Statistics of energy loss and charge exchange of penetrating particles: Higher moments and transients

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Recent work on mean energy loss and straggling of ions in the presence of charge exchange has been extended to higher moments. The transient behavior of charge-exchange straggling has been determined as well as the skewness of the energy-loss profile. Formulas have been found for the two- and three-state cases where terms that have been well known in principle could also be written in a way that illustrates their respective origin. In addition to the frequently analyzed case of negligible energy loss in charge-changing events, we also mention explicitly the opposite situation where all energy loss is associated with charge exchange. The role of transients and skewness is very different in the two extremes. As in a previous paper by one of us, the notation has been kept general such as to allow for both collisional and spontaneous events, and no distinction needs to be made between charge exchange and change of excitation state. Finally we compare our calculations to recently obtained experimental results.

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I. INTRODUCTION

A general theory has recently been outlined for the statistics of energy loss of charged particles in the presence of charge exchange [1,2]. The scheme was directed primarily at swift particles penetrating thin layers of matter, but it is sufficiently flexible to also apply to particles interacting with surfaces as well as to other physical situations that are governed by similar rate equations.

For a beam of swift particles penetrating through a thin layer of material, quantities calculated include the mean energy loss and its fluctuation (straggling). It was found that, with increasing target thickness, the mean energy loss approaches a linear dependence with a slope independent of the initial charge state but an intercept that does depend on the initial state.

It is well documented that charge exchange produces a contribution to the spread in the energy-loss spectrum which is not accounted for by conventional theory of collisional straggling. The development of this area of research is described in Ref. [2], including an extensive list of references. For more recent related work see [3]. A general expression was derived for the fluctuation in energy loss in the presence of charge exchange [2]. This expression was found to be closely related to the zero-thickness intercept in the mean rate of energy loss. For the specific case of a two-state system with continuous stopping, well-known results were reproduced.

In connection with an experimental study of the electronic energy loss of slow ions scattered from surfaces, the claim has been made that charge exchange may be a major source of skewness in an energy-loss spectrum [4]. That claim was supported by model calculations that ought to represent a special case of the scheme outlined in [1]. It is well established that for swift heavy ions, charge-exchange straggling may overshadow collisional straggling [5]. A similar statement applying to skewness, if proven more generally true, would be of importance in ion beam physics. In this paper we concentrate on deriving expressions for skewness in equilibrium and transients for straggling. A detailed comparison with the results of Ref. [4], which involves time-dependent transition rates, will be published separately, including expressions for full energy-loss spectra.

By way of analogy, one expects skewness introduced by charge exchange to be related to the transient behavior of charge-exchange straggling. The latter has been found to be measurable recently in experiments with swift heavy ions [6].

On the basis of these considerations, we found it desirable to carry on the analysis performed in [2] to the next moment. As a result, we determine the stationary value of the skewness and the intercept of the straggling. In accordance with previous practice, an explicit analysis has been carried out for the particularly transparent two- and three-state cases.

II. INPUT AND OUTPUT

The key input is a set of differential transition rates $d\Lambda_{IJ}(T)/dT$ between accessible projectile states I and J, defined such that $[d\Lambda_{IJ}(T)/dT]dT\delta t \equiv \delta t d\Lambda_{IJ}(T)$ is the probability in a small time interval δt for a transition from state I to state J under simultaneous loss of kinetic energy (T, dT). In standard penetration theory [1], only collisional interactions are considered so that transition rates reduce to $d\Lambda_{IJ}(T) = Nv d\sigma_{IJ}(T)$, where N is the density of scattering centers, v the projectile velocity,

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and $d\sigma_{IJ}(T)$ the differential cross section. The notation in terms of transition rates allows for both spontaneous and collisionally induced events [2].

The most general output is a transfer matrix $\mathbf{F}(\Delta E,t)=\{F_{IJ}(\Delta E,t)\}$. Here $F_{IJ}(\Delta E,t)d(\Delta E)$ is the probability for a projectile occupying state I at $t=0$ to occupy state J at time t and to have lost kinetic energy $(\Delta E, d(\Delta E))$ by an arbitrary sequence of events. $\mathbf{F}(\Delta E,t)$ has been found to obey a generalized Bethe-Landau formula [1]

$$\mathbf{F}(\Delta E,t)=\frac{1}{2\pi}\int_{-\infty}^{\infty} dk e^{ik\Delta E}\, e^{t[\mathbf{Q}-\mathbf{\Lambda}(k)]}, \tag{1}$$

where $Q_{IJ}=\int d\Lambda_{IJ}-\delta_{IJ}\sum_L\int d\Lambda_{IL}$ and $\Lambda_{IJ}(k)=\int d\Lambda_{IJ}(1-e^{-ikT})$. Equation (1) assumes the individual events to be statistically independent and transition rates $d\Lambda_{IJ}(T)/dT$ to be independent of time.

