I. SIMULATION OF IONS IN A PENNING TRAP

Ions are confined radially by a magnetic field $\mathbf{B}$, with an ideal quadrupolar trapping potential of V_T. The potential and field near the centre of the trap is approximated as

$$\Phi_T(x,y,z) = V_T(\gamma' - \frac{\alpha'}{2l^2}(x^2+y^2-2z^2)) \qquad \mathbf{E} = -\nabla\Phi_T(x,y,z) = \frac{\alpha}{l^2}(-x\mathbf{i} - y\mathbf{j} + 2z\mathbf{k}) \tag{1}$$

where $\gamma' = 1/3$ and $\alpha' = 2.77373$ are geometric factors for the cubic trap, and l is the edge length[1]. The force experienced by an ion in the trap is

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v}\times\mathbf{B}) \tag{2}$$

Charges and mass are simulated in atomic units, lengths in nm and time in ns.

A. Integration scheme

The code uses the Boris integrator[2] as formulated in Birdsall and Langdon[3]. This is a modified leapfrog scheme in which positions are calculated at times $..., n-1, n, n+1, ...$ and velocities at times $..., n^{-1/2}$, $n^{+1/2}, ...$

$$\mathbf{v}^- = \mathbf{v}^{n-1/2} + \frac{q\mathbf{E}}{m}\frac{\Delta t}{2} \tag{3}$$

$$\mathbf{v}' = \mathbf{v}^- + \mathbf{v}^- \times \mathbf{t} \qquad \mathbf{t} = \frac{q\mathbf{B}}{m}\frac{\Delta t}{2} \tag{4}$$

$$\mathbf{v}^+ = \mathbf{v}^- + \mathbf{v}' \times \mathbf{s} \qquad \mathbf{s} = \frac{2\mathbf{t}}{1+t^2} \tag{5}$$

$$\mathbf{v}^{n+1/2} = \mathbf{v}^+ + \frac{q\mathbf{E}}{m}\frac{\Delta t}{2} \tag{6}$$

B. Ion motion

The cyclotron frequency ω_c is predicted by $\omega_c = \frac{qB}{m}$[1] (S.I. units - see Table IV). To achieve 1% phase error in simulated cyclotron frequency requires $\Omega\Delta t \lesssim 0.3$[3], [4]. The cyclotron radius r is predicted by $r = \frac{mv}{|q|B}$ and is measured in simulation for a single particle by the distance between maxima in the x dimension.

The electric field gives rise to a magnetron motion of a lower frequency ω_z. In a quadrupolar trapping potential of V_T, the modified cyclotron frequency ω_+ is predicted by

$$\omega_+ = \frac{\omega_c}{2} + \sqrt{\frac{\omega_c^2}{4} - \frac{\omega_z^2}{2}} \qquad \omega_z = \left(\frac{2\alpha q V_T}{ml^2}\right)^{1/2} \tag{7}$$

The modified cyclotron frequency is measured by peaks in the Fourier transform of the induced current time signal.

C. Induced current

FTICR-MS measures the current induced between detector plates on opposite walls of the cube parallel to the magnetic field. In the simulation, current is induced by the movement of the 'image' $\mathbf{E}_{image}(\mathbf{r})$ associated with each ion, that is, the difference in the electric field generated by the ion at each of the two detector plates[1].

$$I = \sum_{i=1}^{N} q_i \mathbf{v}_i \cdot \mathbf{E}_{image}(\mathbf{r}_i) \qquad \mathbf{E}_{image}(\mathbf{r}) = -\frac{\beta'}{l} r_j \qquad \beta' = 0.72167 \tag{8}$$

D. Evaluation of electrostatic potential and forces

In addition to the influence of the trapping field and the ion-image interaction, each ion experiences a repulsive Coulomb force from every other ion in the packet. The calculation of these forces is nominally $O(N^2)$, which makes it infeasible for simulation of large ion packets unless some approximation is used to reduce the computational complexity. Ion excitation and detection is typically performed in a vacuum, or in an environment of low-pressure neutral gas particles. To produce a detectable ICR signal, it is necessary to excite the ions so as to produce a highly coherent circular motion. Thus the distribution of charged particles within the FT-ICR chamber is highly non-uniform. Previous simulations have either used the particle-in-cell approximation[5] or virtual particles to reduce the number of interactions to be simulated[6]. However, particle-in-cell simulations are best suited to uniform particle distributions with a low required accuracy[7]. In contrast, the adaptive fast multipole algorithm[8] provides guaranteed error bounds for non-uniform distributions.

