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Diffusion heating and cooling of positrons in constrained media

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Thermalized positrons in media with spatial constraints can be trapped by sinks, and annihilate with electrons into γ quanta with characteristics that are discernibly different from those of positrons annihilating in the bulk. The dependence of the cross sections for scattering in the medium on positron velocity determines whether the fastest or the slowest particles in the velocity distribution disappear preferentially from the volume. This causes the cooling or heating of the positrons remaining in the medium. The diffusion equation is solved to derive the annihilation characteristics of positrons, with the result that diffusion heating and cooling always reduce the effective diffusion coefficient pertinent for trapping relative to that in the infinite medium. The effects on the annihilation characteristics are those of a reduced trapping rate and of an apparent initial positron population in sinks, as it is recorded by an instrument with finite time resolution. The results pertain to positronium diffusion in small gas cells, to the escape of positrons or positronium from small solids, and to the trapping of positrons by vacancies or voids in solids. They are compared with experimental results.

I. INTRODUCTION

When positrons from an external source are implanted in a dense medium, they thermalize before they annihilate with electrons into γ quanta.[1-3] Let the medium be constrained in the sense that the spatial positron distribution must comply with boundary conditions. Such conditions might be imposed by the confining walls of a small gas chamber,[4] the absorbing surface of small solids,[5] or the inner and outer boundaries of domains centered on positron sinks like vacancies or voids in solids.[6,7]

In such situations, three rates must be considered. First, the positron annihilation rate γ_B (lifetime $\tau_B \equiv \gamma_B^{-1}$) in the bulk of the medium; second, the relaxation rate of thermal positron-energy fluctuations γ_E (relaxation time $\tau_E \equiv \gamma_E^{-1}$), through interactions with the medium of temperature T; third, the capture rate κ of positrons by sinks, i.e., the positron escape rate from the medium.

In general, positrons reach thermal equilibrium before annihilation, i.e., $\gamma_E \tau_B > 1$. Their annihilation characteristics, such as their lifetime, the angular correlation between the two 0.511-MeV annihilation γ quanta, or the Doppler-shifted energies of these γ quanta are indicative of the properties of the medium.[8] If $\kappa\tau_B \ll 1$, the constraints have a negligible influence on the positrons, and the annihilation characteristics approach those found in the bulk. If $\kappa\tau_B \gtrsim 1$, a significant fraction of the positrons is absorbed by sinks which constitute, in general terms, the confining walls of the medium. Once absorbed, positrons can annihilate with discernibly different rates $\gamma_W \equiv \tau_W^{-1}$. Thus the annihilation characteristics can yield information about inhomogeneities in the medium. It is normally assumed that thermal relaxation is complete during the trapping process, $\kappa\tau_E \ll 1$, and that the dynamics of the positrons is that of an ensemble of particles with the Maxwell-Boltzmann distribution of velocities v appropriate for the temperature T of the medium. Positron diffusion is then governed by the usual ensemble-average diffusion constant

$$D_T = \tfrac{1}{3}\langle \lambda(v) v\rangle_T \,, \tag{1}$$

where $\lambda(v) = [N_{sc}\sigma(v)]^{-1}$ is the mean free path in terms of the scattering cross section $\sigma(v)$ in a medium containing scatterers at the density N_{sc}.

When the constraints become so closely spaced that $\kappa\tau_E \gtrsim 1$, conditions change. The positrons cannot exchange energy rapidly enough with the medium to reach thermal equilibrium before being trapped at a sink. In consequence, trapping is no longer governed by the ensemble-average diffusion constant D_T, but by different diffusion coefficients, $D(v) = \frac{1}{3}\lambda(v)v$, for particles in different parts of the velocity distribution. For example, if $\sigma(v)$ were to vary with v as $\sigma = Av^m$, where A and m are constants, $D(v)$ would be proportional to v^{1-m}. Values $m > 1$ imply that the slowest particles escape preferentially from the medium, and that the mean kinetic energy of the remaining particles corresponds to an effective temperature T^* that is higher than T. Conversely, if $m < 1$, the fastest particles become trapped preferentially, and T^* is lower than T. Such processes are called "diffusion heating" and "diffusion cooling" in the context of electron transport in gases.[9-12] Only if $m = 1$ does T^* remain equal to T irrespective of any spatial constraints in the medium.