The charge-state distribution $F_{IJ}(t)$ at time t is obtained from Eq. (1) by integration over ΔE,

$$\mathbf{F}(t)=e^{t\mathbf{Q}}.$$

The matrix $\mathbf{Q}$ satisfies the important sum rule

$$\sum_J Q_{IJ}=0. \tag{2}$$

III. MOMENTS

Quantities of primary interest are the mean energy loss, irrespective of the outgoing charge state, as well as the fluctuation and skewness of the associated spectrum. These quantities may be determined from the moments

$$\begin{aligned}\langle \Delta E^n\rangle_I &= \sum_J\int d(\Delta E)(\Delta E)^n F_{IJ}(\Delta E,t)\\ &= \sum_J\left(i\frac{\partial}{\partial k}\right)^n (e^{t[\mathbf{Q}-\mathbf{\Lambda}(k)]})_{IJ}\Big|_{k=0},\end{aligned}$$

where the index I indicates a dependence on the initial state. The first and second moments were determined previously [2] and were shown to reduce to

$$\langle\Delta E\rangle_I=\sum_J\int_0^t dt' F_{IJ}(t')\mathcal{P}_J, \tag{3}$$

$$\begin{aligned}\langle\Delta E^2\rangle_I=&\sum_J\int_0^t dt' F_{IJ}(t')\mathcal{M}_J\\ &+2\sum_{J,K,L}\int_0^t dt'\int_0^{t'} dt'' F_{IJ}(t'-t'')\\ &\times\mathcal{P}_{JK}F_{KL}(t'')\mathcal{P}_L,\end{aligned} \tag{4}$$

where $\mathbf{P}$ is a matrix characterizing the rate of energy loss with the elements $\mathcal{P}_{IJ}=\int T d\Lambda_{IJ}(T)$, and $\mathcal{P}_I=\sum_J\mathcal{P}_{IJ}$. Similarly, $\mathbf{M}$ is a matrix characterizing fluctuations in energy loss with the elements $\mathcal{M}_{IJ}=\int T^2 d\Lambda_{IJ}(T)$, and $\mathcal{M}_I=\sum_J\mathcal{M}_{IJ}$.

The sequence of steps leading to Eqs. (3) and (4) was outlined in [2]. When applied to the third moment it yields

$$\begin{aligned}\langle\Delta E^3\rangle_I=&\sum_J\sum_{n=1}^{\infty}\frac{t^n}{n!}\left(\mathbf{Q}^{n-1}\mathbf{N}\right)_{IJ}+3\sum_J\sum_{n=2}^{\infty}\frac{t^n}{n!}\sum_{\nu=0}^{n-2}\left(\mathbf{Q}^{n-2-\nu}[\mathbf{M}\mathbf{Q}^{\nu}\mathbf{P}+\mathbf{P}\mathbf{Q}^{\nu}\mathbf{M}]\right)_{IJ}\\ &+6\sum_J\sum_{n=3}^{\infty}\frac{t^n}{n!}\sum_{\nu=0}^{n-3}\sum_{\mu=0}^{\nu}\left(\mathbf{Q}^{n-3-\nu}\mathbf{P}\mathbf{Q}^{\nu-\mu}\mathbf{P}\mathbf{Q}^{\mu}\mathbf{P}\right)_{IJ}\\ =&\sum_J\int_0^t dt'\ (e^{t'\mathbf{Q}}\mathbf{N})_{IJ}+3\sum_J\int_0^t dt'\int_0^{t'} dt''\ (e^{(t'-t'')\mathbf{Q}}[\mathbf{M}\,e^{t''\mathbf{Q}}\,\mathbf{P}+\mathbf{P}\,e^{t''\mathbf{Q}}\,\mathbf{M}])_{IJ}\\ &+6\sum_J\int_0^t dt'\int_0^{t'} dt''\int_0^{t''} dt'''\ (e^{(t'-t'')\mathbf{Q}}\,\mathbf{P}\,e^{(t''-t''')\mathbf{Q}}\,\mathbf{P}\,e^{t'''\mathbf{Q}}\,\mathbf{P})_{IJ}\end{aligned}$$

or

$$\begin{aligned}\langle\Delta E^3\rangle_I=&\sum_J\int_0^t dt'\ F_{IJ}(t')\mathcal{N}_J+3\sum_{J,K,L}\int_0^t dt'\int_0^{t'} dt''\ F_{IJ}(t'-t'')\left[\mathcal{M}_{JK}F_{KL}(t'')\mathcal{P}_L+\mathcal{P}_{JK}F_{KL}(t'')\mathcal{M}_L\right]\\ &+6\sum_{J,K,L,M,N}\int_0^t dt'\int_0^{t'} dt''\int_0^{t''} dt'''\ F_{IJ}(t'-t'')\mathcal{P}_{JK}F_{KL}(t''-t''')\mathcal{P}_{LM}F_{MN}(t''')\mathcal{P}_N,\end{aligned} \tag{5}$$

where $\mathbf{N}$ is a matrix related to skewness with the elements $\mathcal{N}_{IJ}=\int T^3 d\Lambda_{IJ}(T)$, and $\mathcal{N}_I=\sum_J\mathcal{N}_{IJ}$.

