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Graphical abstract

The motion of an ion in a synthetic molecular ion channel

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Highlights

- A synthetic channel consists of 14 stack-linked crown ether rings. ► In a NaCl electrolyte solution Na^+ but not Cl^- ions enter the channel.
- The Na^+ ions undergo damped oscillations along the channel axis. ► An electric field changes the oscillation amplitude and frequency.
- The ions exit the channel at a critical value of electric field.

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The motion of an ion in a synthetic molecular ion channel

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ABSTRACT

A molecular dynamics investigation is conducted on the passive transport of Na⁺ ions through a synthetic channel in aqueous NaCl medium, the channel consisting of fourteen 15-crown-5 rings rigidly linked in a stacked configuration. The investigation studies the entry and exit of Na⁺ ions by applied electric fields; the Cl[−] ions are not admitted because of the channel's unfavourable axial electrostatic potential for anions, and the water molecules are too large to enter. The Na⁺ ions exhibit damped oscillatory dynamics, for which frequencies and damping parameters are calculated, and possible applications of the system are discussed.

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1. Introduction

Syntheses of nanochemical molecular systems have resulted in the creation of interesting mechanical devices [1] and may soon create ones sharing features of living cells. Since synthetic materials may well have lower complexities than those of the biological systems which they model, it is hoped that an analysis of the kinetics and energetics of ion transport through a simple molecular ion channel that is designed for such a study may contribute to an understanding of ion migration in biological systems. These systems might include the transport of Na⁺ and Cl[−] ions through protein channels across the membrane of a biological cell, for which a complete structural, kinetic and thermodynamic description is currently beyond the capability of theory and simulation.

In this work a molecular dynamics (MD) investigation will be conducted in which ions are transported through a synthetic, structurally simple molecular channel (Fig. 1) consisting of fourteen stacked 15-crown-ether-5 rings (15-CE-5) in which each CE ring is covalently bonded to a similar one on either side of it in a stacked configuration. A previous work considered a two-dimensional lattice consisting of several 'floppy' channels in which the stacked rings were mutually linked by methylene (CH₂) groups, mounted in a bilayer membrane [2,3]. With the channels connecting two salt solutions it was shown that they allowed the passage of cations, anions and solvent molecules between the layers, but that the Na⁺ ions showed significantly greater mobility than the Cl[−] ions. Water molecules, which were also admitted, played a role

in the migration of the ionic species. In a subsequent work [4] the channel was made rigid by a 'bracket' consisting of an amine segment –CH₂–NH–CH₂– linking the CEs at 10 points on each rings rather than five as for the methylenes. When this rigid channel bridged the two aqueous LiF solutions across the membrane, it acted as a 'cation trap', admitting passage to only the Li⁺ cations from the salt layers. It was concluded that its ability to enter the channels and its subsequent motion were principally of electrostatic origin, for while the cations could do this, the solvent water molecules and even the F[−] ions (whose radius is smaller than that of Na⁺) failed to do so. There was also a suggestion that the Li⁺ would undergo an oscillatory motion in the channel, a feature that will be investigated in this work.

2. The molecular system

2.1. The ion transporter channel

As the channel in this investigation is a solute in an aqueous electrolyte solution it is rendered hydrophilic by OH on one carbon atom of each amine linking segment which becomes –CH–NH–COH– as shown in Fig. 1a. Both C atoms are bonded to a CE ring on either side of the unit (or to just one if they are terminal rings, the remaining site being occupied by a H atom). The structure is thus characterised by two adjacent rings constituting the basic unit that repeats along the length of the channel. The smaller one is the (O–C–C)₅ segments with a diameter 4.10–6.10 Å; the larger has the five 'bracket' segments [–CH–NH–C(OH)–]₅ whose diameter is 7.62–9.24 Å (but these segments are not mutually linked). The ion transporter is thus a molecular channel with overall length

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Fig. 1. The molecular channel containing fourteen stacked 15-crown ether-5 rings viewed (a) along, and (b) perpendicular, to the axis.

35.75 Å and consists of alternating narrow and wide rings which Fig. 1b shows to define 13 molecular chambers or cavities, with a repeat distance of 2.5 Å.

