Observation of Metastable Structural Excitations and Concerted Atomic Motions on a Crystal Surface

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The addition of a small number of lead atoms to a germanium(111) surface reduces the energy barrier for activated processes, and with a tunneling microscope it is possible to observe concerted atomic motions and metastable structures on this surface near room temperature. The formation and annihilation of these metastable structural surface excitations is associated with the shift in position of large numbers of germanium surface atoms along a specific row direction like beads on an abacus. The effect provides a mechanism for understanding the transport of atoms on a semiconductor surface.

Knowledge of atomic scale motions is essential for understanding dynamical phenomena on surfaces, such as diffusion, phase transitions, and epitaxial growth. Observations with field ion microscopy, together with the calculations they have motivated, have greatly improved our understanding of atomic dynamics on metal surfaces (*1*). Very few studies have been conducted on the atomic dynamics on semiconductor surfaces, the understanding of which has become more and more vital as new semiconductor technology demands control at an atomic level. Since its invention, scanning tunneling microscopy (STM) has offered the unprecedented capability to study surface structures with atomic resolution. This has shed much light on the propensity of semiconductor surfaces to adapt crystal structures with unit cell dimensions many times larger than a simple bulk termination would suggest. For example, the reconstructed Si(111) - 7 × 7 and Ge(111) - c(2 × 8) surfaces have unit cells 49 and 16 times larger, respectively, than might be expected. Owing to the development of instruments that operate at high temperatures, the phase transitions on Si(111) - 7 × 7 surfaces (*2*) as well as on Ge(111) - c(2 × 8) surfaces (*3*) have been observed. In both cases, however, atomic motions are too fast to be imaged clearly. There are also room-temperature STM observations of high-temperature Si epitaxial growth on Si(100) surfaces (*4*), but the conclusions reached regarding the anisotropy and activation energy of Si atom diffusion relied on detailed modeling of island growth rather than on direct observation.

It has been demonstrated that the frequency of individual atomic interchanges of Pb and Ge atoms can be measured on the Ge(111) - c(2 × 8) reconstructed semiconductor surface near room temperature (*5*). However, the actual atomic mechanism for this transition has remained unclear except that a large entropic barrier is necessary to explain such slow diffusion with a small activation energy. In this report, we describe how we used a small number of Pb atoms to probe activated processes on the Ge(111) - c(2 × 8) surface using a tunneling microscope. A concerted atomic motion involving an adatom row shift was identified and was shown to be part of a metastable structural surface excitation. This process provides a previously unidentified mechanism for the transport of atoms on this surface and accounts for a number of other phenomena associated with Ge(111) surfaces.

For several reasons Pb/Ge(111) - c(2 × 8) is a good candidate for the atomic scale study of dynamics on reconstructed semiconductor surfaces. The pure Ge(111) - c(2 × 8) surface is a "soft" reconstruction that undergoes a phase transition near 300°C (*3*), where most of the long-range adatom order is lost. This low transition temperature as compared with that of Si(111) - 7 × 7 [~860°C (*2*)] suggests a relatively weak bonding of Ge adatoms to the substrate. Indeed, at room temperature Ge adatoms are mobile on the Pb-doped surface as shown by a previous STM study (*5*). Furthermore, bulk Pb and Ge do not intermix and Pb atoms do not evaporate from the surface below 300°C, so Pb atoms remain at the surface after deposition (*5, 6*). Finally, because it is possible to distinguish Pb from Ge adatoms with the STM, the Pb atoms serve as markers allowing the registry and motion of Ge adatoms to be determined.

In our experiments we used a homemade tunneling microscope in an ultrahigh vacuum chamber with base pressure of 6×10^{-11} torr. The preparation and the structure of a clean Ge(111) - c(2 × 8) surface have been described elsewhere (*5, 7*). On this surface, about 0.02 monolayer of Pb was deposited from an effusion cell with a system pressure below 4×10^{-10} torr. The sample was then resistively heated on the STM stage. By careful control of the sample temperature, thermal drift of the microscope can be reduced to <0.3 Å/s within 3 hours without the use of compensating hardware or software. Typically, a constant tunneling current of 50 pA and a sample bias of +2 V were used to obtain the data presented here, which were selected from more than 1000 images taken at temperatures from 24° to 80°C.