IV. DIAGONALIZATION

Further reduction was found possible by use of the diagonal form of $\mathbf{Q}$. With the eigenvalues $q^{(\nu)}$ of $\mathbf{Q}$, the real parts of which are nonpositive, the charge-state distribution may be written in the form [2]

$$F_{IJ}(t) = \sum_{\nu} F_{IJ}^{(\nu)} e^{tq^{(\nu)}}, \tag{6}$$

where the coefficients $F_{IJ}^{(\nu)}$ can be expressed in terms of the eigenvectors of $\mathbf{Q}$. The explicit form of $F_{IJ}^{(\nu)}$ does not enter so long as only charge-state equilibrium and approach to equilibrium are of interest.

This allows carrying out the time integrals with the result

$$\begin{aligned} \langle \Delta E \rangle_I &= \sum_J \sum_\nu \gamma_\nu(t) F_{IJ}^{(\nu)} \mathcal{P}_J, \\ \langle \Delta E^2 \rangle_I &= \sum_J \sum_\nu \gamma_\nu(t) F_{IJ}^{(\nu)} \mathcal{M}_J + 2 \sum_{J,K,L} \sum_{\nu,\mu} \gamma_{\nu\mu}(t) F_{IJ}^{(\mu)} \mathcal{P}_{JK} F_{KL}^{(\nu)} \mathcal{P}_L, \\ \langle \Delta E^3 \rangle_I &= \sum_J \sum_\nu \gamma_\nu(t) F_{IJ}^{(\nu)} \mathcal{N}_J + 3 \sum_{J,K,L} \sum_{\nu,\mu} \gamma_{\nu\mu}(t) F_{IJ}^{(\mu)} \left[\mathcal{M}_{JK} F_{KL}^{(\nu)} \mathcal{P}_L + \mathcal{P}_{JK} F_{KL}^{(\nu)} \mathcal{M}_L \right] \\ &\quad + 6 \sum_{J,K,L,M,N} \sum_{\nu,\mu,\lambda} \gamma_{\nu\mu\lambda}(t) F_{IJ}^{(\lambda)} \mathcal{P}_{JK} F_{KL}^{(\mu)} \mathcal{P}_{LM} F_{MN}^{(\nu)} \mathcal{P}_N, \end{aligned} \tag{7}$$

where

$$\begin{aligned} \gamma_\nu(t) &= \frac{1}{q^{(\nu)}} (e^{tq^{(\nu)}} - 1), \\ \gamma_{\nu\mu}(t) &= \frac{\gamma_\nu(t) - \gamma_\mu(t)}{q^{(\nu)} - q^{(\mu)}}, \\ \gamma_{\nu\mu\lambda}(t) &= \frac{\gamma_{\nu\lambda}(t) - \gamma_{\mu\lambda}(t)}{q^{(\nu)} - q^{(\mu)}}. \end{aligned}$$

It is easily verified that $\gamma_{\nu\mu}(t)$ and $\gamma_{\nu\mu\lambda}(t)$ are fully symmetric.

V. STATIONARY SOLUTION AND APPROACH TO EQUILIBRIUM

At least one of the eigenvalues $q^{(\nu)}$ must always be vanishing, as follows from Eq. (2). Equation (6) demonstrates that all but those contributions $F_{IJ}^{(\nu)}(t)$ that belong to vanishing eigenvalues $q^{(\nu)}$ decay to zero. Hence vanishing eigenvalues determine charge-state equilibrium, or

$$F_{IJ}(\infty) = F_{IJ}^{(0)},$$

where $\nu = 0$ denotes a vanishing eigenvalue.

The following analysis is formally based on the assumption that there is only one vanishing eigenvalue. The existence of more than one vanishing eigenvalue would indicate a reducible transition matrix, i.e., separate sets of states with all interset transition rates vanishing.

