Maxwellianization of Positrons Cooling in CF_4 and N_2 Gases

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Positron cooling in CF_4 and N_2 gases via inelastic vibrational and rotational (de)excitations is simulated, importantly including elastic positron-positron collisions. For CF_4, it is shown that rotational (de)excitations play no role on the experimental timescale, and further, that in the absence of positron-positron collisions, cooling via excitation of the dipole-active ν_3 and ν_4 modes alone would lead to a non-Maxwellian positron momentum distribution, in contrast to the observations of experiment. It is shown that the observed Maxwellianization of the distribution may be effected by positron-positron collisions and/or cooling involving the combination of the dipole-inactive ν_1 mode with the dipole-active modes. For N_2, rotational excitations alone are sufficient to Maxwellianize the distribution (vibrational effects are negligible).

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The development of the positron buffer-gas trap [1] has enabled the routine trapping, accumulation, and beam delivery of positrons [2,3]; the study of low-energy antimatter-matter interactions [4,5]; and the formation and exploitation of positronium [6,7] and antihydrogen [8–15]. Positrons from a ^{22}Na source (with energies 0–500 keV) are slowed to eV energies by passing through an ∼8 K solid-neon moderator, then magnetically guided into the three-stage buffer-gas trap. The first two stages contain N_2 gas in which the positrons cool, typically through electronic excitation [16]. In the third stage, a mixture of N_2 and CF_4 (or SF_6) is used to complete the thermalization of the positrons to room temperature, typically via rotational and vibrational excitation of the molecules [17]. Further cooling can proceed in a cryogenic trap, which produces an ultrahigh-resolution (∼7 meV FWHM) beam [18].

Optimization and development of traps, accumulators, beams, and positron-based technologies requires, or could benefit from, theoretical insight and predictive capability. The theory of low-energy positron cooling in atomic and molecular gases, however, lags well behind experiment (see, e.g., Refs. [19,20] for early reviews). Most existing theoretical work has been for noble gases, yielding limited agreement with experiment [21–27]. Recently, however, a Monte Carlo approach employed by one of us that used accurate many-body-theory scattering cross sections gave a complete description of low-energy positron cooling in noble gases, finding excellent agreement with experiment for cooling rates, annihilation rates [28], and γ spectra [29]. For molecular gases, less progress has been made, with cooling even in N_2 and CF_4—the buffer gases of choice in the ubiquitous Surko traps—poorly understood, though some simulations have been performed [30,31].

Natisin *et al.* [37] performed measurements and theoretical modeling of positron cooling from ∼1500 K to room temperature in CF_4, N_2, and CO gases. Their measurements of the positron momentum distribution (PMD) indicated that it remained Maxwellian throughout the cooling. For CF_4, their model included cooling only via excitation of the dominant vibrational ν_3 mode and explicitly assumed the PMD to remain Maxwellian throughout. However, although the model accurately predicted the time evolution of the positron temperature, with only this single cooling channel, the PMD cannot remain Maxwellian: positrons below the excitation threshold cannot cool further, leading to a "pileup" of positrons just below the threshold (see below). Thus, the mechanism(s) causing the "Maxwellianization" observed in the experiment is not yet understood.

Here, we calculate the evolution of the PMD and positron temperature during cooling in CF_4 and N_2 gases. For CF_4, we show that even when both dipole-active vibrational modes (ν_3 and ν_4) are included [38], pileups indeed occur, resulting in a non-Maxwellian PMD. [We also additionally studied octupole and hexadecapole rotational (de)excitations but found they have no additional effect, see below and Supplemental Material [39], Figs. S1–S4]. We explore two mechanisms that could effect the Maxwellianization observed in experiment: (1) *Positron-positron collisions.*—the relative importance of positron-positron and positron-gas collisions is governed by the ratio R of the positron number density to the gas number density. Positron-positron collisions are known to be capable of effecting rapid Maxwellianization at high positron densities [40], but the magnitude of R required for this to occur on the experimental timescale is unclear. We find that $R \gtrsim 10^{-6}$ is sufficient, so the density ratio in the CF_4 experiment [37,41], $R \sim 10^{-7}$–10^{-6} [41], may be sufficient to Maxwellianize the PMD. In higher-density traps [18,42] positron-positron collisions will readily Maxwellianize the PMD. (2) *Excitation of the dipole-inactive ν_1 mode.*—we find that positrons with energies