2.2. Molecular dynamics

Structural geometries were taken from literature values of diffraction and computed quantities on model compounds [5], Refs. in [4,2,3]. Partial atomic charges were obtained from Restricted Hartree-Fock (RHF) calculations performed by the Gaussian package [6] using 6-311 basis sets supplemented by (2p, 2d, 3d and 3f) polarisation functions, on model molecules consisting of a pair of (CH–NH–HOC)-linked 5-CE-15 rings, hydrogenated where necessary. The resulting charges were compared with those obtained from calculations on smaller molecules on which Møller-Plesset (MP2) corrections had been performed. (These were acetic acid CH₃COOH and dimethylamine H₃C–NH–CH₃.) The consistency between the latter and the RHF results was deemed to be sufficient to accept the RHF charges without reviewing their values other than those resulting from the minor adjustments involved in dehydrogenating the 2-ring model molecules that had been deployed as models for the quantum calculations. The problem of atomic charges was discussed in an earlier work [4,3].

Molecular dynamics (MD) calculations were performed using DL-POLY [7] under constant volume-temperature and also constant pressure-temperature conditions (Evans NVT and Hoover NPT thermostats). Simulations of several hundred thousand to a million time-steps, where a time-step was 1 femtosecond (10^{–15} s), were first performed to ensure that the MD system had achieved thermal and dynamic equilibrium, while the running times for the migrations of the ions in the channel were much shorter. The simulation box consisted of a 36 × 36 × 75 Å cell containing the 685-atom channel (Fig. 1) in an aqueous solution of

various molarities (0–5 M) in NaCl, about 3500 water molecules and a varying number of ions depending on the salt concentration.

The bond and non-bond atom-pair interactions were DREIDING (6–12) atomistic potentials [8] except those for the ions, for which those of Åquist [9] were used for Na⁺, and those of Lee and Rasaiah [10] for Cl[–]. As the use of these potentials, together with those of Berendsen's SPC model [11] successfully simulate the solvation of the ions by the water molecules no additional electronic polarisation effects were allowed for (which would be inconsistent with the use of the atomistic potential described). Potential functions for heteroatomic pairs were calculated by the geometric-mean rule. Constant DREIDING values were used for all bonded atom pairs (bonds) and atom triads (bond angles).

3. Results

3.1. Axial electrostatic potential

When the channel is made rigid by the amine 'clamping' structural unit described in Section 1, the principal factor governing the entry of the ions into the channel and their subsequent trajectories is the electrostatic potential along the axis of the channel [4]. As a result, while the deformable channel in the phospholipid membrane [2] distorts to transport the anions and solvent, the rigid channel was found to admit Li⁺ cations but water molecules from the bulk solution, and even the smallest halide ion F[–], were denied entry [4]. (Even when the F[–] ion was inserted in a channel cavity it could not be displaced by more than 0.5 Å by strong electric fields.)

Fig. 2 shows profiles of the channel's axial electrostatic potential plotted for the 35 Å channel length plus 20 Å on either side. The two curves are the potentials for the isolated channel and for that when contributions are included from the aqueous medium consisting of water molecules and ions in a 0.1 M NaCl solution. Despite the particles' translations and reorientations in the bulk

Fig. 2. The electrostatic potential (in volts) along the channel axis.

medium their contribution over 10^6 time steps does not average out to zero. The greater negative values for the case where the solution is included suggests that ions and/or water molecules may be partially immobilised on the channel walls. The small peaks shown by the same trace on either side of the molecular channel's range, where the electrostatic potential is several volts, may have the same origin. The finding that neither the shift in the potential well nor the peaks near the channel termini are eliminated even after 5 million time steps (10 ns) suggests the presence of ions and solvent close to the channel whose mobilities are reduced by the longer relaxation times of the molecular species of the solution in this region. This conclusion is consistent with the pair radial distribution functions (rdf) plotted for the ions in the simulation in Fig. 3, which shows the association of the Na^+ and Cl^- respectively with the negatively charged O and positively charged C atoms of the channel. A comparison of the two rdf traces in the 2–3 Å interval suggests that there is a closer association of the Cl^- than of the Na^+ ion with the channel surface – a fact that would lead to a more negative axial potential. A similar result was found (but not presented in Fig. 3) by rdf curves for the interaction of the oxygen atoms in the water solvent with the channel carbons, indicating that water molecules near the channel are also partially immobilised. Increasing the NaCl concentration in the solution to 5 M (near saturation) produced a potential that was just under 1 V more negative than the one shown for the 0.1 M solution. This may also be explained by the association of anions on the channel surface.

