + \frac{\partial^2 \Psi}{\partial Z^2} = -\sigma \quad (1)$$

where the non-dimensional space-charge density is written

$$\sigma = \frac{1}{2} \sum_i z_i C_i \exp(-z_i \Psi) \quad (2)$$

with $C_i = c_i/I$ being the relative concentration. Other variables are defined in Methods. The summation is taken over all ionic species present in the electrolyte. For a symmetric 1:1 electrolyte system, equation (2) reduces to $\sigma = \sinh \Psi$. The dimensionless parameters

and coordinates are defined in accordance with the usual practice in colloid science¹⁶, $R = \kappa r$; $Z = \kappa z$; $\Psi = e\psi/kT$ and

$$\kappa = \left(\frac{e^2 \sum_i z_i^2 c_i}{\epsilon kT} \right)^{1/2} = \left(\frac{2e^2 N_A I}{\epsilon kT} \right)^{1/2}$$

where κ is the Debye parameter and $1/\kappa$ provides a measure of the range of the electrostatic interactions.

Equation (1) is solved with appropriate boundary conditions for the geometry in question. The non-dimensional parameters of relevance are the reduced potential Ψ , the scaled particle radius κa , the sphere-radius to pore-radius ratio λ , and the scaled distance between sphere centres, D ($D = \kappa d$). The electrostatic force acting on the sphere can be obtained directly by integrating the stress tensor, over the sphere surface¹⁷

$$F_E = \int_s \left[\left(\Pi + \frac{1}{2} \epsilon E^2 \right) \mathbf{I} - \epsilon \mathbf{E} \mathbf{E} \right] \cdot \mathbf{n} ds$$

where $\mathbf{E} = -\nabla \psi$ is the electric field and $ds = a^2 \sin \theta d\theta d\phi$. Owing to symmetry, this becomes

$$F_E = \epsilon \pi (\kappa a)^2 \left(\frac{kT}{e} \right)^2 \int_0^\pi |\nabla \Psi|^2 \cos \theta \sin \theta d\theta$$

The results of the calculations are shown in Fig. 1, which indicates how the force varies with the sphere centre–centre distance for two cases: one where the spheres are isolated with radius $a = 0.325 \mu\text{m}$, $\kappa a = 1.185$ and a surface potential $\Psi_s = 3.0$ (top curve); and the corresponding case in which the spheres are confined within a charged pore of surface potential $\Psi_p = 5.0$ and size ratio $\lambda = 0.13$ (bottom curve). These conditions parallel those used in previous experimental work^{6,10} for interacting spheres close to a charged planar wall.

Curve a in Fig. 1 shows that a purely repulsive interaction occurs at all distances for the isolated spheres. This is the interaction used in DLVO theory. Curve b shows that the situation is different for confined spheres of identical surface potential and with identical solution conditions. In this case, the repulsive force at shorter

Figure 1 Electrostatic force (F_E) as a function of the sphere centre–centre distance (d) for two cases. **a**, Case where the spheres are isolated with $a = 0.325 \mu\text{m}$, $\kappa a = 1.185$ and a surface potential $\Psi_s = 3.0$. **b**, The corresponding case where the spheres are confined within a charged pore of surface potential $\Psi_p = 5.0$ and size ratio $\lambda = 0.13$. These conditions parallel those in previous experimental work^{6,10} for interacting spheres close to a charged planar wall.

sphere–sphere separation distances is essentially the same as that for the isolated spheres. However, as the separation increases, so the repulsive force becomes less than that for the isolated spheres. Eventually, at even greater distances, the force changes sign, that is it becomes attractive. At very large distances, the force approaches zero. The attractive minimum is similar in form to those previously reported experimentally^{6,10}. The magnitude of the attractive interaction potential corresponding to the force–distance curve in Fig. 1 is about an order of magnitude greater than the experimental value^{6,10} for a planar surface due to the different geometry in the calculations (cylindrical) and possibly some uncertainty in the experimental surface potential. It is, however, of the order expected for interactions in concentrated colloidal dispersions²⁰, for which the cylindrical geometry is a useful analogy. It should be noted that the attractive minimum arises naturally when proper account is taken of the presence of the wall in the calculations. It is not necessary to introduce any further assumptions, and the explanation is based on established colloid theory.