The equilibrium state must be independent of the initial state. Therefore we have

$$F_{IJ}^{(0)} = F_{KJ}^{(0)} \equiv F_J^{(0)}.$$

Evaluation of the moments Eq. (7) in the limit of large t requires due consideration of all terms with vanishing eigenvalues. Limiting values of γ_ν and $\gamma_{\nu\mu}$ have been given previously [2]. For $\gamma_{\mu\nu\lambda}$ one finds

$$\gamma_{\nu\mu\lambda}(t) = \begin{cases} t^3/6 & \text{for } q^{(\lambda)} = q^{(\nu)} = q^{(\mu)} = 0 \\ -t^2/[2q^{(\lambda)}] - t/[q^{(\lambda)}]^2 - 1/[q^{(\lambda)}]^3 & \text{for } q^{(\nu)} = q^{(\mu)} = 0 \\ (t + 1/q^{(\nu)} + 1/q^{(\mu)})/[q^{(\nu)} q^{(\mu)}] & \text{for } q^{(\lambda)} = 0 \\ -1/[q^{(\lambda)} q^{(\nu)} q^{(\mu)}] & \text{for all nonvanishing.} \end{cases}$$

When all terms that vanish in the limit of large t are dropped, the nth moment reduces to a polynomial in t of order n. From these expressions, cumulants can be formed which read

$$\begin{aligned} \langle \Delta E \rangle_I &= t \sum_J F_J^{(0)} \mathcal{P}_J - \sum_J \sum_\nu{}' \frac{1}{q^{(\nu)}} F_{IJ}^{(\nu)} \mathcal{P}_J, \\ \langle (\Delta E - \langle \Delta E \rangle)^2 \rangle_I &= t \sum_J F_J^{(0)} \mathcal{M}_J - 2t \sum_{J,K,L} \sum_\nu{}' \frac{1}{q^{(\nu)}} F_J^{(0)} \mathcal{P}_{JK} F_{KL}^{(\nu)} \mathcal{P}_L + \Omega_I^2, \end{aligned}$$

where

$$\Omega_I^2 = -\sum_J \sum_\nu{}' \frac{1}{q^{(\nu)}} F_{IJ}^{(\nu)} \mathcal{M}_J + 2 \sum_{J,K,L} \sum_{\nu,\mu}{}'' \frac{1}{q^{(\nu)} q^{(\mu)}} F_{IJ}^{(\nu)} \mathcal{P}_{JK} F_{KL}^{(\mu)} \mathcal{P}_L$$
$$-2 \sum_{J,K,L} \sum_\nu{}' \frac{1}{[q^{(\nu)}]^2} \left[F_{IJ}^{(\nu)} \mathcal{P}_{JK} F_L^{(0)} + F_J^{(0)} \mathcal{P}_{JK} F_{KL}^{(\nu)} \right] \mathcal{P}_L - \left(\sum_J \sum_\nu{}' \frac{1}{q^{(\nu)}} F_{IJ}^{(\nu)} \mathcal{P}_J \right)^2 .$$

Primes and double primes in a sum indicate omission of vanishing eigenvalues. Moreover,

$$\langle (\Delta E - \langle \Delta E \rangle)^3 \rangle_I = t \sum_J F_J^{(0)} \mathcal{N}_J - 3t \sum_{J,K,L} \sum_\nu{}' \frac{1}{q^{(\nu)}} \left[F_J^{(0)} \mathcal{M}_{JK} F_{KL}^{(\nu)} \mathcal{P}_L + F_J^{(0)} \mathcal{P}_{JK} F_{KL}^{(\nu)} \mathcal{M}_L \right]$$
$$-6t \sum_{J,K,L,M} \sum_\nu{}' \frac{1}{[q^{(\nu)}]^2} F_J^{(0)} \mathcal{P}_J F_K^{(0)} \mathcal{P}_{KL} F_{LM}^{(\nu)} \mathcal{P}_M$$
$$+6t \sum_{J,K,L,M,N} \sum_{\nu,\mu}{}'' \frac{1}{q^{(\nu)} q^{(\mu)}} F_J^{(0)} \mathcal{P}_{JK} F_{KL}^{(\nu)} \mathcal{P}_{LM} F_{MN}^{(\mu)} \mathcal{P}_N + (\text{const})_I ,$$

where the intercept $(\text{const})_I$ has not been evaluated explicitly.

VI. GENERATING FUNCTION

In Ref. [2], it was demonstrated that the expression $\mathbf{f}(s) = s\,(s\mathbf{1} - \mathbf{Q})^{-1}$, where $\mathbf{1}$ is the unit matrix, can serve as a generating function for the sums over eigenvalues occurring in the above moments and cumulants. Indeed, from the Laplace transform of Eq. (6),

$$(s\mathbf{1} - \mathbf{Q})^{-1} = \sum_\nu \mathbf{F}^{(\nu)} \frac{1}{s - q^{(\nu)}} ,$$

one readily deduces that $\mathbf{F}^{(0)} = \mathbf{f}(0)$ and

$$\sum_\nu{}' \frac{1}{[q^{(\nu)}]^n} \mathbf{F}^{(\nu)} = -\frac{1}{n!} \frac{d^n}{ds^n} \mathbf{f}(s) \bigg|_{s=0} .$$