It is the purpose of this paper to study diffusion heating and cooling of positrons in constrained media, to discuss experimental situations in which these effects can influence positron annihilation characteristics, and to develop means for extracting information about the dynamics of positrons and the nature of the sinks in different media.[13] In Sec. II solutions of the diffusion equation for positrons in constrained media are developed and, in Sec. III, are applied to the representative model $\sigma = Av^m$ for the scattering cross section. Section IV presents adaptations suitable for the analysis of experiments and discusses recent measurements of positronium diffusion in small gas samples[4] and of the annihilation characteristics of positrons in metals containing vacancies.[14,15] The general implications of our work are summarized in Sec. V. Appendix A delineates the parametric dependence of the diffusion modes on the spatial constraints in the medium, and Appendix B gives the trapping rates in the limit of receding constraints.

II. DIFFUSION EQUATION

Consider the distribution $\hat{f}(E,\vec{r},t)$ of particles with kinetic energy E in the position $\vec{r}$ at time t in a medium of temperature T where they annihilate with rate γ_B. The distribution is determined by a Boltzmann equation, subject to boundary conditions due to spatial constraints in the medium. We expand $\hat{f}$ in Legendre polynomials in velocity space and, on retaining the first two terms in the usual way,[16] obtain for the isotropic part $\hat{f}_0$ the equation

$$E^{-1/2}\frac{\partial}{\partial E}\left[E^{3/2}\omega^*\left(\hat{f}_0 + kT\frac{\partial \hat{f}_0}{\partial E}\right)\right] + \frac{E}{kT}\frac{\Lambda_E^2}{\omega^*}\nabla_{\vec{r}}^2\hat{f}_0 = \tau_E\left(\frac{\partial \hat{f}_0}{\partial t} + \gamma_B \hat{f}_0\right), \quad (2)$$

where $\omega^* \equiv \omega/\omega_0$ is a reduced scattering-collision frequency in terms of a temperature-dependent reference frequency ω_0, and k is the Boltzmann constant. The particle-energy relaxation length Λ_E and the corresponding relaxation time τ_E contain the information about the scattering and energy-exchange processes between the diffusing particles and the medium. Specifically, if elastic scattering dominates, one has

$$\Lambda_E = (MkT/3m_+^2\omega_0^2)^{1/2}, \qquad \tau_E = M/(2m_+\omega_0) = (M/2m_+)\tau_{\text{col}}, \quad (3)$$

where M is the effective mass of the scatterers in the medium,[17] m_+ the effective positron mass, and $\tau_{\text{col}} = \omega_0^{-1}$ the collision time. We note that the ratio

$$\Lambda_E^2/\tau_E = \tfrac{2}{3}kT/m_+\omega_0 \quad (4)$$

is equal to D_T, Eq. (1), for the case $m=1$ where $\omega = \omega_0 E/kT$.

Inasmuch as the positron annihilation rate γ_B is independent of E,[18] we can set $\hat{f}_0 = f_0\exp(-\gamma_B t)$ and write, in terms of the reduced quantities

$$\vec{\rho} \equiv \vec{r}/\Lambda_E, \quad \tau \equiv t/\tau_E, \quad u \equiv E/kT, \quad (5)$$

Eq. (2) as

$$u^{-1/2}\omega^*\frac{\partial}{\partial u}\left[u^{3/2}\omega^*\left(f_0 + \frac{\partial f_0}{\partial u}\right)\right] + u\nabla_{\vec{\rho}}^2 f_0 = \omega^*\frac{\partial f_0}{\partial \tau}. \quad (6)$$