The attractive force arises as a result of a redistribution of the static electrical double layers around the spheres caused by the presence of the wall. This is apparent in Fig. 2, where isopotential lines are shown for the problem considered. Each part of the figure shows a half-section which, because of symmetry, is sufficient to describe the physical reality. (Numerical computation also makes use of the plane of symmetry between the spheres.) Figure 2a shows the calculated potential distribution for the isolated spheres; Fig. 2b shows the calculated potential distribution for the spheres confined in a pore. Comparison shows that in the latter case the potential distribution is disturbed both between the spheres and on opposing sides of the spheres. It is this modified distribution that results in a net attractive force due to the presence of the pore wall. This modified distribution is shown quantitatively in Fig. 3, which shows the potential along the midplane between the spheres for the two cases. In the absence of the wall, the potential along this plane is low at all distances. However, the presence of the wall induces a significant potential between the spheres (Fig. 3, inset).

Our calculations confirm speculation that the attraction between confined spheres may result from the electrostatic influence of the confining plates⁸. Further, the case of two interacting spheres in a tube could be taken as a very first approximation to multiparticle interactions in concentrated systems. The attractive minima calcu-

lated here could therefore provide the basis of an explanation for phase separation and the formation of ordered structures in some concentrated colloidal systems^{6,7}. On this basis, curve b of Fig. 1 also shows that the repulsive force between particles in concentrated systems is expected to be less than that for isolated pairs of spheres, even for separations at which no attractive force exists, as has been found experimentally. The assessment provided here is in agreement with previous qualitative explanations of phase separation¹⁸. Other workers have also shown theoretically that a purely repulsive screened-Coulomb (DLVO) interaction between charged colloidal spheres is compatible with phase separation at low ionic strength¹⁹. It is not necessary to introduce a new description of interaction, such as a Sogami–Ise potential, as has been suggested²⁰. Indeed, the Sogami–Ise approach^{11,12} indicates a long-range attractive potential even for a pair of isolated spheres, which we do not find.

Our calculations indicate that further experimental and theoretical investigations of these phenomena could be very rewarding, for long-range attraction may have an important influence on the properties of colloids of industrial significance. Our results also show that the existence of such attraction does not in itself lead to a requirement to reformulate the basis of existing theories of colloidal systems. □

Methods

Variables. a , particle radius (m); c_i , concentration of ion species i (kmol m⁻³); C_i , relative concentration of ion species (c_i/I); d , centre–centre separation distance (m); D , reduced centre–centre distance; e , electronic charge (1.602×10^{-19} C); E , electric field (V m⁻¹); F_E , electrostatic force (N); I , ionic strength of the electrolyte, in kmol m⁻³ ($= (\sum z_i^2 c_i)/2$); $\mathbf{I}$, unit tensor; k , Boltzmann constant (1.381×10^{-23} J K⁻¹); $\mathbf{n}$, outward normal; N_A , Avogadro's number (6.022×10^{26} kmol⁻¹); r , radial coordinate (m); R , dimensionless coordinates ($R = \kappa r$); s , particle surface area (m²); T , absolute temperature (K); z , axial coordinate (m); Z , dimensionless coordinates ($Z = \kappa z$); z_i , charge number of ion species (i); ϵ , permittivity of the electrolyte ($= \epsilon_0 \epsilon_r$), in F m⁻¹; ϵ_0 , permittivity of vacuum (8.854×10^{-12} in F m⁻¹); ϵ_r , relative permittivity (dielectric constant); κ , Debye parameter (m⁻¹); θ , angle subtended at a centre of circle by an arc (rad); λ , sphere–radius/pore–radius ratio; Π , difference in local osmotic pressure (N m⁻²); σ , non-dimensional space charge density; ϕ , azimuth angle in a plane normal to the axis (rad); ψ , electric potential (V); Ψ , reduced potential; Ψ_s , reduced potential at sphere surface; Ψ_p , reduced potential at pore wall.