The ~13 V potential drop between the channel ends and its centre would be expected to provide a favourable negative electrostatic environment for the migrating cations. As the water molecules and the Cl^- ions show no sign of entry into the channel, the present work will report the transport of only the Na^+ ions and its analysis. In their migrations from the bulk solution to the channel, the ions leave the low energy environment associated with

their hydrated condition to another low energy that is the channel interior [4]. Between these two regions (i.e. at the entrances to the channel) there is an interface region with steep energy walls forming an energy barrier, where the migrating ions' stabilities do not benefit either from the full negative potential on the channel axis nor from the hydration in the aqueous solution.

3.2. The ion migration

It was found that the initiation time taken for a Na^+ ion to approach the terminal ring of the molecular channel sufficiently closely to effect entry from the bulk electrolyte solution was long in comparison with the time intervals that are permitted by MD running times (~1 ns). Accordingly, the dynamics were made tractable in time by placing equal numbers of Na^+ and Cl^- ions in the vicinity of the channel ends and entry was made possible by applying stationary electric fields along the axis (z) of the channel. Although the response of the ions to an electric field is in itself interesting, its investigation is mainly to overcome the problems associated with the long MD times awaiting a successful ion entry. Where possible, effects of the field will be eliminated in the analysis of the ion migrations particularly for those properties that do not depend explicitly on electric field.

3.3. Oscillations in the channel

Since the determination of the response of the Na^+ ion to the electric fields requires it to be maintained at a definite orientation, the channel was held in position by freezing the coordinates of one H atom in each of its terminal CE rings. In those sections of the work in which an external electric field is not applied these H atoms were unclamped and the whole molecular channel was allowed to float freely in the aqueous NaCl solution.

It was found that Na^+ ions in the bulk of the aqueous solution did not enter the channel when the electric field applied along the axis was less than $2 \text{ V } \text{\AA}^{-1}$. This was a substantially higher field than those to be described below, that control the exit from the channel. The field confers velocities of up to $200 \text{ \AA fs}^{-1}$ on the ions, values which are an order of magnitude greater than those controlling transport within the channel, and several times that required to expel Na^+ from the channel. Consequently after entry the ion would 'drop' to the bottom of the 12 V electrostatic energy well, thereby gaining sufficient kinetic energy (and velocity in the direction of the applied field) to propel it through the channel and to exit at the downfield end.

Fig. 3a monitors the axial position of the Na^+ ion during a 5000 time-step (5 ps) interval in smaller axial electric fields 0.0, 0.5, 0.7 and $1.0 \text{ V } \text{\AA}^{-1}$. As the channel's z coordinate goes from 35.3 to 2.89 Å the figure shows that application of a field of 0.7 or more

Fig. 3. Radial distribution functions for the associations of migrant ions with the molecular channel. (a) Na^+ with channel oxygen atoms and (b) Cl^- with channel H atoms.

is required to permit the exit of the Na^+ ion from the channel. The trajectories of the low-field cases are characterised by an apparent oscillation of the ion between sites in the channel that are defined by the molecular chambers between the CE rings.

Oscillations are found for all conditions in which the ions are retained by the channel, including, as we shall see below, those where no electric field was applied. However they are more prominent in certain ranges of electric field ($0.4\text{--}0.6\text{ V \AA}^{-1}$) and the $\mathcal{E} = 0.5$ trace selected for illustration in Fig. 3b. The shapes of the waves make it clear that the oscillations are highly damped and are not harmonic. This can be explained as follows. When the motion of the Na^+ ion is in the same direction as that of the electric field, the ion is swept downfield towards the opposite end of the channel. There it is brought to rest by the wall of the electrostatic energy well, before reversing its motion describing the upfield part of the cycle, and returning towards the channel end from which it first entered. The resulting asymmetric waves are explained by the shape of the electrostatic energy well. The sharp maxima are the result of the steep walls of the upper portion of the energy well while the ion's trajectory near the minima are blunt as the forward motion is resumed by its reflection at the gentler slopes of the walls in this region. Fig. 3b shows that the ion finally comes to rest in a downfield region of the well (at 0.84 of the channel length).