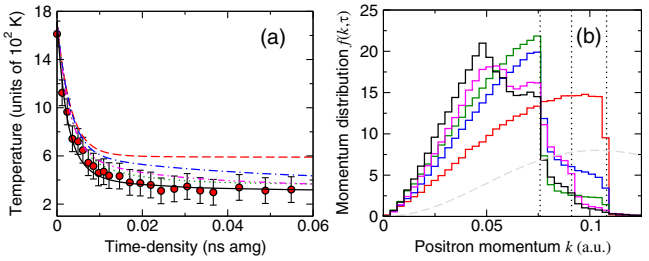

FIG. 1. Positron cooling in CF_4, neglecting positron-positron collisions. (a) Temperature: ν_3 (dashed red), $\nu_3+\nu_4$ (dot-dashed blue), $\nu_3+4\nu_4$ (dotted green), $\nu_3+\nu_4+\nu_1$ (dot-dash-dotted magenta), and $\nu_3+4\nu_4+4\nu_1$ (solid black) approximations (see text), and experiment [37] (red circles). (b) PMD $f(k,\tau)$ at $\tau=0.06$ ns amg, colored as in (a); the initial MB for $T=1700$ K (dashed gray line); the vibrational excitation thresholds (dotted vertical lines).

below the lowest vibrational threshold (ν_4) can lose further energy by exciting ν_1 and subsequently deexciting ν_4, enabling the PMD to "relax" closer to Maxwellian.

For N_2, we find that the PMD remains Maxwellian during cooling via rotational excitations of the molecules, even without positron-positron collisions. Overall, we obtain excellent agreement with experiment for the time evolution of the positron temperature for both CF_4 and N_2.

Simulation procedure.—PMD $f(k,\tau)$, where k is the momentum and $\tau\equiv n_g t$ is the *time-density* (n_g being the gas number density and t the time), normalized as $\int_0^\infty f(k,\tau)dk=1$, is calculated using the ANTICOOL program [43], modified to include vibrational and rotational inelastic positron-gas collisions and positron-positron collisions. We employ a grid in τ with constant step size $\Delta\tau\equiv n_g\Delta t$. The initial momentum of each positron is sampled from a Maxwell-Boltzmann distribution (MB) at ~1500 K, corresponding to the experiment [37]. For each τ and each positron, the collision probability is $P=W\Delta t$, where $W=n_g[\int u\sigma_{eg}(u)f_g(\mathbf{v}')d\mathbf{v}'+R\int u\sigma_{ee}(u)f_e(\mathbf{v}')d\mathbf{v}']$, u is the collision speed, σ_{eg} and σ_{ee} are the positron-gas and positron-positron scattering cross sections, respectively, $f_g(\mathbf{v}')$ and $f_e(\mathbf{v}')$ are the gas and positron velocity distributions, respectively, and $\Delta\tau$ is chosen such that $W\Delta t\ll 1$ [44]. We approximate $\int u\sigma_{eg}(u)f_g(\mathbf{v}')d\mathbf{v}'$ by $v_{eg}\sigma_{eg}(v_{eg})$, where v_{eg} is the relative speed of the positron and a single gas molecule whose velocity is sampled from a MB at room temperature, $T_R=300$ K. We calculate $\int u\sigma_{ee}(u)f_e(\mathbf{v}')d\mathbf{v}'$ using a self-consistent method similar to that of Ref. [45], using a screened positron-positron cross section σ_{ee} [46] (see the Supplemental Material for full details [39]). A random number $r\in[0,1]$ is drawn and if $r<P$, a collision is deemed to occur. Additional random numbers are compared with the relevant cross sections to determine the target type (molecule or positron) and scattering channel (a transition between two specific molecular states, or the velocity of the target positron), and the projectile positron's momentum is updated accordingly. The positron temperature at a given τ is calculated from the rms momentum of the positrons. More details of the simulation procedure are given in the Supplemental Material [39].

Positron cooling in CF_4 gas.—We investigate positron cooling from $T=1700$ K ($k_BT=146$ meV) to T_R ($k_BT=26$ meV), corresponding to the experiment [37].