Figure 2 Calculated isopotential lines for the problem considered. A half-section of the physical geometry is shown, with the line of symmetry lying at the bottom. **a**, Isolated spheres; **b**, spheres confined in a pore. The pore wall is at the top.

Figure 3 Potential along the midplane between two spheres: isolated spheres (square symbols) and spheres confined in a pore (circles). Zero distance corresponds to the line of centres of the spheres. On the right-hand side of the main graph, the pore wall is reached at $\Psi = 5.0$.

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Non-volatile holographic storage in doubly doped lithium niobate crystals

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Photorefractive materials are being widely investigated for applications in holographic data storage¹. Inhomogeneous illumination of these materials with an optical interference pattern redistributes charge, builds up internal electric fields and so changes the refractive index. Subsequent homogeneous illumination results in light diffraction and reconstructs the information encoded in the original interference pattern. A range of inorganic and organic photorefractive materials are known², in which thousands of holograms of high fidelity can be efficiently stored, reconstructed and erased. But there remains a problem with volatility: the read-out process usually erases the stored information and amplifies the scattered light. Several techniques for 'fixing' holograms have been developed^{3–6}, but they have practical disadvantages and only laboratory demonstrators have been built^{7–10}. Here we describe a resolution to the problem of volatility that should lead to the realization of a more practical system. We use crystals of lithium niobate—available both in large size and with excellent homogeneity—that have been doped with two different deep electron traps (iron and manganese). Illumination of the crystals with incoherent ultraviolet light during the record-

Figure 1 Band diagram of LiNbO₃ doped with iron (a) and doubly doped with iron and manganese (b). CB, conduction band; VB, valence band. Manganese has a deeper energy level than iron. Both elements occur in two different valence states. Electrons are excited into the conduction band from Fe²⁺ either by visible light or by ultraviolet light, or from Mn²⁺ by ultraviolet light only. Conduction-band electrons can recombine with Fe³⁺ or with Mn³⁺.

ing process permits the storage of data (a red-light interference pattern) that can be subsequently read, in the absence of ultraviolet light, without erasure. Our crystals show up to 32 per cent diffraction efficiency, rapid optical erasure of the stored data is possible using ultraviolet light, and light scattering is effectively prevented.

Build-up of space-charge fields in photorefractive materials requires redistribution of charge. Transition-metal ions can occur in inorganic crystals in different valence states: for example, iron is present in LiNbO₃ as Fe²⁺ and Fe³⁺ (ref. 11). The energy level of such a centre is located in the gap between valence and conduction band; Fig. 1a illustrates this. Iron is a deep centre, and hence thermal excitations are negligible. Light, however, excites electrons from Fe²⁺, the electrons migrate in the conduction band and finally they are trapped somewhere else by Fe³⁺ sites. The dominant charge driving force in LiNbO₃ is the bulk photovoltaic effect, which causes the excited electrons to migrate in a preferred direction. Drift and diffusion can also contribute to the movement of the charge carriers. Reconstruction of stored information, which requires homogeneous illumination with light of the recording wavelength, causes uniform electron excitation. As a result, the charge pattern is 'washed out' and the hologram becomes erased.

One approach to obtaining non-volatile storage is to copy the space-charge pattern into a pattern of immobile ions³ ('thermal fixing'). Ions become mobile if the crystals are heated; they migrate to compensate the space-charge field and after cooling they become immobile again. The resulting ion pattern cannot be erased by light. Alternatively, the recorded space-charge field can be copied into ferroelectric domains⁴ ('electrical fixing'). This is accomplished through application of external electric fields, which switch ferroelectric domains in the regions where the external and internal fields add up. The domain pattern is also stable against further illumination. Unfortunately, heating or application of large external fields is not practical and rapid refreshing of the memory is not possible. Two-step recording⁵ is an all-optical approach for non-volatile storage: recording light of low photon energy and sensitizing light