When the applied field applied is not greater than $0.6\text{ V \AA}^{-1}$ the Na^+ ion is subject to forces that accelerate it to points on the downfield wall that are short of the critical z-coordinate (the broken line at $z = 37.9\text{ \AA}$) that lets it escape from the channel. An electric field of $\mathcal{E} \approx 0.65$ succeeds in imparting this critical force. The $\mathcal{E} = 0.7$ trace in Fig. 4a shows the route taken by the Na^+ ion as it penetrates the channel without oscillating, reaches the broken-line position at a speed greater than 'escape velocity' and emerges into the aqueous solution.

The series of $2.5\text{ \AA}$ -interval chambers (cavities) that constitute the CE channel described in Section 2, present possible halting sites to the migrating Na^+ ion. That the binding of the ion at these sites is small is illustrated by the ion's initial oscillation amplitudes in an applied electric field shown in Fig. 4 and the amplitudes of the hops that it undergoes in its thermally quenched state in the absence of an external electric field in Fig. 4c. Further comments on the $\mathcal{E} = 0$ behaviour will be described in the next subsection.

In order to test whether the oscillations might be an artifact of the thermal coupling of the MD system to the thermostat, dynamics simulations were conducted for Evans and for Hoover NVT (constant volume) thermostats and for Hoover and Berendsen (constant pressure) thermostats. The simulations were performed wherever possible at different time constants which control the thermal coupling between the MD system at temperature $T(t)$ and the thermostat at T_0 . The barostat coupling time was kept constant at 2 ps. In the thermostat mechanism used here this time constant τ is specified by the first-order relaxation expression

$$\frac{dT(t)}{dt} = \frac{T_0 - T(t)}{\tau}$$

At long imposed relaxation times τ the thermal coupling is ineffective and the system is essentially a microcanonical ensemble whose total energy is conserved but whose temperature is not maintained at the required value. At short τ the temperatures at the various timesteps show that they are over-compensated and again it is hard for the system to achieve T_0 . The τ interval in the test was from 0.01 to 0.5 ps, times which are shorter than those of the Na^+ ion's hops ($\sim 0.8\text{ ps}$) that we saw in Fig. 4. The result of the exercise with an applied electric field $\mathcal{E} = 0.5$ produced trajectories which for the entire τ interval oscillated in the manner of Fig. 4b. While there were differences in the oscillation amplitudes, the frequencies were largely the same as those in the figure. We

Fig. 4. The trajectory of a Na^+ ion in (a) the axial electric fields shown (in $\text{V \AA}^{-1}$), (b) $0.5\text{ V \AA}^{-1}$, and (c) zero field. In fields smaller than $0.7\text{ V \AA}^{-1}$ the ion oscillates. In larger fields it exits the channel.

therefore believe that the behaviour found for the cations in the channel is not directly correlated with the thermostat relaxation mechanism.

3.4. Temperature

Fig. 5 shows that the behaviour of the Na^+ ion as it escapes from the channel is, as might be expected, dependent on temperature. The $0.5\text{ V \AA}^{-1}$ trajectory that we discussed in relation to Fig. 4b continues to be oscillating until about 350 K . At this point the kinetic energy due to the axial motion is augmented by the higher thermal energy and helps to expel the ion from the channel. (Simply conducting the dynamics at zero electric field would require impossibly high temperatures to achieve this.) Where the ion does not have the critical escape energy, then having been released from its position on the channel wall which it occupied immediately after entering the channel, it first acquires some kinetic energy when it drops towards the base of the well. Then, as its thermal energy dissipates it hops between sites of progressively smaller ranges which reduce to a loose vibration at a single channel site.

