Stochastic treatment of charge states for ion stopping in solids

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We describe the evolution of the charge state of a fast atomic projectile under the equilibrium conditions as a stationary continuous-time Markov process with discrete values. The time scale of the charge-state autocorrelation function is governed by the rate of charge-changing collisions in the target. Describing the collective electron excitations in the target by a linear-response formalism, we show that the finite response time of the electron gas makes the mean stopping power and the mean self-energy of the projectile sensitive to the charge-state correlation effects. We evaluate these effects for light projectiles by using a two-level model for the Markov process and simple models for the dielectric function of the electron gas.
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Interrelation between the charge states and the energy loss of atomic particles, moving through the solid targets, is a much-studied problem, which has been extensively reviewed recently.[1–3] Significant progress has been reported on the evaluation of the electron capture and loss cross sections, σ_c and σ_L, for atomic projectiles in solids.[1,4,5] Equilibrium charge fractions, resulting from those cross sections, have been used to evaluate the mean stopping power of a projectile as a weighted (incoherent) superposition of the stopping powers associated with each charge state, as well as the stopping powers associated with charge-changing events.[6] A more complete statistical theory of charged-particle stopping in the presence of charge exchange has been developed using differential energy loss rates that allow for transitions within an arbitrary number of projectile states.[2,7] Such a theory yields the mean energy loss as a weighted average over the instantaneous charge-state distribution of the projectile, in both the preequilibrium and equilibrium regimes. Inherent in these approaches is the assumption that the elementary energy-loss events depend on the instantaneous charge state of the projectile, and the assumption of the statistical independence of different charge-changing events. It should be noted that the charge-state problem is further complicated for fast heavy ions,[8] where the screening of the ion by the bound electrons leads to a nontrivial dependence of the stopping power S on the (fixed) ion charge Z, even though the scaling $S \propto Z^2$ is implied by the perturbation theory at high ion velocities.[3] Consequently, it may be difficult to relate the concept of the effective charge Z_{eff} to the charge-state distribution for heavy ions, based on assumption that the average ion stopping power scales as $\propto Z_{eff}^2$.[9]

In the present paper, we focus on the energy loss of fast light ions, such as H^+ and He^+, due to the electron excitations of the solid, in the presence of the charge-changing collisions with the target atoms. For high projectile speeds, the energy loss is dominated by the collective electron excitations, which are well described by the linear-response formalism.[1] We model the projectile as a structured, point-charge perturber, moving with a constant velocity **v** through an electron gas. Charge-changing collisions may be considered as instantaneous events on the time scale of the electron-gas response. The stopping power S of a projectile with a *fixed* charge Z_1 scales as $S \propto Z_1^2$ and represents the drag force due to the polarization of the medium in a form of a stationary wake pattern in the frame of reference attached to the projectile. If the projectile charge is suddenly switched to the value Z_2, there will be a temporal response in the polarization of the medium, which propagates on the time scale of $1/\omega_p$, where ω_p is the electron plasma frequency. The drag force on the projectile will not instantaneously follow the change of the charge from Z_1 to Z_2, but rather will retain some memory of the preceding charge Z_1. We consider the equilibrium conditions, where the charge state of the projectile is usually assumed to frequently oscillate about the mean value Z_{eq}, obtained as a balance of the electron capture and loss processes. In fact, the charge state $\zeta(t)$ of the projectile is a stationary continuous-time Markov process,[10] which takes discrete values Z_j. Each realization of the process $\zeta(t)$ is a staircase function of time, with jumps at discrete points in time t_n, which are distributed in such a way that the past has no influence on the future if the present value of $\zeta(t)$ is defined. With this picture in mind, the survival time of a given charge value Z_j is given by $1/\Gamma_j$, where $\Gamma_j = N_{at} v \sigma_j$, N_{at} being the atomic density of the target and σ_j the total cross section for the transitions leading out of the charge state Z_j. That time may be long enough compared to the response time of the electron gas, $1/\omega_p$, that a significant correlation between various charge-state values may arise in the stopping power. We examine below the role of this correlation in the stopping power and the self-energy of the projectile, using atomic units.