Figure 1 shows four consecutive images of 90 Å by 90 Å, taken at 45°C, with each

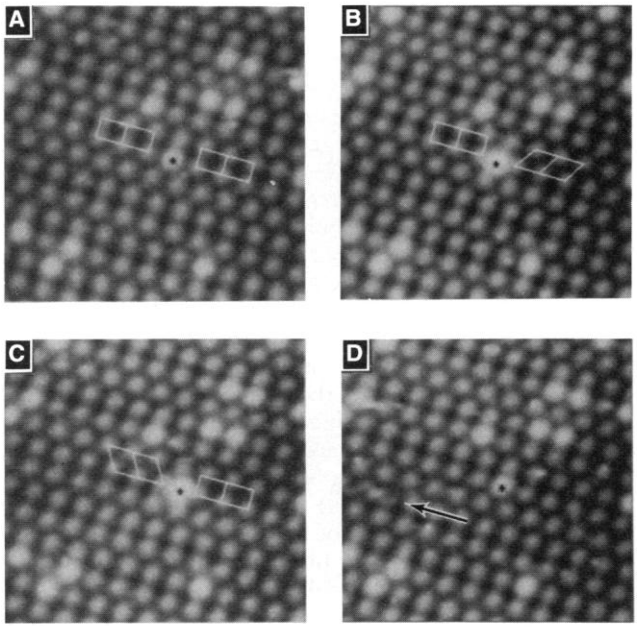

Fig. 1. (**A** to **D**) Four consecutive STM images taken at 45°C, separated by 65 s each. The images in (B) and (C) show metastable states with Pb atom * sitting on two different H_3 sites. Notice the Ge adatom structure change on both sides of Pb atom *. The 2 × 2 and c(4 × 2) structures transform into each other through an adatom row shift. In (D) the metastable state relaxes, and a new adatom row shift occurs below during data acquisition (indicated by an arrow).

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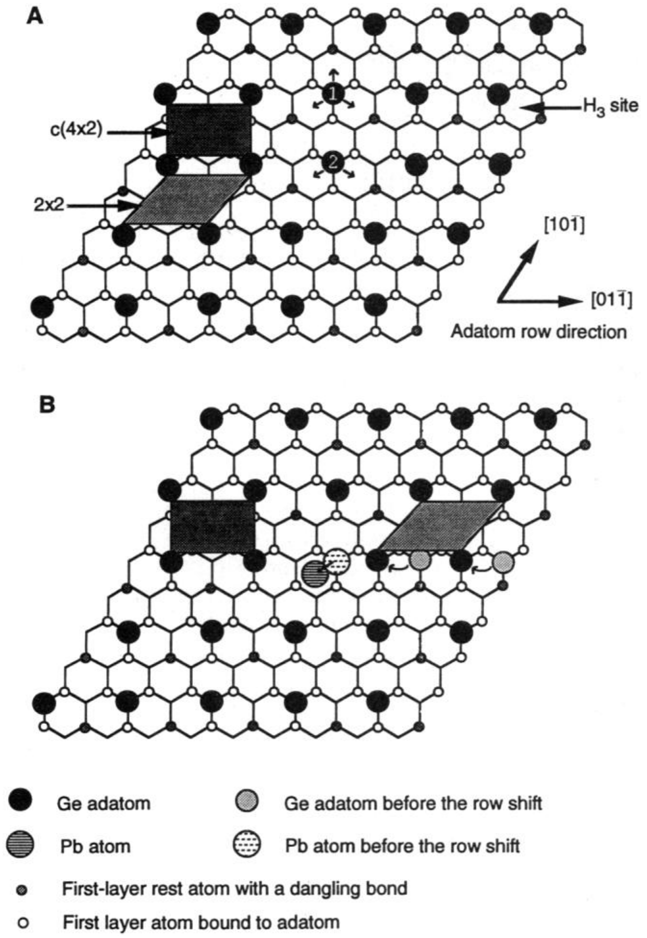

Fig. 2. (**A**) A simple adatom model of Ge(111) - c(2 × 8). We define the row direction as [01$\bar{1}$]. Subunits of 2 × 2 and c(4 × 2) are indicated by shaded areas. There are two inequivalent adatom sites. A substitutional Pb atom on adatom site 1 can hop to three adjoining H_3 sites, whereas it can hop to only two on adatom site 2, because of the availability of rest atom dangling bonds. (**B**) A model for a metastable surface structural excitation. The Pb atom moves from a T_4 site to an adjoining H_3 site, accompanied by a cascade of Ge atom transitions along the adatom row.