By standard separation of variables, $f_0 = R(\vec{\rho})F(u)T(\tau)$, we obtain

$$\nabla_{\vec{\rho}}^2 R(\vec{\rho}) = -q^2 R(\vec{\rho}), \quad (7)$$

$$\frac{dT(\tau)}{d\tau} = -\theta T(\tau), \quad (8)$$

$$u^{-1/2}\omega^*\frac{d}{du}\left[u^{3/2}\omega^*\left(F + \frac{dF}{du}\right)\right] + (\theta\omega^* - q^2u)F = 0, \quad (9)$$

where q^2 and θ are separation constants. As shown in Appendix A, the eigenvalues of Eq. (7), $q \propto \Lambda_E/L$, are proportional to the ratio of the positron-thermalization length Λ_E and a characteristic dimension L of the medium. The eigenvalues q incorporate the spatial boundary conditions on $R(\vec{\rho})$ into the secular equation, Eq. (9), for the particle-energy distribution function $F(u)$. The eigenvalues of Eq. (9), then, determine the reduced rates θ for the trapping of the positrons at the boundaries, yielding by Eq. (8), for each rate θ, a component of the time spectrum describing the positron disappearance from the medium,

$$\hat{T} = Te^{-\gamma_B t} = e^{-(\gamma_B + \theta\gamma_E)t} = e^{-(\gamma_B + \kappa)t}, \quad (10)$$

where $\kappa \equiv \theta\gamma_E$ is the trapping rate.

It is convenient to separate out the Boltzmann factor e^{-u} by setting

$$F(u) = e^{-u}G(u), \quad (11)$$

which transforms Eq. (9) into the Sturm-Liouville equation for the function $G(u)$,

$$\frac{d}{du}\left(P(u)\frac{dG}{du}\right) + [\theta S(u) + Q(u,q)]G = 0, \quad (12)$$

with the abbreviations

$$P(u) \equiv u^{3/2}\omega^* e^{-u}, \quad (13)$$

$$Q(u,q) \equiv -q^2(u^{3/2}/\omega^*)e^{-u}, \quad (14)$$

$$S(u) \equiv u^{1/2}e^{-u}. \quad (15)$$

It is instructive to recast Eq. (12) into a Schrödinger-like equation

$$\frac{d^2\Psi}{dx^2}+[\theta_q - V(x,q)]\Psi=0 \qquad (16)$$

through the substitutions

$$\Psi \equiv (PS)^{1/4}G, \quad x\equiv \int du\left(\frac{S}{P}\right)^{1/2}. \qquad (17)$$

The potential-energy-like term $V(x,q)$ has the form

$$V(x,q)=-\frac{Q}{S}-\frac{3}{16}\left[\left(\frac{P'}{P}\right)^2+\left(\frac{S'}{S}\right)^2\right]+\frac{1}{8}\frac{P'}{P}\frac{S'}{S}+\frac{1}{4}\left(\frac{P''}{P}+\frac{S''}{S}\right) \qquad (18)$$

in terms of $P'\equiv dP/dx$, etc.

The spatial boundary conditions on $\hat{f}$, epitomized by q, appear in $V(x,q)$ through the dependence on $Q(q)$. For a given eigenvalue of Eq. (7), q_ν^2, where $\nu=1,2\ldots$, Eq. (16) has, in general, a series of positive eigenvalues which we denote as $\theta_{q_\nu \xi}\equiv\theta_{\nu\xi}$, $\xi=1,2,\ldots$, so constituting a spectrum of increasing trapping rates. The corresponding eigenstates $\Psi_{\nu\xi}(x)$ of Eq. (16) determine the energy distribution of the diffusing particles through

$$F_{\nu\xi}(u)=e^{-u}G_{\nu\xi}(u)=e^{-u}(PS)^{-1/4}\Psi_{\nu\xi}. \qquad (19)$$

The distribution function becomes, with $\kappa_{\nu\xi}\equiv\theta_{\nu\xi}\gamma_E$,

$$\hat{f}_0=e^{-\gamma_B t}\sum_{\nu\xi}A_{\nu\xi}R_\nu(\vec{\rho})F_{\nu\xi}(u)e^{-\kappa_{\nu\xi}t}, \qquad (20)$$

where the coefficients $A_{\nu\xi}$ are fixed by the initial conditions.