With this, we find

$$\begin{aligned}
\langle \Delta E \rangle_I &= t\, \mathrm{Tr}[\mathbf{f}(s)\mathbf{P}] + \frac{d}{ds} [\mathbf{f}(s)\mathbf{P}]_I , \\
\langle (\Delta E - \langle \Delta E \rangle)^2 \rangle_I &= t\, \mathrm{Tr}[\mathbf{f}(s)\mathbf{M}] + t \frac{d}{ds} \mathrm{Tr}[\mathbf{f}(s)\mathbf{P}\, \mathbf{f}(s)\mathbf{P}] \\
&\quad + \frac{d}{ds} [\mathbf{f}(s)\mathbf{M}]_I + \frac{d^2}{ds^2} [\mathbf{f}(s)\mathbf{P}\, \mathbf{f}(s)\mathbf{P}]_I - \left(\frac{d}{ds} [\mathbf{f}(s)\mathbf{P}]_I \right)^2 , \\
\langle (\Delta E - \langle \Delta E \rangle)^3 \rangle_I &= t\, \mathrm{Tr}[\mathbf{f}(s)\mathbf{N}] + 3t \frac{d}{ds} \mathrm{Tr}[\mathbf{f}(s)\mathbf{M}\, \mathbf{f}(s)\mathbf{P}] + t \frac{d^2}{ds^2} \mathrm{Tr}[\mathbf{f}(s)\mathbf{P}\, \mathbf{f}(s)\mathbf{P}\, \mathbf{f}(s)\mathbf{P}] + (\text{const})_I ,
\end{aligned} \tag{8}$$

all expressions being taken at $s = 0$. Here, the notations

$$\mathrm{Tr}[\mathbf{X}] = \sum_J X_{JJ} \quad \text{and} \quad (\mathbf{X}\mathbf{P})_I = \sum_J X_{IJ} \mathcal{P}_J$$

have been used.

VII. SPECIAL CASES

The following definitions will be used throughout this section:

$$\langle \mathcal{P} \rangle = \sum_J F_J^{(0)} \mathcal{P}_J , \quad \langle \mathcal{M} \rangle = \sum_J F_J^{(0)} \mathcal{M}_J ,$$
$$\langle \mathcal{N} \rangle = \sum_J F_J^{(0)} \mathcal{N}_J , \quad \langle \mathcal{P}^2 \rangle = \sum_{JK} F_J^{(0)} \mathcal{P}_{JK} \mathcal{P}_K ,$$
$$\langle \mathcal{M}\mathcal{P} \rangle = \sum_{JK} F_J^{(0)} \mathcal{M}_{JK} \mathcal{P}_K , \quad \langle \mathcal{P}\mathcal{M} \rangle = \sum_{JK} F_J^{(0)} \mathcal{P}_{JK} \mathcal{M}_K ,$$
$$\langle \mathcal{P}^3 \rangle = \sum_{JKL} F_J^{(0)} \mathcal{P}_{JK} \mathcal{P}_{KL} \mathcal{P}_L , \quad \text{and} \quad (\mathcal{P}^2)_I = \sum_J \mathcal{P}_{IJ} \mathcal{P}_J .$$

A. The two-state case

The generating function for the two-state case has been given in [2]. Its derivatives are found to obey the relations

$$\frac{d}{ds} \mathbf{f}(s) \bigg|_{s=0} = \frac{1}{\Lambda} [\mathbf{1} - \mathbf{f}(0)] ,$$
$$\frac{d^2}{ds^2} \mathbf{f}(s) \bigg|_{s=0} = -\frac{2}{\Lambda^2} [\mathbf{1} - \mathbf{f}(0)] ,$$

where $\Lambda = \Lambda_{12} + \Lambda_{21}$. All traces and intercepts can then easily be evaluated and read

$$\langle \Delta E \rangle_I = t\langle \mathcal{P} \rangle + \frac{1}{\Lambda}(\mathcal{P}_I - \langle \mathcal{P} \rangle), \tag{9}$$

$$\begin{aligned}\langle (\Delta E - \langle \Delta E \rangle)^2 \rangle_I = t\langle \mathcal{M} \rangle + t\frac{2}{\Lambda}\left(\langle \mathcal{P}^2 \rangle - \langle \mathcal{P} \rangle^2\right) \\ +\frac{1}{\Lambda}(\mathcal{M}_I - \langle \mathcal{M} \rangle) + \frac{1}{\Lambda^2}(\mathcal{P}_I - \langle \mathcal{P} \rangle)^2 \\ -\frac{4}{\Lambda^2}(\langle \mathcal{P}^2 \rangle - \langle \mathcal{P} \rangle^2) \\ +\frac{2}{\Lambda^2}[(\mathcal{P}^2)_I - (\mathcal{P}_I)^2],\end{aligned} \tag{10}$$