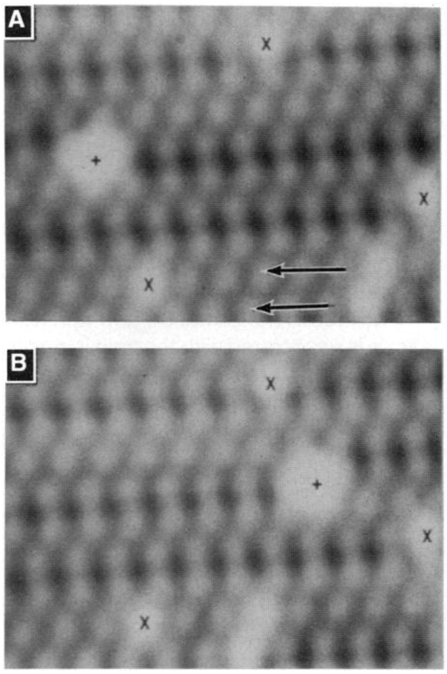

Fig. 3. Long jumps of Pb atoms. The image in (**B**) was taken about 100 s after that in (**A**). Three Pb atoms marked with an "x" serve as reference atoms in the figure. An H_3-site Pb atom (indicated by a "+") moves 44 Å along the row and ends up on another H_3 site. Two substitutional Pb atoms move 24 Å down the rows, as indicated by arrows. This H_3-site Pb atom is not as well resolved as that in Fig. 1 because there are fewer pixels per unit surface area. The corrugation of the three nearest neighbor Ge adatoms is somewhat masked by the much brighter H_3-site Pb atom.

image separated from the next by 65 s (which is essentially the time needed to take each picture). Dark and bright atoms represent Ge and Pb atoms, respectively. Atomic motions associated with structural changes and relaxation are shown in Fig. 1, A through D. These motions are observed only 10 to 20% as often as the simple interchange of Pb and Ge atoms, which has been reported previously (5).

One can analyze the motions observed in Fig. 1 in terms of an atomic model of a perfect Ge(111) - c(2 × 8) reconstruction (Fig. 2A). On a perfect c(2 × 8) reconstruction, each Ge adatom resides on a T_4 (top) site and forms three bonds with the layer underneath, which is not reconstructed (7). The STM images show only the adatoms, which are the large black circles in the figure. This structure is composed of two alternating rows of 2 × 2 and c(4 × 2) subunit cells, as indicated in the figure. The rows can be along one of three equivalent ⟨01$\bar{1}$⟩ directions in the surface plane. We define the adatom row direction in Fig. 2A as [01$\bar{1}$]. On a real Ge(111) - c(2 × 8) reconstruction, extra rows of adatoms are often present and result in three or more adatom rows in 2 × 2 or c(4 × 2) local reconstruction (7). There is another potential binding site for Pb and Ge adatoms on Ge(111) indicated in Fig. 2A, namely, the H_3 (hollow) site. This binding site is in general less favorable energetically than the T_4 site and, to our knowledge, has never before been identified as occupied in previous STM studies.

One image shows a c(2 × 8) surface with two extra adatom rows (Fig. 1A). All Pb atoms appear to replace Ge adatoms in the c(2 × 8) reconstruction. We call these "substitutional Pb atoms." However, a Pb atom (marked with an asterisk) shifts left to an H_3 site in Fig. 1B. Then we call it an "H_3-site Pb atom" to distinguish it from a substitutional Pb atom. Also, on the same row and to the right of the Pb atom, a string of Ge adatom shifts left concertedly by one primitive vector to the next T_4 sites. We call this an "adatom row shift." Notice that 2 × 2 and c(4 × 2) rows of subunit cells transform into each other by this atomic row shift, as indicated in the figure; a detailed model of this concerted motion is shown in Fig. 2B. Figure 1C shows the same Pb atom shifted right to another H_3 site accompanied by another adatom row shift (presumably after the structure relaxed back to that in Fig. 1A). The structure finally relaxes back to the original structure in Fig. 1D. Usually, we see individual excitations either like Fig. 1B or like Fig. 1C, and then the structure relaxes.