To be more specific, we adopt a two-level model of the Markov process, which may be quite appropriate for fast H and He projectiles. Namely, we have $Z_1 = 1$ for He^+ and $Z_2 = 2$ for He^{2+}, or $Z_1 = 0$ for H and $Z_2 = 1$ for H^+. Defining

$P_j(t)$ as the probability that the charge state $\zeta(t)$ has the value Z_j at time t, one has the familiar rate equations[4,8]

$$\dot{P}_1(t) = -\Gamma_L P_1(t) + \Gamma_C P_2(t), \qquad \dot{P}_2(t) = -\Gamma_C P_2(t) + \Gamma_L P_1(t), \tag{1}$$

where the transition rates $\Gamma_{C,L} = N_{at} v \sigma_{C,L}$ are defined in terms of the electron capture and loss cross sections, σ_C and σ_L. In the stationary regime, the state probabilities are $\overline{P_1} = \Gamma_C/\Gamma$ and $\overline{P_2} = \Gamma_L/\Gamma$, where $\Gamma = \Gamma_C + \Gamma_L$. The mean value of the charge state in equilibrium is $\langle \zeta(t) \rangle \equiv Z_{eq} = Z_1 \overline{P_1} + Z_2 \overline{P_2}$, while the autocorrelation function for the charge states at times t and t' is given by[10]

$$\langle \zeta(t)\zeta(t')\rangle = Z_{eq}^2 + Q\, e^{-\Gamma|t-t'|}, \tag{2}$$

where $Q \equiv (Z_2 - Z_1)^2 \overline{P_1}\,\overline{P_2} = (Z_2 - Z_{eq})(Z_{eq} - Z_1)$. We may call the two terms on the right-hand side of Eq. (2) the uncorrelated and the correlated part of $\langle \zeta(t)\zeta(t')\rangle$, with the correlation time in the latter part defined by $1/\Gamma$.

We now study the polarization of the electron gas by a point-charge perturber, with the density $\rho(\mathbf{r},t) = \zeta(t)\delta(\mathbf{r} - \mathbf{v}t)$, by using the linear-response formalism.[1] The corresponding current density is $\mathbf{J}(\mathbf{r},t) = \mathbf{v}\rho(\mathbf{r},t)$, and the rate of the energy dissipation in the electron gas is given by

$$\dot{W}(t) = \int d\mathbf{r}\, \mathbf{J}(\mathbf{r},t)\cdot \mathbf{E}_{ind}(\mathbf{r},t), \tag{3}$$

where the induced electric field is given in terms of the induced potential, $\mathbf{E}_{ind}(\mathbf{r},t) = -\nabla \phi_{ind}(\mathbf{r},t)$. The solution of the Poisson's equation in the medium, described by a dielectric function $\epsilon(k,\omega)$, gives for the space-time Fourier transform of the induced potential

$$\phi_{ind}(\mathbf{k},\omega) = \frac{4\pi}{k^2}\rho(\mathbf{k},\omega)\left[\frac{1}{\epsilon(k,\omega)} - 1\right], \tag{4}$$

where the same transform of the perturber density is given by $\rho(\mathbf{k},\omega) = \zeta(\omega - \mathbf{k}\cdot\mathbf{v})$, $\zeta(\omega)$ being the time Fourier transform of the process $\zeta(t)$. Going to the space Fourier transform in Eq. (3), we obtain

$$\dot{W}(t) = -i\int \frac{d\mathbf{k}}{(2\pi)^3}\frac{4\pi}{k^2}\mathbf{k}\cdot\mathbf{v}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\left[\frac{1}{\epsilon(k,\omega+\mathbf{k}\cdot\mathbf{v})} - 1\right] \times \int_{-\infty}^{\infty} dt'\, e^{-i\omega(t-t')}\zeta(t)\zeta(t'). \tag{5}$$

The mean value of the energy dissipation rate, $\langle \dot{W}(t)\rangle$, is obtained as an ensemble average over all possible realizations of the process $\zeta(t)$ in terms of the autocorrelation function (2). Based on the decomposition of the autocorrelation function (2) into the uncorrelated and the correlated part, we can write the mean value of the stopping power as $\mathcal{S} \equiv -\langle \dot{W}(t)\rangle/v = Z_{eq}^2 S_0 + Q S_c$. Here, Z_{eq}^2 and Q are the statistical weighting factors of the uncorrelated and correlated parts, while the stopping factors S_0 and S_c describe the dynamics of the corresponding interactions with the electron gas. Using the causal properties of the dielectric function, we obtain for the correlated stopping factor

$$S_c = \frac{1}{\pi^2 v}\int d\mathbf{k}\frac{\mathbf{k}\cdot\mathbf{v}}{k^2}\int_0^{\infty} d\omega\, C(\omega - \mathbf{k}\cdot\mathbf{v})\,\mathrm{Im}\left[\frac{-1}{\epsilon(k,\omega)}\right], \tag{6}$$

with $C(\omega) = (\Gamma/\pi)/(\omega^2 + \Gamma^2)$. The uncorrelated stopping factor S_0 is given by the right-hand side of Eq. (6), with the function $C(\omega - \mathbf{k}\cdot\mathbf{v})$ replaced by $\delta(\omega - \mathbf{k}\cdot\mathbf{v})$, corresponding to the limit $\Gamma \to 0$ in C. Note that S_0 is then the standard expression for the stopping power of a fixed-unit-point charge.[1]