The electric dipole and quadrupole moments of CF_4 are zero, and thus rotational (de)excitation primarily proceeds through octupole and hexadecapole transitions that couple states differing by 3 and 4 units of angular momentum, respectively. We performed converged simulations using Born cross sections [39,47–49] including the dense manifolds, considering up to 150 rotational states. At room temperature the Boltzmann occupation numbers peak at $J\sim 30$, owing to the large $(2J+1)^2$ degeneracy of the spherical-top states, but the (Boltzmann-weighted) rotational cross sections are orders of magnitude smaller than the vibrational cross sections (see below and Supplemental Material [39], Figs. S1–S4). We found that for the energies and timescales considered here, rotational octupole and hexadecapole transitions have negligible effect, and that cooling in CF_4 is predominantly by vibrational (de)excitations of the molecules (see Supplemental Material [39], Figs. S1–S4).

Vibrational modes ν_1 and ν_2, with energies $\varepsilon_1=113$ and $\varepsilon_2=53.9$ meV, are dipole inactive, while ν_3 and ν_4, with energies $\varepsilon_3=159$ and $\varepsilon_4=78.4$ meV, are dipole active [50]. We consider only fundamental transitions, and, initially, we consider only the dipole-active modes and neglect positron-positron collisions. The true positron-molecule interaction is characterized by strong positron-molecule correlations; whilst *ab initio* many-body theory has recently enabled calculations of binding and elastic scattering on ground-state molecules [51,52], the accurate *ab initio* calculation of inelastic cross sections remains a formidable and open problem. To proceed, we make use of the Born-dipole cross sections $\sigma_{0\rightleftarrows 3,4}$ for transitions between the ground state and dipole-active modes ν_3 and ν_4 [32,39,53]. Coupled-channel calculations [33] and measurements [54] found $\sigma_{0\rightarrow 3}$ to be similar in shape and magnitude to the Born-dipole calculation [55], but coupled-channel calculations [33] found $\sigma_{0\rightarrow 4}$ to be approximately 4 times larger than the Born-dipole calculation (see Fig. 6 in Ref. [33]). Thus, to effectively approximate the *ab initio* calculation, we also perform simulations using the Born-dipole $\sigma_{0\rightarrow 4}$ scaled by 4.

Figure 1(a) shows the calculated time-dependent positron temperature compared with experiment [37,56]. The simulation used 200 000 positrons with $\Delta\tau=2\times10^{-6}$ ns amg. The figure separately shows the results for when only $0\rightleftarrows 3$ transitions are included, and when $0\rightleftarrows 3$ and $0\rightleftarrows 4$ transitions are included (denoted ν_3 and $\nu_3+\nu_4$, respectively). Also shown are the results for when $\sigma_{0\rightleftarrows 4}$ is scaled by 4 (denoted

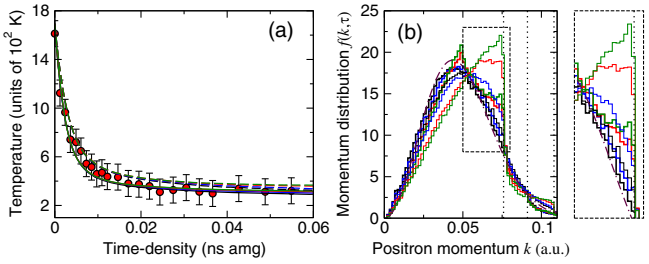

FIG. 2. Positron cooling in CF_4, including positron-positron collisions. (a) Temperature: dashed (solid) lines are $\nu_3 + 4\nu_4$ ($\nu_3 + 4\nu_4 + 4\nu_1$) approximation, with R as follows: 1×10^{-6} (black), 5×10^{-7} (blue), 1×10^{-7} (red), 1×10^{-8} (green); red circles, experiment [37]. (b) PMD $f(k,\tau)$ at $\tau = 0.06$ ns amg: thin (thick) lines are $\nu_3 + 4\nu_4$ ($\nu_3 + 4\nu_4 + 4\nu_1$) approximation, colored as in (a); dot-dashed maroon line is MB for $T_R = 300$ K; inset shows magnified view below the lowest (ν_4) threshold.

