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I. Calculation of the collisional temperature

For a linear quadrupole rf trap, an ion with charge *e* and mass *m* located at a radius *r* from the symmetry axis will perform an oscillatory motion around its equilibrium position with an average kinetic energy of

$$E_{\text{avg}}(r) = \frac{1}{4}\frac{e^2 U_{\text{rf}}^2}{\omega_{\text{rf}}^2 r_0^4 m} r^2, \tag{1}$$

where U_{rf} is the amplitude of the rf voltage applied to the quadrupole electrodes (180° out of phase for neighboring electrodes), ω_{rf} is the rf drive frequency, and r_0 is the distance from the central rf-field-free axis to the electrodes. This oscillation is termed micromotion. For an spheroidal Coulomb crystal with a major radial axis equal to *b*, this leads to an average kinetic energy E_{avg} of the ions with radial positions between *t* (<*b*) and *b* (see Suppl. Fig. S1) given by

$$E_{\text{avg}} = \frac{(2b^2 + 3t^2)}{20}\frac{e^2 U_{\text{rf}}^2}{\omega_{\text{rf}}^2 r_0^4 m}. \tag{2}$$

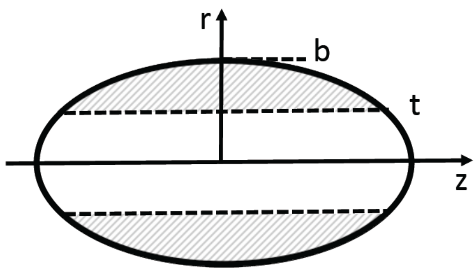
This formula has been used for calculating the average micromotion energy of the molecular ions from crystal projection images.

Assuming now that these molecular ions are colliding with a thermalized helium buffer gas at a temperature of T_{He}, then one can derive the average collision energy in the centre-of-mass frame to be

$$E_{\text{coll}} = \frac{3m}{2(m_{\text{He}} + m)} k_{\text{B}} T_{\text{He}} + \frac{m_{\text{He}}}{m_{\text{He}} + m} E_{\text{avg}}. \tag{3}$$

Finally, assuming the collisional speed distribution is close to a thermal one (see below), then it is possible to assign a collisional temperature T_{coll} given by

$$T_{\mathrm{coll}} = \frac{2}{3k_{\mathrm{B}}} E_{\mathrm{coll}} = \frac{m}{(m_{\mathrm{He}} + m)} T_{\mathrm{He}} + \frac{2m_{\mathrm{He}}}{3(m_{\mathrm{He}} + m)} \frac{E_{\mathrm{avg}}}{k_{\mathrm{B}}}. \tag{4}$$



Supplementary Figure S1: Stylistic cross section of an spheroidal ion Coulomb crystal with cylindrical symmetry around the z axis. The shaded areas indicate the regions for which Eq. (2) holds.

II. Calculation of the collisional speed distribution

Assuming that the velocity distribution of the helium buffer gas can be described by a thermal distribution at a temperature T_{He}, then along any spatial direction the velocity distribution $g_{\mathrm{He}}(v)$ of the He atoms is given by

$$g_{\mathrm{He}}(v) = \sqrt{\frac{m_{\mathrm{He}}}{2\pi k_{\mathrm{B}} T_{\mathrm{He}}}} \exp\left(-\frac{m_{\mathrm{He}} v^2}{2k_{\mathrm{B}} T_{\mathrm{He}}} \right). \tag{5}$$

Since the micromotion is harmonic and only along a single axis, the corresponding velocity distribution for the ion along this axis can be written

$$f(v,r)=\frac{1}{\pi}\frac{1}{\sqrt{v_0^2(r)-v^2}},\quad v\in\left[-v_0(r),v_0(r)\right], \tag{6}$$

where $v_0(r)$ is given by

$$v_0(r)=\frac{eU_{\mathrm{rf}}}{\omega_{\mathrm{rf}}r_0^2 m}r. \tag{7}$$

Along the local micromotion axis, the collisional velocity distribution $h(v,r)$ is hence

$$h(v,r)=\sqrt{\frac{m_{\mathrm{He}}}{2\pi^3 k_{\mathrm{B}}T_{\mathrm{He}}}}\int_{-v_0(r)}^{v_0(r)}\frac{\exp\left(-\frac{m_{\mathrm{He}}(v-v')^2}{2k_{\mathrm{B}}T_{\mathrm{He}}}\right)}{\sqrt{v_0^2(r)-v'^2}}dv'. \tag{8}$$

In any direction perpendicular to this local axis, the collisional velocity distribution is given by Eq. (5). Consequently, the collisional speed distribution $H(v,r)$ for ions at a given radius r can formally be written

$$H(v,r)=\sqrt{\frac{2m_{\mathrm{He}}}{\pi^3 k_{\mathrm{B}}T_{\mathrm{He}}}}v\cdot\exp\left(-\frac{m_{\mathrm{He}}v^2}{2k_{\mathrm{B}}T_{\mathrm{He}}}\right)\int_{-v_0(r)}^{v_0(r)}\frac{\exp\left(-\frac{m_{\mathrm{He}}v'^2}{2k_{\mathrm{B}}T_{\mathrm{He}}}\right)\sinh\left(\frac{m_{\mathrm{He}}vv'}{k_{\mathrm{B}}T_{\mathrm{He}}}\right)}{v'\sqrt{v_0^2(r)-v'^2}}dv'. \tag{9}$$

Furthermore, by spatially averaging over the region delimited by t and b (cf. Fig. S1), one finally arrives at the following expression for the effective collisional speed distribution

$$\bar{H}(v)=3(b^2-t^2)^{-3/2}\int_t^b H(v,r)r\sqrt{b^2-r^2}dr, \tag{10}$$

for the ions contained within the aforementioned region.

Since the thermal velocities of the ions in the Coulomb crystals are always at least one order of magnitude lower than the thermal helium velocities, we have neglected those in the present analysis.