In the high-speed regime, one may use for the stopping power calculations the plasmon-pole approximation[1] for the dielectric function, $\mathrm{Im}[-1/\epsilon(k,\omega)] = (\pi\omega_p^2/2\omega_k)[\delta(\omega - \omega_k) - \delta(\omega + \omega_k)]$, where the plasmon dispersion is given by $\omega_k^2 = \omega_p^2 + 3v_F^2 k^2/5 + k^4/4$, with v_F the Fermi velocity of the electron gas. Then, $S_0 = (\omega_p/v)^2 \ln(k_2/k_1)$, where k_1, k_2 are the positive roots of the equation $\omega_k^2 = k^2 v^2$ with $k_1 < k_2$, while the expression (6) for the correlated stopping factor S_c is reduced to a single integration. Note that the cross sections $\sigma_{C,L}$ generally depend on the projectile speed v, as do the rates $\Gamma_{C,L}$ and the statistical factors Z_{eq}^2 and Q in the stopping power $\mathcal{S}$. In order to single out the velocity dependence of the charge correlation effect on the dynamics of the interaction with the electron gas, we choose to evaluate the ratio S_C/S_0, which may also be a useful factor in attempting to derive the effective charge Z_{eff} in the form $Z_{eff}^2 \equiv \mathcal{S}/S_0 = Z_{eq}^2 + Q(S_c/S_0)$, in an analogy to the procedure outlined in Ref. 9. Using parameters for an Al target, we have evaluated the ratio S_C/S_0 for the velocity range $2 < v < 10$ and the values of the total charge-exchange rate $\Gamma < 1$. The results, shown on Fig. 1, indicate substantial dependence of the charge correlation effect on both the ion speed and the rate Γ. In particular, one finds[1] for the He projectile in the Al target, that Γ remains close to about 0.16 in the velocity range $2 < v < 5$, giving the ratio S_c/S_0 of about 0.9. However, the values of the ratio of the statistical weighting factors, Q/Z_{eq}^2, are found[1] to decrease from about 0.12 to about 0.03 in the same velocity range, which renders the correlation part of the stopping power relatively small, but noticeable, for He in Al.

Let us now derive the expression for the projectile self-energy due to the collective electron excitations in the target in the presence of charge-changing collisions. We start with the general definition,

$$\Sigma(t) = \frac{1}{2}\int d\,\mathbf{r}\,\rho(\mathbf{r},t)\phi_{ind}(\mathbf{r},t), \tag{7}$$

and proceed along the same lines as in the derivation of Eq. (5). The mean value of the self-energy is again decomposed into an uncorrelated and correlated part, $\mathcal{E} \equiv \langle \Sigma(t)\rangle = Z_{eq}^2\mathcal{E}_0 + Q\mathcal{E}_c$, with

$$\mathcal{E}_c = \frac{1}{2\pi^2}\int \frac{d\mathbf{k}}{k^2}\int_0^{\infty} d\omega\, C(\omega - \mathbf{k}\cdot\mathbf{v})\,\mathrm{Re}\left[\frac{1}{\epsilon(k,\omega)} - 1\right], \tag{8}$$

and $\mathcal{E}_0$ being obtained by replacing $C(\omega - \mathbf{k}\cdot\mathbf{v}) \to \delta(\omega - \mathbf{k}\cdot\mathbf{v})$. In the high-speed limit, one may use the classical dispersionless frequency-dependent dielectric function