$\nu_3 + 4\nu_4$). For ν_3 and $\nu_3 + \nu_4$, the positrons do not thermalize to T_R. The reason for this is seen by considering $f(k,\tau)$ for $\tau = 0.06$ ns amg, when equilibrium has been reached, as shown in Fig. 1(b) (see also `CF4-video` [57]). In the ν_3 approximation, only positrons above the threshold can lose energy; thus, in equilibrium we observe a pileup in $f(k,\tau)$ just below the threshold, with $f(k,\tau) \sim 0$ above the threshold, and the positron temperature decreases no further. In the $\nu_3 + (4)\nu_4$ approximations, we observe pileups below both thresholds. Both diminish on longer timescales than considered here: positrons below the $0 \to 3$ threshold can cool via $0 \to 4$ excitation; those below the $0 \to 4$ threshold can actually cool further, but only via at least two $4 \to 0$ deexcitations (since $2\varepsilon_4 < \varepsilon_3 < 3\varepsilon_4$) followed by a $0 \to 3$ excitation. Only in the $\nu_3 + 4\nu_4$ approximation is the temperature in agreement with experiment.

In all of the ν_3, $\nu_3 + \nu_4$, and $\nu_3 + 4\nu_4$ approximations, the equilibrium PMD is markedly non-Maxwellian, in contrast to what is observed in experiment [37]. We now consider, therefore, the role of positron-positron collisions. Figure 2(a) shows the time dependence of the positron temperature in the $\nu_3 + 4\nu_4$ approximation with positron-positron collisions included, for $R = 10^{-8}$–10^{-6} (the experimental value being understood to be $R \sim 10^{-7}$–10^{-6} [41]). Figure 2(b) shows $f(k,\tau)$ for $\tau = 0.06$ ns amg. For $R = 10^{-6}$, the positron-positron collisions clearly Maxwellianize the PMD, eliminating the pileup at the $0 \to 4$ threshold almost completely. For $R = 10^{-7}$, however, the effect of positron-positron collisions is much smaller, and for $R = 10^{-8}$, the PMD is essentially the same as it was without positron-positron collisions [cf. Fig. 1(b)]. Also, for all R, positron-positron collisions play a negligible role in the early stage of the cooling. Even the PMD for $R = 10^{-6}$ does not noticeably differ from the PMD without positron-positron collisions until $\tau \sim 0.01$ ns amg, by which time, the temperature has already dropped to ~450 K (see `CF4-pospos-video` and `CF4-pospos-nonu1-video` in Refs. [58,59]). This is because $\sigma_{ee}(u) \sim 1/u^4$, where u is the relative speed of the colliding pair [39,46]; as the temperature decreases, the likely relative speed of a colliding pair decreases, so σ_{ee} increases. In the experiment [37] it is estimated that $R \sim 10^{-7}$–10^{-6} [41], so positron-positron collisions may indeed play a significant role in Maxwellianizing the PMD [60].

We now consider the possible role of excitation of the dipole-inactive ν_1 mode in Maxwellianizing the PMD. We are unaware of any existing investigation of positron-impact excitation cross section for ν_1, so we turn to a set of measurements of $\sigma_{0\to1,3,4}$ for electron impact [61] and assume the positron-impact cross sections to be similar (as is predicted for ν_3 and ν_4 [33]). The shape of each measured electron cross section is similar, differing in the threshold energy and magnitude. The peak in the measured $\sigma_{0\to1}$ is approximately 3.1 times higher than the peak in the measured $\sigma_{0\to4}$ (see Fig. 1 in Ref. [61]). Thus, we estimate $\sigma_{0\rightleftarrows1}$ using the Born-dipole $\sigma_{0\rightleftarrows4}$ scaled by 3.1, with the threshold shifted. We include ν_1 along with ν_3 and ν_4 in two approximations, viz., without scaling of cross sections (denoted $\nu_3 + \nu_4 + \nu_1$), and with $\sigma_{0\rightleftarrows4,1}$ scaled by a factor of 4 (denoted $\nu_3 + 4\nu_4 + 4\nu_1$; see above). (We neglect the possible role of the other dipole-inactive mode, ν_2, because we are unaware of any existing theoretical or experimental investigation of $\sigma_{0\rightleftarrows2}$.) Figure 1(a) shows that inclusion of ν_1 (neglecting positron-positron collisions) enables faster cooling than ν_3 and ν_4 alone, with the $\nu_3 + 4\nu_4 + 4\nu_1$ approximation giving near-perfect agreement with experiment. Figure 1(b) shows that including ν_1 significantly reduces the pileups in the PMD at the ν_4 and ν_3 thresholds. This is because the ν_1 mode enables positrons below the lowest $(0 \to 4)$ threshold to cool further via a *single* deexcitation and excitation of the molecule: a positron with energy ε, where $\varepsilon_1 - \varepsilon_4 < \varepsilon < \varepsilon_4$, can induce a $4 \to 0$ deexcitation followed by a $0 \to 1$ excitation, reducing its energy by $\varepsilon_1 - \varepsilon_4$; another pathway is a $1 \to 0$ deexcitation followed by a $0 \to 3$ excitation. Since the deexcitation cross sections are orders of magnitude smaller than the excitation ones above the excitation thresholds [39], cooling via a single deexcitation and excitation is much more probable than via multiple deexcitations followed by excitation. Indeed, the peak in $f(k,\tau)$ at $k \approx 0.05$ a.u. corresponds to the energy $\varepsilon_1 - \varepsilon_4$, below which positrons can cool further only via the improbable multiple-deexcitations pathway. The doorway provided by ν_1 thus enables an accurate cooling timescale and room-temperature thermalization. Still, inclusion of ν_1 without positron-positron collisions is insufficient to fully Maxwellianize the PMD: the equilibrium PMD ($\tau = 0.06$ ns amg) has a lingering pileup at the $0 \to 4$ threshold (see also `CF4-video` [57]).