To obtain the positron-lifetime spectrum, we integrate Eq. (20) term by term over the particle energies and over the volume Ω of the medium, to calculate the strength of the decay mode (ν,ξ),

$$n_{\nu\xi}=\frac{2}{\sqrt{\pi}}A_{\nu\xi}\int\frac{d^3\rho}{\Omega}R_\nu(\vec{\rho})\int du\, u^{1/2}F_{\nu\xi}(u). \qquad (21)$$

The fraction $p_B(t)$ of positrons surviving in the bulk, of the medium at time t becomes

$$p_B(t)=\sum_{\nu\xi}n_{\nu\xi}e^{-(\gamma_B+\kappa_{\nu\xi})t}. \qquad (22)$$

If all positrons are deposited initially in the bulk one has $\sum_{\nu\xi}n_{\nu\xi}=1$. The fraction

$$F_B=\int_0^\infty\gamma_B p_B(t)\,dt=\sum_{\nu\xi}\frac{n_{\nu\xi}}{1+\kappa_{\nu\xi}\tau_B} \qquad (23)$$

annihilates in the bulk.

The positron fraction $p_W(t)$ annihilates outside Ω in a domain which we refer to as the "wall," with rate γ_W. Since[19,20]

$$\frac{dp_W}{dt}=-\gamma_W p_W+\sum_{\nu\xi}n_{\nu\xi}\kappa_{\nu\xi}e^{-(\gamma_B+\kappa_{\nu\xi})t}, \qquad (24)$$

one obtains

$$p_W(t)=\sum_{\nu\xi}\Phi_{\nu\xi}n_{\nu\xi}(e^{-\gamma_W t}-e^{-(\gamma_B+\kappa_{\nu\xi})t}), \qquad (25)$$

with the abbreviation

$$\Phi_{\nu\xi}=\kappa_{\nu\xi}/(\kappa_{\nu\xi}+\gamma_B-\gamma_W). \qquad (26)$$

The positron fraction

$$F_W=\int_0^\infty\gamma_W p_W(t)\,dt=1-F_B=\sum_{\nu\xi}\frac{n_{\nu\xi}\kappa_{\nu\xi}\tau_B}{1+\kappa_{\nu\xi}\tau_B} \qquad (27)$$

annihilates in the wall.

The observable lifetime spectrum becomes

$$p(t)=p_B(t)+p_W(t)=\sum_{\nu\xi}n_{\nu\xi}(1-\Phi_{\nu\xi})e^{-(\gamma_B+\kappa_{\nu\xi})t}+\sum_{\nu\xi}n_{\nu\xi}\Phi_{\nu\xi}e^{-\gamma_W t}. \qquad (28)$$

Equation (28) has a distinctly new content when compared with the results given in Refs. 19 and 20. The index ξ enumerates lifetime components indicative of the distribution in particle energies which in the presence of sinks differs from the Boltzmann distribution e^{-u}.

In the limit $q_\nu\to 0$, that is, in weakly constrained media where $\Omega\gg\Lambda_E^3$, $F(u)$ approaches e^{-u}. In this limit only $A_{\nu 1}$ in Eq. (20) is populated and $\theta_{\nu 1}\propto q_\nu^2$, as shown in Appendix B. Only the summation over ν in Eq. (28) remains, and we retrieve Eq. (9) of Ref. 19 exactly.

III. MODELS

For the sake of definiteness in what follows, we assume that the reduced collision frequency $\omega^*\equiv\omega/\omega_0$ in Eq. (2) has the form

$$\omega^*=u^{1+\alpha}, \qquad (29)$$

where $u=E/kT$, and α is a model parameter independent of E. Consequently, since $\omega=N_{sc}v\sigma$, the scattering cross section σ varies with v as

$$\sigma=Av^m, \qquad (30)$$

where A is a constant and $m=1+2\alpha$.

In this model, D_T, Eq. (1), becomes

$$D_{\alpha T}=\frac{1}{3}\left\langle\frac{v^2}{\omega}\right\rangle_T=\frac{4}{3\sqrt{\pi}}\frac{kT}{m_+\omega_0}\int_0^\infty du\,u^{1/2-\alpha}e^{-u}=[\Gamma(\tfrac{3}{2}-\alpha)/\Gamma(\tfrac{3}{2})]D_{0T}, \qquad (31)$$

where $\Gamma(x)$ is the gamma function, and $D_{0T}=\Lambda_E^2\gamma_E=\frac{2}{3}kT/m_+\omega_0$ is given by Eq. (4).