$$\begin{aligned}\langle (\Delta E - \langle \Delta E \rangle)^3 \rangle_I = t\langle \mathcal{N} \rangle + t\frac{3}{2\Lambda}\langle (\mathcal{M} - \langle \mathcal{M} \rangle)(\mathcal{P} - \langle \mathcal{P} \rangle) \rangle \\ +t\frac{3}{2\Lambda}\langle (\mathcal{P} - \langle \mathcal{P} \rangle)(\mathcal{M} - \langle \mathcal{M} \rangle) \rangle \\ +t\frac{6}{\Lambda^2}\langle (\mathcal{P} - \langle \mathcal{P} \rangle)^3 \rangle + (\mathrm{const})_I.\end{aligned} \tag{11}$$

1. Ignoring energy loss in charge exchange

An instructive limiting case is found by decoupling the possible processes into either energy loss or charge exchange, i.e. [1,7],

$$d\Lambda_{IJ}(T)/dT = \Lambda_{IJ}\delta(T) + \delta_{IJ}d\Lambda_I(T)/dT.$$

This makes the matrices **P**, **M**, and **N** diagonal and causes the last term in Eq. (10) to drop out. Then, Eqs. (9)–(11) reduce to

$$\langle \Delta E \rangle_1 = t(f_1\mathcal{P}_1 + f_2\mathcal{P}_2) + \frac{f_2}{\Lambda}(\mathcal{P}_1 - \mathcal{P}_2), \tag{12}$$

$$\begin{aligned}\langle (\Delta E - \langle \Delta E \rangle)^2 \rangle_1 = t(f_1\mathcal{M}_1 + f_2\mathcal{M}_2) \\ +\frac{2t}{\Lambda}f_1f_2(\mathcal{P}_1 - \mathcal{P}_2)^2 \\ +\frac{f_2}{\Lambda}(\mathcal{M}_1 - \mathcal{M}_2) \\ +\frac{f_2(f_2 - 4f_1)}{\Lambda^2}(\mathcal{P}_1 - \mathcal{P}_2)^2,\end{aligned} \tag{13}$$

$$\begin{aligned}\langle (\Delta E - \langle \Delta E \rangle)^3 \rangle_1 = t(f_1\mathcal{N}_1 + f_2\mathcal{N}_2) \\ +\frac{6tf_1f_2}{\Lambda}(\mathcal{M}_1 - \mathcal{M}_2)(\mathcal{P}_1 - \mathcal{P}_2) \\ -\frac{6t}{\Lambda^2}f_1f_2(f_1 - f_2)(\mathcal{P}_1 - \mathcal{P}_2)^3 \\ +(\mathrm{const})_1,\end{aligned} \tag{14}$$

with $f_1 \equiv f_1(0) = \Lambda_{21}/\Lambda$ and $f_2 \equiv f_2(0) = \Lambda_{12}/\Lambda$. The corresponding relations for state 2 are found by interchanging indices.

Here, the expression Eq. (12) is contained in the results of Ref. [2]; the equilibrium term proportional to t in Eq. (13) is well known and was first derived in Ref. [8], while the intercept was not previously known; in Eq. (14), only the equilibrium term is given, which is also new.

2. Energy loss only by charge exchange

The opposite extreme is a situation where all energy loss goes into charge exchange. Such a model was proposed by Firsov [9] to describe electronic energy loss by slow heavy ions in gases. In that case, all diagonal elements in the three matrices vanish. For the two-state system, the terms proportional to t read, then,

$$\langle (\Delta E - \langle \Delta E \rangle)^2 \rangle = t(f_1\mathcal{M}_1 + f_2\mathcal{M}_2) - \frac{2t}{\Lambda}(\mathcal{P}_1 - \mathcal{P}_2)(f_1^2\mathcal{P}_1 - f_2^2\mathcal{P}_2), \tag{15}$$

$$\begin{aligned}\langle (\Delta E - \langle \Delta E \rangle)^3 \rangle = t(f_1\mathcal{N}_1 + f_2\mathcal{N}_2) - \frac{3t}{\Lambda}(\mathcal{P}_1 - \mathcal{P}_2)(f_1^2\mathcal{M}_1 - f_2^2\mathcal{M}_2) - \frac{3t}{\Lambda}(\mathcal{M}_1 - \mathcal{M}_2)(f_1^2\mathcal{P}_1 - f_2^2\mathcal{P}_2) \\ +\frac{12t}{\Lambda^2}(\mathcal{P}_1 - \mathcal{P}_2)(f_1\mathcal{P}_1 + f_2\mathcal{P}_2)(f_1^2\mathcal{P}_1 - f_2^2\mathcal{P}_2).\end{aligned} \tag{16}$$

These expressions differ significantly from Eqs. (13) and (14).