Apart from the energetically difficult process of entering and exiting the channel, the Na^+ ions encounter low energy barriers as they migrate between their sites. As predicted by collision the-

Fig. 5. The effect of temperature (K) on the path of the Na⁺ ion migrating in a 0.5 V Å⁻¹ electric field.

ory [12], raising the temperature of the dynamics system has a greater effect on the range of the hopping than on its frequency. Fig. 4 shows the dependence of the $\varepsilon = 0.5$ trajectory on temperature. Recall our discussion of the results in Fig. 4a that the kinetic energy of the Na⁺ ion had to be above a critical value in order that it could be ejected from the channel. At room temperature this energy was provided by an external field of $\varepsilon = 0.65$ V Å⁻¹. The ion trajectories for the $\varepsilon = 0.5$ field at different temperatures are plotted Fig. 5. It shows that with a $\varepsilon = 0.5$ field the critical kinetic energy is provided by temperatures of 360 K and above – at this and at higher temperatures the Na⁺ ion is swept through the channel and out into the surrounding electrolyte medium.

Fig. 6 presents the Na⁺ ion trajectories at different temperatures when no electric field is applied ($\varepsilon = 0$). At all temperatures its release from the near end of the channel to drop into the electrostatic well in the interior gives the ion an initial kinetic surge and it rebounds through a ~ 5 Å range (two CE cavities). Its site after relaxation depends on the temperature; the figure shows the ion occupying one or other of two sites that are in adjacent cavities.

3.5. Ion velocities

Fig. 7a–c shows the velocities of a migrating Na⁺ ion under the same set of electric fields as illustrated for their trajectories in Fig. 4. The mean thermal velocity $\bar{v}$ of a Na⁺ ion *in vacuo* (from $\frac{1}{2}m\bar{v}^2 = \frac{3}{2}kT$) is about 6 Å ps⁻¹ at normal temperatures (600 m s⁻¹). We discussed above that the ion's velocity increases

rapidly with applied electric field before exhibiting damped oscillations, and a plot of the maximum velocities against field in Fig. 7d shows an ionic mobility of about 10⁻² cm² V⁻¹ s⁻¹. For comparison the Na⁺ ion's mobility in water at infinite dilution is 5.2 × 10⁻⁴ cm² V⁻¹ s⁻¹ [13] and that of the Rb⁺ ion in the fast ion conductor RbAg₅I₅ is 2 × 10⁻⁴ cm² V⁻¹ s⁻¹ [14]. In an amphiphilic electroactive monolayer on the liquid–vacuum interface of an aqueous NaCl solution a Na⁺ ion mobility of 3.6 × 10⁻³ cm² V⁻¹ s⁻¹ was calculated [15]; the progress of the ion through the molecular channel thus appears to be faster than the instances quoted.

We discussed how, in the absence of an applied field, the Na⁺ ion, after first jumping between the more widely separated sites, then settles down to a thermal oscillation between adjacent channel cavities (Fig. 4c). During this event the ion velocity v shown in Fig. 7a diminishes from ones in which the ion was initially travelling at about twice thermal speed until v reaches thermal values. When a 0.5 V Å⁻¹ electric field is implied as shown in Fig. 7b, the higher oscillation velocities do not reach the escape minimum that would enable the Na⁺ ion to exit the channel. It does so, however, when the slightly higher velocity of 100 Å ps⁻¹ conferred by $\varepsilon = 0.7$ shown in part (c) enables the ion to exit the channel after 500 ps. After losing the gas-like environment of the channel interior and entering the aqueous medium its velocity decreases to values associated with a liquid medium. When the critical kinetic energy that corresponds to an escape velocity is converted to a potential energy the magnitude of the latter implies the presence of an energy barrier of 1150 kJ mol⁻¹ (11.9 eV) for the ion to exit the channel.

The energy barrier of 12 eV derived above that is imposed by the channel ends would naturally be too high to permit a spontaneous exit of the ion. Its origin is the steep rise of the potential from the centre of the channel to the walls (Fig. 1). The 11 V rise shown in the figure, implying a 11 eV in the electrostatic energy of a unit positively charged ion to migrate from the centre to the end of the channel, is so close to the 12 eV calculated above from the ionic velocity strongly suggests that the dominating contribution to the energy barrier is electrostatic. This conclusion is consistent with that from an earlier work [4] where it was found that while the differently-sized cations Li⁺, Na⁺ and K⁺ would enter and migrate along the channel, while the solvent water molecules and even the small F⁻ ion failed to do so.