The range of α is circumscribed by physical processes which underlie thermal-positron scattering,[2,6,21,22] and are summarized in Table I.

For this model, the variable x, Eq. (17), be-

TABLE I. Range of model parameters α and m in Eqs. (29) and (30), respectively, for various positron scattering processes. The corresponding dependences of the characteristic collision frequency ω_0 and the diffusion coefficient $D_{\alpha T}$, Eq. (31), on the medium temperature T, are also listed.

Positron scattering partners	α	$m=1+2\alpha$	ω_0	$D_{\alpha T}$
Electrons [a]	1	3	T^2	T^{-1}
$(\sigma \propto v)$	0	1	T	T^0
Phonons [b]	$-\frac{1}{2}$	0	$T^{3/2}$	$T^{-1/2}$
Neutral atoms [c]	-1	-1	T^0	T
Crystal imperfections [d] $(\sigma \cong \pi ƛ_+^2)$	$-\frac{3}{2}$	-2	T^{-1}	$T^{3/2}$

[a] References 2 and 6.
[b] References 21 and 25.
[c] Reference 22.
[d] References 6 and 21; $ƛ_+ = \hbar/m_+ v$.

comes

$$x=\int \frac{du}{u^{1+\alpha/2}} = \begin{cases} -(2/\alpha)u^{-\alpha/2}, & \alpha \neq 0 \\ \ln u, & \alpha = 0, \end{cases} \tag{32}$$

and, from Eq. (18), we derive

$$V_\alpha(x,q)=q^2u^{-\alpha}+\tfrac{1}{16}[3(\alpha+1)(\alpha+3)u^\alpha - 4(5+2\alpha)u^{1+\alpha}+4u^{2+\alpha}]. \tag{33}$$

This function is displayed in Fig. 1 for $q=1$ and various α values (cf. Table I). The horizontal lines in the "potentials" for $\alpha=0$ and $\alpha=-1$ illustrate the eigenvalues $\theta_{q\zeta}(q=1)$, $\zeta=1,2\ldots.$ The requirement $u \geq 0$ limits the domain of x, by Eq. (32), to $x>0$ if $\alpha<0$ and to $x<0$ if $\alpha>0$; the variable x ranges from negative to positive values only if $\alpha=0$. We shall now discuss the implications for positron trapping.

(i) $\alpha=0$: The positrons maintain the Boltzmann distribution irrespective of constraints. Equation (33) becomes

$$V_0(x,q)=q^2+\tfrac{9}{16}-\tfrac{5}{4}e^x+\tfrac{1}{4}e^{2x}, \tag{34}$$

which appears to have only one discrete eigenvalue $\theta_{q1}=q^2$, corresponding to the solution of Eq. (16)

$$\Psi_{q1}(x)=\exp(\tfrac{3}{4}x-\tfrac{1}{2}e^x)=u^{3/4}e^{-u/2}. \tag{35}$$

With this result and Eqs. (13) and (15), Eq. (17) yields $G=1$ independent of q. Thus, by Eq. (11), $F=e^{-u}$. Equation (6) reduces to the ordinary diffusion equation, with a diffusion constant $D_{0T} = \Lambda_E^2\gamma_E$ which is independent of T. The positron annihilation characteristics for $\alpha=0$, therefore, are exactly those one predicts by neglecting entirely the influence of the constraints on the particle-energy distribution, as derived for media with external surfaces, in Ref. 19, and for media