The above case demonstrates that there are two possible neighboring H_3 sites to which the Pb atom can hop. Both structures in Fig. 1, B and C, are metastable; they can last minutes at low temperatures before relaxation. We denote this process as a metastable structural surface excitation. Surprisingly, it involves the motion of very many adatoms. The length of an adatom row shift usually extends beyond our scan area. Occasionally it terminates at a preexisting defect or a domain boundary. We have never observed the creation of a vacancy, which might be expected from a partial row shift. The longest row shift we observed involves 21 Ge adatoms (corresponding to 168 Å), and the end is still beyond our scan area.

Long jumps (movements of more than one atomic spacing) of Pb atoms along the [01$\bar{1}$] row direction were also observed (Fig, 3), which shows that the previously reported "long jump" diffusion (5) can involve the adatom row shift we described above.

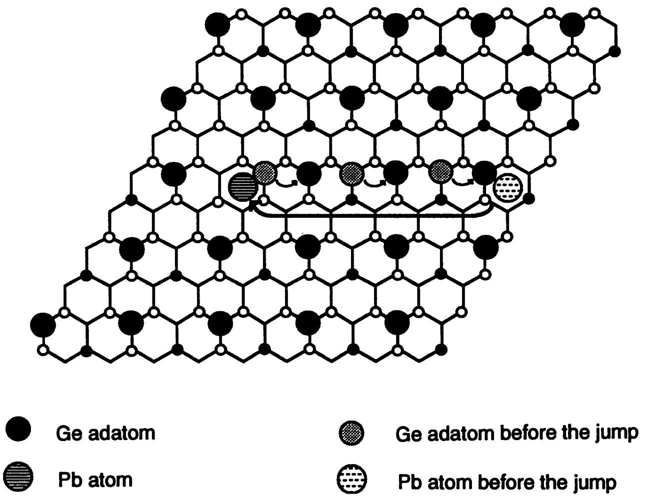

Fig. 4. Model for a long jump of an H_3-site Pb atom along an adatom row.

Two consecutive STM images of 65 Å by 90 Å taken at 50°C, separated in time by 100 s, show an H_3-site Pb atom hopping along the row 44 Å to another H_3 site (Fig. 3, A and B). A structure change [$2 \times 2 \leftrightarrow c(4 \times 2)$] attributable to adatom row shifts occurs on both sides of the H_3-site Pb atom. Also, two substitutional Pb atoms making long jumps (24 Å) down the row in Fig. 3 are indicated by arrows. More commonly, only a single substitutional Pb atom is seen making such a maneuver. As in the case of single interchanges of Pb and Ge atoms (*5*), most of the long jumps of Pb atoms are along the [$01\bar{1}$] row direction. The row direction is an easy pathway for Pb atom diffusion, and the adatom row shift can provide a mechanism for such an anisotropic motion.

Negligible mutual bulk solubility of Pb in Ge and the desorption of Pb from Ge(111) surfaces at 400°C (*6*) indicate that the Pb–Ge bond is very weak. As a result, the substitutional Pb atoms, which appear to occupy T_4 sites in STM images, can hop easily to neighboring H_3 sites by breaking one Pb–Ge bond and forming a new bond with a neighboring rest atom (see adatoms 1 and 2 in Fig. 2A). The energy barrier for this hopping should be about that of breaking one Pb–Ge bond. The total binding energy of one Pb atom on a Ge(111) adsorption site (T_4 site) has been measured by isothermal desorption to be about 1.35 eV (*6*). If a Pb atom forms three bonds with the substrate, one Pb–Ge bond energy is about 0.45 eV. This level of bonding is very weak compared with a Ge–Ge covalent bond [1.6 eV in the bulk (*8*)]. Thus, substitutional Pb atoms might jump rapidly between the T_4 sites and neighboring H_3 sites, whereas Ge atoms should be less likely to do so. Taking 0.45 eV as the activation energy, we can use the Arrhenius equation to estimate the mean lifetime for substitutional Pb atoms to stay on T_4 sites, without any other atoms moving. The mean lifetime is