3.6. Analysis of the oscillations

We have already accounted for the axial motion of the Na⁺ ion in terms of the principal contributions from the forces on the ion that arise from (1) the electrostatic potential described by the energy well, (2) the applied electric field $\varepsilon(z)$ and (3) thermal energy.

Fig. 6. The channel migration of a Na⁺ ion at zero electric field.

Fig. 7. (a–c) The velocity of the Na^+ ion at the electric fields shown. When $\mathcal{E}$ reaches $0.7 \text{ V \AA}^{-1}$ the ion's velocity decays sharply to small values as the ion exits the channel into the surrounding aqueous medium. (d) Fitting the maximum velocities to calculate a mobility.

Except for very small electric fields contribution (3) is much less than the other two, and the following treatment will be for conditions dominated by (1) and (2). The classical motion can be accounted for in the language describing a spring balance model that oscillates harmonically in a gravitational field, which is analogous to our electric field.

When the ion is at axial coordinate z it experiences a force f from the energy well f_w and another $f_{\mathcal{E}}$ from the field $\mathcal{E}$ given by $f_{\mathcal{E}} = \mathcal{E}q$. Although we remarked on the inharmonicity implied by the oscillation traces, in order to obtain approximate quantities to describe the ion's motion it will be assumed that the energy well is harmonic. When the forces are balanced and the ion is at the ax-

ial coordinate z_0 , then we have $f_w = -kz_0$. We would then have $f \equiv f_w + f_e = 0$, which implies that

$$z_0 = \mathcal{E}q/k$$

Under general conditions the ion is at a position z . If this corresponds to a displacement ζ from its equilibrium position ($\zeta = z - z_0$), then $z = \zeta + \mathcal{E}q/k$ the force f is [16,17]

$$f(\zeta) = f_e + f_w = -k\zeta$$

in which the explicit dependence on the field is removed (but is actually implicit in z_0). The equation

$$m\ddot{\zeta} = -k\zeta \quad (1)$$

has solutions $\zeta(t) = A \cos(\omega_0 t + \phi)$ (2)

where the oscillation's angular frequency is given by

$$\omega_0 = \sqrt{\frac{m}{k}}$$

and ϕ is a phase term. As a result (1) becomes

$$m\ddot{\zeta} + m\omega_0^2 \zeta = 0$$

or

$$\ddot{\zeta} + \omega_0^2 \zeta = 0 \quad (3)$$

The clear damping of the waves in Fig. 3 indicates a dissipation of the energy of the oscillations. We shall suppose that the damping mechanism is described [17] by adding a friction term to the force Eq. (1). There is little consensus on how friction on an atomic scale should be described. Friction force microscopy [18] (in which sliding velocities are much greater than those of the ions described here) establish a logarithmic dependence of frictional force on velocity; calculations on sliding polymer surfaces [19] find, for different polymers, linear, logarithmic and no dependence of the force on sliding velocity. We shall suppose that the friction force is proportional to the cation's velocity as in fluid mechanics. With proportionality constant γ Eq. (3) is extended to

$$\ddot{\zeta} + \gamma\dot{\zeta} + \omega_0^2 \zeta = 0 \quad (4)$$

The solution to (3) should bear a periodic component as in (2) and also a decay (damping) factor, both of which can be found by substituting $\zeta(t) = Ce^{\alpha t}$ into (4) which leads to the condition

$$\alpha = 1/2 \left[-\gamma \pm \sqrt{\gamma^2 - 4\omega_0^2} \right] \quad (5)$$

In the no-damping limit ($\gamma = 0$), (5) implies

$$\zeta(t) = Ce^{i\omega_0 t}$$

which is the general solution from which (2) can be derived. A condition in which $\gamma \geq 2\omega_0$ means that α is real, and there is no oscillation. This is the 'overdamping' limit. If $\gamma = 2\omega_0$ we have a critical damping condition with $\zeta(t) = Ce^{1/2\gamma t}$, but again the ion does not oscillate.