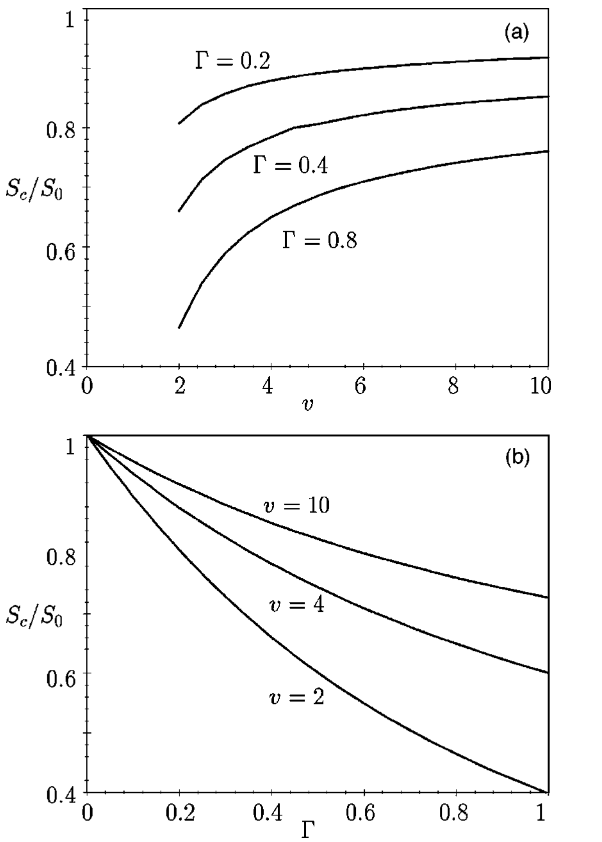

FIG. 1. Dependence of the ratio of the correlated to the uncorrelated stopping, S_C/S_0, on the ion speed v (in a.u.) and the total rate of charge-changing collisions Γ (in a.u.). (a) S_C/S_0 versus v for $\Gamma=0.2$, 0.4, and 0.8. (b) S_C/S_0 versus Γ for $v=2$, 4, and 10.

$\epsilon(k,\omega)=1-\omega_p^2/\omega(\omega+i\gamma)$, with the damping constant $\gamma \to 0^+$, to obtain $\mathcal{E}_0=-(\pi/4)(\omega_p/v)^1$ and $\mathcal{E}_c/\mathcal{E}_0=1-(2/\pi)\arctan(\Gamma/\omega_p)$. Thus, this simple analytical result clearly shows that the dominant parameter in estimating the role of the charge-state correlation in the plasmon excitations of the electron gas is the ratio Γ/ω_p, which compares the frequency of the charge-changing collision events to the plasma frequency. Moreover, this ratio may be cast in the form l_w/λ, where $l_w=v/\omega_p$ is the characteristic length scale of the wake pattern in the electron-gas polarization, and $\lambda=1/(N_{at}\sigma)$ is the total mean free path for the charge-changing collisions, with the cross section $\sigma=\sigma_C+\sigma_L$.

Let us examine the two important extreme cases of the charge-state correlation effects on the stopping power and the self-energy. If the charge-state collisions are very frequent, $\Gamma \gg \omega_p$, the electron gas will not respond to the fluctuations in $\zeta(t)$, so that the charge states appear uncorrelated, $\langle\zeta(t)\zeta(t')\rangle \simeq Z_{eq}^2$, and, consequently, $\mathcal{S}\simeq Z_{eq}^2 S_0$ and $\mathcal{E}\simeq Z_{eq}^2\mathcal{E}_0$. In the opposite extreme of the infrequent collisions, $\Gamma \ll \omega_p$, the charge-state correlations are substantial in Eq. (2), and the electron gas will respond efficiently to the fluctuations in $\zeta(t)$. Since $S_c \simeq S_0$ and $\mathcal{E}_c \simeq \mathcal{E}_0$ in the limit $\Gamma \to 0$, we have an entirely different scaling with the equilibrium charge state, which may be expressed as $\mathcal{S}\simeq Z_{eff}^2 S_0$ and $\mathcal{E}\simeq Z_{eff}^2\mathcal{E}_0$, where $Z_{eff}^2 \equiv Z_{eq}^2+Q=(Z_1+Z_2)Z_{eq}-Z_1Z_2$.

In conclusion, we have described the projectile charge-state evolution in equilibrium as a stationary continuous-time Markov process and showed that the time scale of the charge-state autocorrelation function is governed by the cross sections of charge-changing collisions. Because of the finite response time of the electron gas to a fast perturber, undergoing random sudden changes in its charge level, there are significant interference effects in the excitation pattern of the target. Using the two-state model of the Markov process, we have described the collective electron excitations of the target by the linear-response formalism, and rederived the expressions for the mean stopping power and the mean self-energy of the projectile. The charge-state correlation effects on these quantities appear through statistical weighting factors, as well as through the modifications of the dynamical interaction with the electron gas, compared to the case of a fixed-charge projectile. Stopping power and the self-energy have been evaluated for simple models of the dielectric function, showing that the charge correlation effects on the interaction with the electron gas are primarily governed by the ratio of the total rate for the charge-changing collisions in the target to the electron plasma frequency. Interesting conclusions about the scaling with the equilibrium projectile charge may be drawn for the stopping power and the self-energy, in the limits of fast and slow charge-changing events.

It is possible to extend the present theory to the case of fast heavy ions by using a general, multiple-state, Markov process[10] description of the projectile charge states. In that case, the projectile must be described by a charge-state–dependent density distribution, taking into account the ion screening by the bound electrons.[3] Finally, a further effort is required to obtain a complete energy-loss spectrum of the projectile, with the charge state described by a Markov process, using approach similar to that in Ref. 11.

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