$$t = R^{-1} = \nu^{-1} \exp(E_D/k_BT)$$

where R is the transition rate for an adatom to hop away from its original low-energy site, E_D is the activation energy, ν is the attempt frequency ($\sim 10^{13}$ s^{-1}), k_B is the Boltzmann constant, and T is temperature. This gives a mean lifetime of 10^{-5} s at room temperature (*9*). Our STM tip scans at about 1000 Å/s, which is too slow to image this motion. There are two inequivalent adatom sites in the $c(2 \times 8)$ reconstruction, as indicated in Fig. 2A. A Pb atom on site 1 might appear round, whereas a Pb atom on site 2 might appear elongated if it has about the same probability to occupy the T_4 and H_3 sites. However, in the STM images Pb atoms on both sites appear the same, centered on the T_4 sites. Therefore, we conclude that each substitutional Pb atom is hopping back and forth rapidly between its T_4 site and neighboring H_3 sites with a mean lifetime that is at least an order of magnitude longer on the former site. When a Ge adatom row shift occurs and traps the Pb atom on an H_3 site, a metastable structure as shown in Fig. 1 is formed (*10*). Consistent with the above conclusion regarding the substitutional Pb atoms, we have never observed the trapping of a Pb atom on an H_3 site by a neighboring substitutional Pb atom.

There is a possibility that a substitutional Pb atom hops away down the row after it goes to an H_3 site, instead of simply hopping back to its T_4 site. This causes Pb atom diffusion along the row, as observed by the STM (*5*). The vacancy that the Pb atom leaves behind can propagate through a partial adatom row shift until it recombines with the Pb atom. This idea explains the long jumps of substitutional Pb atoms along the row direction, as seen in Fig. 3. An H_3-site Pb atom of the metastable structure can also make a long jump along the row direction, so that it ends up on a different H_3 site similarly through an adatom row shift (or a partial adatom row shift). A model is drawn in Fig. 4.

Row shifts may also play an important role in the phase transition of Ge(111) - $c(2 \times 8)$ observed between 200° and 300°C. In a recent hot STM study of this phase transition fuzzy rows were observed, which were ascribed to the hopping motion of the adatoms during the imaging process (*3*). We believe that those are the adatom row shifts we report here. We did not observe this motion on the clean Ge(111) surface at temperatures between 24° and 80°C. However, the weak Pb–Ge bonding reduces the activation energy of this process so that we can observe the atomic motions at low temperatures. On a clean Ge(111) surface, Ge adatom row shifts can also occur at high temperatures, for Ge adatoms then have a good chance to hop to H_3 sites by themselves. We believe Ge adatoms form rows upon cooling from the transition temperature of $c(2 \times 8)$, and through appropriate row shifts the $c(2 \times 8)$ reconstruction forms with the occasional occurrence of three or more adatom rows in 2×2 or $c(4 \times 2)$ local arrangement. This adatom row shift also represents a previously unrecognized mechanism for atomic transport on crystal surfaces and may explain the roughness of the steps in STM images of this surface. Moreover, the accommodation of Pb atoms into substitutional sites after deposition may be accomplished by this concerted shifting of Ge adatom rows toward domain boundaries.

In addition to the adatom row shifts, we also observed cases that involve atomic motions across the rows. Some of these can even break the adatom row structure locally; Pb atom diffusion associated with these motions was also observed. These events are much less frequent than the motions involving adatom row shifts in the temperature range we have studied. A full report will be presented elsewhere (*11*).

Finally, we have tried to reduce the influence of the scanning tip of the STM by operating at very low tunneling current. Concerted motions were observed along the adatom rows irrespective of the scanning direction and thus should be characteristic of the original system. The influence of the scanning process on the diffusion of Pb atoms has also been carefully examined and has been found to have a negligible effect (*5*).

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9. This energy barrier is not exactly equal to the Pb-Ge bond energy. The barrier also depends on the configuration of surrounding adatoms and rest atom dangling bonds. Here we just want to get a crude estimate of the mean lifetime of substitutional Pb atoms on T_4 sites. Furthermore, this energy barrier should be less than 0.54 eV, the activation energy for Pb atom diffusion (*5*), for the diffusion involves breaking more than one Pb–Ge bond. Taking 0.54 eV as E_D in the Arrhenius equation, we get 0.17 ms (at room temperature), an upper bound for the mean lifetime. It is still much too fast for the scanning tip to resolve this motion.
10. A detailed discussion of the role of nearby domain walls, stacking faults, and point defects in enhancing or pinning the row shift needed to form this metastable structure will be given elsewhere (*11*).
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Direct Mechanical Measurements of the Elasticity of Single DNA Molecules by Using Magnetic Beads

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Single DNA molecules were chemically attached by one end to a glass surface and by their other end to a magnetic bead. Equilibrium positions of the beads were observed in an optical microscope while the beads were acted on by known magnetic and hydrodynamic forces. Extension versus force curves were obtained for individual DNA molecules at three different salt concentrations with forces between 10^{-14} and 10^{-11} newtons. Deviations from the force curves predicted by the freely jointed chain model suggest that DNA has significant local curvature in solution. Ethidium bromide and 4′,6-diamidino-2-phenylindole had little effect on the elastic response of the molecules, but their extent of intercalation was directly measured. Conversely, the effect of bend-inducing *cis*-diamminedichloroplatinum (II) was large and supports the hypothesis of natural curvature in DNA.