We finally consider the roles of ν_1 and positron-positron collisions together. Figure 2(a) shows the time evolution of the positron temperature in the $\nu_3 + 4\nu_4 + 4\nu_1$ approximation. This approximation gives slightly better agreement

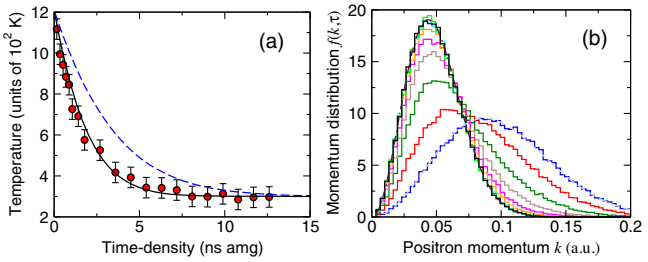

FIG. 3. Positron cooling in N_2. (a) Temperature: calculations using unscaled cross sections (dashed blue) and scaled cross sections (solid black); experiment [37] (red circles). (b) PMD $f(k,\tau)$ for values of τ as follows (in ns amg): 0 (blue), 0.9 (red), 2.1 (dark green), 3.3 (brown), 4.5 (magenta), 5.7 (orange), 8.1 (cyan), 10.5 (light green), 12.9 (black); also shown in the initial MB for $T = 1200$ K (dashed gray line) and the MB for $T_R = 300$ K (dot-dashed maroon line).

with experiment than the $\nu_3 + 4\nu_4$ approximation, for all R considered. Figure 2(b) shows $f(k,\tau)$ for $\tau = 0.06$ ns amg. For $R = 10^{-6}$ and 5×10^{-7}, the difference in the PMDs for the $\nu_3 + 4\nu_4$ and $\nu_3 + 4\nu_4 + 4\nu_1$ approximations is much smaller than it is for $R = 10^{-7}$ or 10^{-8}, or neglecting positron-positron collisions [cf. Fig. 1(b)]. Therefore, for $R \gtrsim 10^{-6}$, positron-positron collisions play the predominant role in Maxwellianizing the PMD, while for $R \lesssim 10^{-7}$, cooling below the lowest vibrational threshold due to the presence of ν_1 (see above) is more important.

Positron cooling in N_2 *gas*—N_2 has no electric dipole moment, and its vibrational mode is dipole inactive. We assessed the role of the vibrational mode, turning to a close-coupling calculation of the *electron*-impact cross section for this process [62], but found that its inclusion had little effect (see Supplemental Material [39], Fig. S7 and S8). Thus, we consider cooling in N_2 via quadrupole rotational excitations only. To a good approximation, the energy of a rotational level with angular momentum J is $\varepsilon_J = BJ(J+1)$, where B is the rotational constant. For N_2, we take $B = 9.2 \times 10^{-6}$ a.u. [63]. We use the Born-quadrupole cross sections for the $J \rightleftarrows J+2$ transitions [34,64] with quadrupole moment from Ref. [65], finding that including up to $J = 60$ gives converged results [39]. Since R is ~30 times smaller in the experiment for N_2 than in the experiment for CF_4 [37], positron-positron collisions are unlikely to play a significant role, so we neglect them.