In the 'under-damped' condition that is implied by the oscillations, $\gamma < 2\omega_0$.

Then

$$\alpha = -1/2\gamma \pm i\omega_u \quad (6)$$

where

$$\omega_u = \omega_0 \sqrt{1 - \left(\frac{\gamma}{2\omega_0}\right)^2} \quad (7)$$

A linear combination of the two solutions defined by (6) leads to

$$\zeta(t) = e^{-1/2\gamma t} (C_+ e^{i\omega_u t} + C_- e^{-i\omega_u t}) \quad (8)$$

where the real character of the trajectory $\zeta(t)$ requires that $C_+ = C_- (=C)$. Finally

$$\zeta(t) = Ce^{-1/2\gamma t} \cos(\omega_u t + \phi)$$

or

$$\zeta(t) = Ce^{-t/\tau} \cos \omega_u t \quad (8)$$

where the damping time constant $\tau \equiv 2/\gamma$ is introduced and the phase factor ϕ omitted. Fitting the periodic part of the function described by (8) to the oscillations for the $\mathcal{E} = 0.5$ data of Fig. 3b yields $\omega_u = 0.018 \text{ fs}^{-1}$, while the envelope of the oscillation amplitudes that decay with time provides a time constant for the damping of $\tau = 1818 \text{ fs}$ ($\tau \sim 2 \text{ ps}$ or $\gamma = 0.0011 \text{ fs}^{-1}$). Eq. (7) implies that the smallness of γ compared to the oscillation frequency implies that the value derived for ω_u would be close to that (ω_0) for the 'natural' (undamped) system.

The picoseconds timescale for atomic friction that we find damping the oscillations is consistent with relaxation time measurements on nanotribology studies on sliding surfaces [20].

3.7. Energy dissipation

The instantaneous energy of a harmonic oscillator is the sum of its kinetic and potential energies,

$$E = \frac{1}{2} m \dot{\zeta}^2 + \frac{1}{2} k \zeta^2 \quad (11)$$

where k is the force constant as in (1) ($k = m\omega_0^2$) and the displacement $\zeta \equiv \zeta(t)$ is given by (10). Substituting these quantities into (1) leads to

$$E = \frac{1}{2} m \dot{\zeta}_{\max}^2 e^{-\gamma t} \left(\frac{\gamma^2}{4} \cos 2\omega_u t + \frac{\gamma\omega_u}{2} \sin 2\omega_u t + \omega_0^2 \right)$$

In the slow-decay condition, which is valid for the $\mathcal{E} = 0.5$ oscillation conditions at least, which led to $\omega_u = 0.018 \text{ fs}^{-1}$ and $\gamma = 0.0011 \text{ fs}^{-1}$ the ion's trajectory gives rise to several cycles before the ion comes to rest. The first two terms in the bracket then average to zero in a time that is shorter than the characteristic time γ^{-1} , so that we can follow the dissipation of the mean energy as

$$\bar{E} = 1/2 m \dot{\zeta}_{\max}^2 e^{-\gamma t}$$

with the same decay constant γ as was determined for the trajectory oscillations.

3.8. Power

Let us calculate the power output of the radiation from the oscillations, treating them classically. The power P emitted by an electric dipole p oscillating with angular frequency ω radiates is given [17] by

$$P = \frac{p^2}{12\pi\epsilon_0} \frac{\omega^4}{c^3} \quad (12)$$

In the analogous quantum mechanical system, the power is expressed by an equivalent expression but with the dipole moment replaced by $p_{ab}^z = \iint \psi_a^* z \psi_b dx dy dz$, the transition moment integral for a quantized transition between states with wave functions ψ_a and ψ_b (z is the direction of the polarisation of the radiation). Since ours is a classical system we can use (12) in which the dipole moment p results from the displacements of the charge e of the Na^+ ion as it oscillates along the channel's z axis. Substituting an amplitude of $30 \text{ \AA}$ and $\omega = 1.8 \times 10^{13} \text{ Hz}$ from the $\mathcal{E} = 0.5$ data that we

considered above permits a figure to be calculated for the power P associated with the oscillations which is $2.7 \times 10^{-18} \text{ J s}^{-1}$ per channel molecule contained in the sample.