B. Three-state case

In the notation of Ref. [2], and after introduction of the quantities

$$\mathcal{E}_{IJ} \equiv \sum_K \frac{\Lambda_{IK}}{\beta}(\mathcal{P}_{IJ} - \mathcal{P}_{KJ}) \quad \text{and} \quad \mathcal{E}_I \equiv \sum_J \mathcal{E}_{IJ},$$

the expressions for the three-state case can be brought into the following form:

$$\langle \Delta E \rangle_I = t\langle \mathcal{P} \rangle + \frac{\alpha}{\beta}(\mathcal{P}_I - \langle \mathcal{P} \rangle) - \mathcal{E}_I, \tag{17}$$

$$
\begin{aligned}
\langle(\Delta E-\langle\Delta E\rangle)^2\rangle_I = {} & t\langle\mathcal{M}\rangle + t\frac{2\alpha}{\beta}\left(\langle\mathcal{P}^2\rangle-\langle\mathcal{P}\rangle^2\right) - 2t\sum_{JK} f_J P_{JK}\mathcal{E}_K + \frac{\alpha}{\beta}(\mathcal{M}_I-\langle\mathcal{M}\rangle) - \sum_J \frac{\Lambda_{IJ}}{\beta}(\mathcal{M}_I-\mathcal{M}_J) \\
& + \frac{\alpha^2}{\beta^2}(\mathcal{P}_I-\langle\mathcal{P}\rangle)^2 + \frac{2\alpha^2}{\beta^2}[\langle\mathcal{P}^2\rangle_I-\langle\mathcal{P}_I\rangle^2] - \frac{4\alpha^2}{\beta^2}(\langle\mathcal{P}^2\rangle-\langle\mathcal{P}\rangle^2) + \frac{2}{\beta}\langle\mathcal{P}\rangle(\mathcal{P}_I-\langle\mathcal{P}\rangle) \\
& + \frac{2}{\beta}(\langle\mathcal{P}^2\rangle-\langle\mathcal{P}\rangle^2) + \frac{4\alpha}{\beta}\sum_{JK} f_J\mathcal{P}_{JK}\mathcal{E}_K - \frac{2\alpha}{\beta}\sum_J \mathcal{E}_{IJ}(\mathcal{P}_J-\langle\mathcal{P}\rangle) \\
& + \frac{2\alpha}{\beta}\sum_J \mathcal{P}_{IJ}(\mathcal{E}_I-\mathcal{E}_J) + 2\sum_J \mathcal{E}_{IJ}\mathcal{E}_J + (\mathcal{E}_I)^2,
\end{aligned} \tag{18}
$$

where $\alpha = \sum_{IJ}\Lambda_{IJ}$, $\beta = \sum_I \mu_I$, $\mu_1 = \Lambda_{32}\Lambda_{21} + \Lambda_{23}\Lambda_{31} + \Lambda_{21}\Lambda_{31}$, and μ_2 and μ_3 are obtained from μ_1 by cyclic permutation. With this, $f_I = \mu_I/\beta$. The constant terms in Eq. (18) were obtained from Eq. (9) by means of computer algebra. The t-dependent terms are equivalent to the result given in Ref. [2]. For the special case of $\Lambda_{13} = \Lambda_{31} = 0$, that result reduces to the one given in Ref. [10]. We have not evaluated the third moment for the three-state case.

VIII. DISCUSSION

While the notation in this paper as well as in [2] has been chosen such as to allow for collision-induced and/or spontaneous events, conclusions will be made here for collision-induced events only. For this purpose, we list a translation of the above results into conventional notation in particle penetration,

$$d\Lambda = Nv\,d\sigma,\quad \mathcal{P} = NvS,\quad \mathcal{M} = NvW,\quad \mathcal{N} = NvQ,$$

with indices added where appropriate. Here, N is the atom density in the penetrated medium and v the projectile speed, $S = \int T d\sigma$ a stopping cross section, $W = \int T^2 d\sigma$ a straggling parameter, and $Q = \int T^3 d\sigma$ a skewness parameter.

A. Straggling

The first problem mentioned in the Introduction is the transient in charge-exchange straggling. Ignoring the terms containing $\mathcal{M}_I$, one deduces from Eq. (13) that for the two-state case, charge-exchange straggling saturates for

$$vt \gg \frac{1}{N(\sigma_{12}+\sigma_{21})}\frac{|4f_1-f_2|}{2f_1}, \tag{19}$$

if the initial charge state was 1. This is to be compared with the transient thickness for the mean energy loss which emerges from Eq. (12),

$$vt \gg \frac{1}{N(\sigma_{12}+\sigma_{21})}\frac{f_2|S_1-S_2|}{f_1S_1+f_2S_2}. \tag{20}$$

Unlike Eq. (19), this depends sensitively on the partial stopping cross sections.