The ability of DNA to pack and fold into chromosomes or to serve as a template during transcription and replication depends on the particular elastic properties of the molecule as modified by local interactions. Light scattering, sedimentation velocity, viscometry, electro-optics, and ligase-catalyzed cyclization have been used to characterize these properties, but these bulk methods have several limitations (*1*). First, the elastic parameters are not directly observed in these measurements and must be obtained through model-dependent theories. Second, these macroscopic measurements represent ensemble averages over all accessible molecular configurations, providing little information about unlikely, extended states of the molecule. Third, measurements are often restricted to a limited range of ionic strength, temperature, and other variables.

Real-time fluorescence microscopy of single DNA molecules in solution (*2–6*) suggests that it should be possible to determine directly the strain-stress relation of single DNA molecules (*7*). These mechanical measurements could: (i) reveal the molecular mechanisms responsible for the elastic response of the molecule over a full range of forces and extensions; (ii) provide a more strict test of theories of polymer elasticity with molecules of known composition and size over a broad range of experimental conditions; and (iii) help improve present theories of gel electrophoresis (8), linear dichroism (9), and charge density (*10*).

The freely jointed chain model (FJC) treats the polymer as a chain of statistically independent (Kuhn) segments of length b whose orientations are uncorrelated in the absence of external forces. A force F acting on the free end of a molecule whose other end is attached to a fixed point stretches the polymer as each segment tends to align with the force. The external force is opposed by the polymer because of thermal agitation, which tends to disorder the segments. In this model, the elastic response of the molecule is purely entropic, and the force-dependent end-to-end distance, $\langle x \rangle$, in terms of the molecular contour length (L), the temperature T, and the Boltzmann constant k_B is (*11*):

$$\langle x \rangle = L\left(\coth\frac{Fb}{k_BT} - \frac{k_BT}{Fb}\right) = L\,\mathscr{L}\left(\frac{Fb}{k_BT}\right) \tag{1}$$

The expression in brackets is the Langevin function ($\mathscr{L}$). This relation can be inverted to give:

$$F = \frac{k_BT}{b}\mathscr{L}^{-1}\left(\frac{\langle x \rangle}{L}\right) \tag{2}$$

This model accounts for the bending rigidity of the molecule in terms of the single parameter b. The stiffer the molecule, the longer the Kuhn segment. An alternative description, the worm-like chain (WLC) (*12*), uses persistence length as a measure of chain stiffness. In the absence of external forces the Kuhn segment corresponds to twice the persistence length of the molecule (*12*).

Individual multimers of λ-DNA (48.5 kbp) were chemically attached by one of their ends to a glass slide and by their other end to a magnetic bead (*13*). A cover slip was used to enclose the anchored molecules into a fluid microchamber that fits on a microscope stage (Fig. 1A). The tethered beads were subjected to various combinations of magnetic and hydrodynamic forces applied along perpendicular directions by using movable magnets and variable flows (Fig. 1A). Arbitrarily large forces could be applied with flow, but their magnitude was difficult to determine directly because flow shear next to the glass surfaces made fluid velocity difficult to estimate there. Conversely, magnetic forces are typically not greater than 1 piconewton (pN) but can be made arbitrarily small and are easier to measure (see below). Flow forces could then be calibrated against the measured magnetic forces.

During an experiment, each combination of magnetic and hydrodynamic force displaced the bead and extended the molecule along a particular angle θ relative to the direction of the magnetic force (Fig. 1B). The greater the flow, the larger the angle with the horizontal axis. As opposite directions of the magnetic and flow forces were combined, the bead positions described a characteristic "ellipse" (Fig. 1B). Positions were observed on a television monitor and recorded by means of a computer cursor (*14*). From these data, the extension of the molecule from its point of attachment to the glass and the relative magnitudes of the magnetic and hydrodynamic forces were obtained.

Four ethidium-stained λ-dimers tether-

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