3.9. A pulsed electric field?

The oscillations, damped by friction with the channel walls, could be maintained indefinitely by a series of pulsed fields. Rather than deploy electric fields of the strengths described above we might examine the feasibility of producing the field by irradiating the sample with pulsed radiation of the appropriate intensity and frequency [17].

The intensity of a beam is the time-averaged mean of the Poynting vector

$$\mathbf{S}(t) = \frac{1}{\mu_0} \mathcal{E}(t) \times \mathcal{B}(t)$$

where $\mathcal{E}$ and $\mathcal{B}$ are respectively the beam's electric and magnetic field vectors, which are related by $\mathcal{E} = \mathcal{B}c$. The magnitude of the Poynting vector is therefore given by

$$s = \varepsilon_0 \mathcal{E}^2 c$$

and the time-averaged intensity is

$$I = 1/2 \varepsilon_0 c (\mathcal{E}_{\max})^2 \quad (13)$$

which is the power per unit area of the beam. A high-power klystron, which is a source of microwave radiation, may deliver pulsed power up to 100 MW. Concentrating such a beam onto a 1 cm^2 target would, by (13) generate electric fields of $\sim 10^8 \text{ V m}^{-1}$ whose strengths are just an order of magnitude below those described in this work.

4. Conclusions and discussion

An axial electric field applied to ions near the end of a CE channel confers a velocity that causes them to enter the channel and to bypass the shallow energy traps associated with the constituent cavities. Unless the field exceeds a critical value, the ions are temporarily brought to rest by the steep walls of the electrostatic energy well which initiates damped oscillating ionic trajectories. The ions, after the dissipation of their kinetic energies, come to a final stop on the channel wall at a site near the downfield end of the channel. Although the ions' oscillatory motions may occur in the absence of an applied electric field, a field significantly enhances the amplitudes of the oscillations

If the field were applied in pulses, as from a **terahertz** source, subsequent cycles would regenerate the oscillations. For the $\mathcal{E} = 0.5$ case radiation would be generated with a frequency of $1.8 \times 10^{13} \text{ Hz}$ (infra red) and a power output of $2.7 \times 10^{-18} \text{ W}$ for each channel molecule in the system. Thus a 10 cm^3 sample of a millimolar channel solution could produce radiation with a maximum power of **16 W**. This would of course only be so for a case in which all the ion channel solute molecules in the sample were parallel to the imposed electric field and were to radiate simultaneously. However since a solute in a low viscosity solution should present any direction to an externally applied one in a relaxation timescale of the order of 0.1 ns the response that has been described for the system would occur in a sufficient number of solute molecules at any instant for the radiation to be detectable. A spectral analysis of such output might contain useful information of the Na^+ ion's interactions with the CE channels.

While MD studies have been conducted that simulate ion migration in biological transporters [21], if in *synthetic* systems, molecular-mechanical devices are to be designed that operate on a **nano-scale** such as those described in Ref. [1] a detailed under-

standing is necessary of the fine details that describe how the component units respond to internal and externally-imposed conditions, and to determine the extent to which the behaviour of the components approaches that of an ideal macroscopic, mechanical system. As an attempt to achieve this, the system presented in this work (a Na^+ ion penetrating a rigid tube-like molecule whose diameter is a little greater than the size of the ion) has components that are sufficiently simple for their operating conditions to be closely controlled. As well as temperature, the controllable conditions in this system could be, for the migrant: its identity, size and charge, its velocity and direction of propagation. For the channel it would be possible to vary its shape and rigidity, the atomic species that constitute it, the partial charges on these atoms and the interactions that are inherent between these atoms and the migrant species. The work reported here, as an approach to this goal, is necessarily confined to passive ion transport through a rigid channel. Bearing in mind the role played by phonons (as local deformations of the environmental medium) in charge transport, e.g. in DNA chains [22], an important feature to consider will be a non-rigid channel whose conformational motions may play an active part in the transport of migrants. Such investigations are currently under way in our laboratory.

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