B. Skewness

Next, consider skewness. Ignore all collisional straggling and collisional skewness as well as energy loss to charge exchange. Then, Eqs. (13) and (14) reduce to

$$\left.\frac{\langle(\Delta E-\langle\Delta E\rangle)^3\rangle}{\langle(\Delta E-\langle\Delta E\rangle)^2\rangle}\right|_{\text{chex}} = -\frac{3}{\sigma_{12}+\sigma_{21}}(f_1-f_2)(S_1-S_2). \tag{21}$$

This may be compared with the collisionally induced skewness

$$\left.\frac{\langle(\Delta E-\langle\Delta E\rangle)^3\rangle}{\langle(\Delta E-\langle\Delta E\rangle)^2\rangle}\right|_{\text{coll}} = mv^2 \tag{22}$$

for straight Coulomb stopping, where m is the electron mass. In the energy range where Eq. (22) applies, that ratio is much greater than Eq. (21), since stopping cross sections are made up by energy losses $\ll mv^2$, and since charge-exchange cross sections are of similar or higher magnitude as energy-loss cross sections. Hence, for swift ions, skewness introduced by charge exchange is negligible in comparison with the skewness introduced by violent Coulomb collisions. This is not too surprising in view of the width of the Rutherford spectrum.

The situation is different in the opposite extreme where energy loss is caused mainly by charge-changing events. Here, the corresponding estimate based on Eqs. (15) and (16) leads to

$$\left.\frac{\langle(\Delta E-\langle\Delta E\rangle)^3\rangle}{\langle(\Delta E-\langle\Delta E\rangle)^2\rangle}\right|_{\text{chex}} = -\frac{6}{\sigma_{12}+\sigma_{21}}(f_1S_1+f_2S_2), \tag{23}$$

where the occurrence of the mean stopping cross section on the right-hand side indicates that this term is much more significant than Eq. (21).

In the low-velocity limit, which was dealt with in Ref. [4], the above arguments concerning Coulomb stopping do not apply and hence charge exchange *does* contribute to skewness. This is consistent with the findings in Ref. [4].

C. Comparison with experiments

We apply the calculations presented for straggling in the three-state case to experiments [6] using 17.6 MeV/u Br^{33+} beams penetrating through 1 μm Si foils. The states involved are Br^{31+} (1), Br^{32+} (2), and Br^{33+} (3) with equilibrium occupations of 0.2, 0.4, and 0.4, respectively. Brackets define the notation for the states. Stopping powers are 4.06, 4.33, and 4.6 MeV/μm, respectively.

These numbers were obtained by scaling the measured average energy loss of 4.6 MeV with q^2 [6]. From an estimated mean free path of 0.5 μm for loss of an L-shell electron one obtains a transition rate from state 2 to state 3 of $\Lambda_{23} = 2\ (\mu\text{m})^{-1}$. If only one-electron processes are allowed (i.e., $\Lambda_{13} = \Lambda_{31} = 0$), the remaining transition frequencies can be extracted from the equilibrium occupations and read $\Lambda_{23} = \Lambda_{32} = \Lambda_{21} = 2$ and $\Lambda_{12} = 4$, all in $(\mu\text{m})^{-1}$.

Insertion of these numbers in Eq. (18) gives the equilibrium straggling $(\Omega^2)^{\text{eq}}_{\text{chex}} = 0.029\,16$ MeV^2 and a contribution from the intercept $\Delta(\Omega^2)_{3,\text{chex}} = -0.0173$ MeV^2. Taking into account the Bohr straggling ($\Omega_{\text{Bohr}} = 137$ keV) finally leads to a total straggling of $\Omega_{\text{tot}} = 175$ keV which is to be compared to the experimental value of $\Omega_{\text{expt}} = 178$ keV. This excellent agreement is not unexpected since the transition frequencies input into Eq. (18) were determined from the same experiment to which we compare the straggling number. The resulting equation for straggling in this case reads

$$\langle \Omega^2 \rangle = 0.029\,16x - 0.0159 \quad \text{MeV}^2,$$

where the thickness x is in μm.

IX. SUMMARY

We extended previously presented calculations on mean energy loss and straggling of ions penetrating matter to the third moment. The general result is given in Eq. (5).

For the equilibrium limit we derived general formulas for the first three cumulants [Eqs. (8)] which we evaluated explicitly for the two- and three-state systems in Secs. VII A and VII B, respectively.

We derived new expressions for the intercept in straggling and for the equilibrium in skewness.

Finally we focused on the contributions coming from charge exchange for the two-state system in two limiting cases (no energy loss in charge exchange and energy loss in charge exchange only) and applied our results to recently obtained experimental data involving three charge states.

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