E. Simulation results

B 4.7 V 1.0 edgeLength 0.01 radius 0.003 dt 25.0 steps 2097152 logSteps 2097152 fmmDensity 60 fmmTerms 10 species glutamine 147.07698 1 1 species lysine 147.11336 1 1

TABLE I

REPLICATING: HAN AND SHIN[9]. INPUT, PREDICTED AND MEASURED SIMULATION PARAMETERS

$B = 0.7646T, V_T = 1.0V, l = 0.047, \Delta t = 25ns$											
				predicted		**measured**		**error: timestep**			
species	**charge**	**mass**	v_0 **(m/s)**	$\omega_+/2\Pi$ **(Hz)**	r **(mm)**	$\omega'_+/2\Pi$ **(Hz)**	r' **(mm)**	Δt **(ns)**	$\epsilon : \Delta t$	$\epsilon : \Delta t$ **/ 10**	$\epsilon : \Delta t$ *** 10**
HCO^+	1	29.0182	10^4	394,022	3.933	404,220	3.933	118			
CH_3CO^+	1	43.04462	10^4	262,028	5.835	272,460	5.835	175			

TABLE II

REPLICATING: LEACH ET AL.[5]. INPUT, PREDICTED AND MEASURED SIMULATION PARAMETERS

$B = 7.0T, V_T = 1.0V, l = 0.0508, \Delta t = 25ns$											
				predicted		**measured**		**error: timestep**			
species	**charge**	**mass**	v_0 **(m/s)**	$\omega_+/2\Pi$ **(Hz)**	r **(mm)**	$\omega'_+/2\Pi$ **(Hz)**	r' **(mm)**	Δt **(ns)**	$\epsilon : \Delta t$	$\epsilon : \Delta t$ **/ 10**	$\epsilon : \Delta t$ *** 10**
Cs^+	1	132.9054	2.7×10^4	807,826	5.313	807,680	5.319	59			
$Xx^+(\frac{m}{q} = 150)$	1	150.0	2.7×10^4	715,652	5.996	715,840	5.997	67			

F. Comparison with experiment: amino acids

We performed a scan of a [TODO mole/volume fraction?] mixture of lysine and glutamine on a Bruker Apex 4.7T FT-ICR mass spectrometer at the ANU. The core of this machine is a Penning trap of 4.7T / 1.0V of side length 1cm. We performed a molecular dynamics simulation for an equimolar mixture of N singly-charged ions in total. The simulation parameters and results are in table III.

TABLE III

AMINO ACIDS IN ANU MASS SPECTROMETER. INPUT, PREDICTED AND MEASURED SIMULATION PARAMETERS

$B = 4.7T, V_T = 1.0V, l = 0.01, \Delta t = 25ns$											
				predicted		**measured**		**error: timestep**			
species	**charge**	**mass**	v_0 **(m/s)**	$\omega_+/2\Pi$ **(Hz)**	r **(mm)**	$\omega'_+/2\Pi$ **(Hz)**	r' **(mm)**	Δt **(ns)**	$\epsilon : \Delta t$	$\epsilon : \Delta t$ **/ 10**	$\epsilon : \Delta t$ *** 10**
glutamine	1	147.07698	9.25×10^3	450,313	3.0	489,407	3.0	106			
lysine	1	147.11336	9.25×10^3	450,190	3.0	489540	3.0	106			

G. Peak coalescence

Vladimirov et al.[10] give an expression for the minimum number of ions required for coalescence of (singly-charged) clouds of similar masses m_1 and m_2:

$$N = 4.87 \times 10^8 \frac{a^2 R B^2 (m_2 - m_1)}{m^2} \tag{9}$$

(For a, R in mm, m_1, m_2, m in Da, B in Tesla.)

Applying this formula to the experiment described in section I-F, where ion cloud major axis $a = 1$ mm, ion cyclotron radius $R \approx 3$ mm, and average mass $m = 147.09517$, we find the minimum number of ions required for coalescence is ≈ 55000.

TABLE IV

CONVERSION FACTORS

property	**unit**	**SI unit**
mass	amu	$1.660538921 \times 10^{-27} kg$
charge	e	$1.60217653 \times 10^{-19} C$

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