Figure 3 shows the calculated time-dependent positron temperature during cooling from $T = 1200$ K ($k_B T = 103$ meV) [37,66] to T_R. We use 200 000 positrons and $\Delta\tau = 5 \times 10^{-4}$ ns amg. The calculation (dashed blue line) predicts slower cooling than the experiment (red circles). This was also seen in the theoretical model of Natisin *et al.* [37], suggesting that the Born-quadrupole cross sections underestimate the true ones. Natisin *et al.* found that scaling the Born-quadrupole cross sections by 1.8 gave better agreement between their model and experiment [37], and yielded a magnitude for $\sigma_{0\to2}$ in better agreement with calculation [67]. We likewise find that scaling the Born-quadrupole cross sections by 1.8 (solid black line) yields excellent agreement with the experiment, the thermalization time being consistent with the 14 ns amg measured in Ref. [68]. In contrast to CF_4, the PMD for cooling in N_2 remains near-Maxwellian as τ proceeds. Indeed, for the final value of τ shown, viz., $\tau = 12.9$ ns amg, $f(k,\tau)$ follows a MB for T_R closely. The small energy spacing between the N_2 rotational levels relative to that between the CF_4 vibrational levels allows the positrons to lose or gain energy in relatively small discrete amounts, so the PMD can relax to a MB easily. Thus, positron-positron collisions will have little effect.

Conclusions.—The development of positron traps, accumulators, and high-energy-resolution beams (e.g., for shorter temporal pulses in lifetime spectroscopy, colder positrons for antihydrogen formation, and higher densities for positronium BEC production) will benefit from fundamental theoretical insight [42,69]. However, currently positron cooling even in CF_4 and N_2 gases—the buffer gases of choice in the ubiquitous Surko traps—is not fully understood. Using Born-multipole collision cross sections (scaled to effectively approximate *ab initio* calculation where possible), this Letter has elucidated the mechanisms of cooling and the role of positron-positron interactions in positron cooling in CF_4 and N_2 gases, successfully simulating the experiment of Natisin *et al.* [37].

For CF_4, we found that rotational (de)excitation plays no appreciable role in cooling on the thermalization timescale, and that cooling only via excitation of the dipole-active vibrational modes would lead to a non-Maxwellian PMD that exhibits pileups below the thresholds, in contrast to the observations of experiment [37]. We showed that Maxwellianization can be effected by positron-positron collisions and/or further cooling below the lowest dipole-active (ν_4) threshold by deexciting ν_4 and subsequently exciting the dipole-inactive ν_1 mode (this is possible because, fortuitously, $\varepsilon_1 < 2\varepsilon_4$) [70]. For N_2, we found that even without positron-positron collisions, the PMD remains near-Maxwellian throughout the cooling process.

Overall, we have elucidated interesting cooling dynamics in these molecules, including the effect of cooling via a combination of deexcitation and excitation, and positron-positron interactions, specifically showing that in next-generation higher-density traps [18,42] (i.e., traps that support larger R than considered here) positron-positron interactions will readily Maxwellianize the PMD (simplifying modeling).

Positron-molecule correlations may modify the inelastic cross sections and rotational dynamics. However, *ab initio* calculation of positron-molecule inelastic scattering cross sections is a challenging, long-standing open problem (our recently developed positron-molecule many-body theory [51] may be extended to calculate *ab initio* inelastic

cross sections, but this remains unsolved; we also note excellent recent progress coupling electronic and vibrational degrees of freedom in electron scattering on molecular hydrogen [71]), and the suitability of Born cross sections has been highlighted [47] (note that we do use *ab initio* coupled-channel cross sections where available). Positron annihilation during cooling is another process that can affect the overall PMD and positron temperature [28,29], but for CF_4 or N_2 the annihilation cross sections are relatively small, thus this will have negligible effect on the timescales considered [72].

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