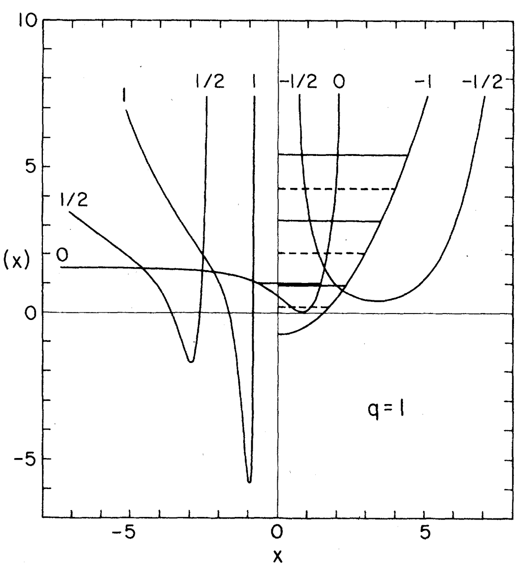

FIG. 1. Potential-energy-like function $V_\alpha(x,q)$ in Eq. (16) vs the positron kinetic-energy parameter x, Eq. (17). It is calculated according to Eq. (33) for the collision-frequency model given by Eq. (29). The curves are for the value $q=1$, i.e., for a medium where [see Eqs. (A6)–(A8)] the positron-thermalization length is comparable to the dimensions of the constraints. The effects of positron diffusion cooling or heating are expected to be significant for $q \gtrsim 1$ (see Fig. 2). The curve labels are the values of the model parameter α, ranging from $\alpha<0$ (diffusion cooling) to $\alpha>0$ (diffusion heating) as explained in the text [Sec. III, (i)–(iii)]. The eigenvalues θ_1 of Eq. (16), indicating the rate of positron trapping at the boundaries, are drawn for $\alpha=0$ and $\alpha=-1$ as horizontal lines. Only those indicated by solid lines are physically acceptable.

with internal surfaces, in Ref. 20.

(ii) $\alpha < 0$: Diffusion cooling. As seen in Table I, this α range covers most of the processes investigated. The problem can be solved exactly for $\alpha = -1$, and discussion of this case may suffice to sketch the behavior for all $\alpha < 0$. Equation (33) becomes

$$V_{-1}(x, q) = -\tfrac{3}{4} + \tfrac{1}{4}(q^2 + \tfrac{1}{4})x^2 , \qquad (36)$$

which is a harmonic-oscillator-type "potential" applicable here for $x \geq 0$, with minimum value $-\frac{3}{4}$. Acceptable solutions of Eq. (16) must vanish at $x = 0$, so that only the eigenvalues ($\zeta = 1, 2, \ldots$)

$$\theta_{q\zeta} = [(2\zeta - 1) + \tfrac{1}{2}]\beta(q) - \tfrac{3}{4} \qquad (37)$$

appear, with state functions

$$\Psi_{q\zeta} = e^{-\beta u} H_{2\zeta-1}\{[2\beta(q)u]^{1/2}\} , \qquad (38)$$

where $\beta(q) \equiv (q^2 + \frac{1}{4})^{1/2}$; H_i is the Hermitian polynomial of order i. Equation (19) gives the components of the particle-energy distribution,

$$F_{q\zeta}(u) = u^{-1/2} e^{-[\beta(q)+1/2]u} H_{2\zeta-1}\{[2\beta(q)u]^{1/2}\} , \qquad (39)$$

This result is identical with that given by Parker[10] in terms of Laguerre polynomials.

It is illuminating to display the lowest mode, $\zeta = 1$,

$$F_{q1}(u) = 2^{3/2}\beta^{1/2}(q) e^{-[\beta(q)+1/2]u} , \qquad (40)$$

because it resembles a Boltzmann distribution with effective temperature $T^* < T$ in that

$$T/T^* = \beta + \tfrac{1}{2} = (q^2 + \tfrac{1}{4})^{1/2} + \tfrac{1}{2} > 1 . \qquad (41)$$

The trapping rate

$$\kappa_{q1} \equiv \theta_{q1}\gamma_E = \tfrac{3}{4}[(1 + 4q^2)^{1/2} - 1]\gamma_E \qquad (42)$$

is always smaller than the limiting value

$$\kappa_{q1} = \frac{\Gamma(\frac{5}{2})}{\Gamma(\frac{3}{2})} q^2 \gamma_E, \quad \text{for } q^2 \to 0 , \qquad (43)$$

appropriate when $\alpha = -1$ in weakly constrained media.

(iii) $\alpha > 0$: Diffusion heating. In this parameter range, $V_\alpha(x, q)$ extends only in the $x < 0$ plane. In tightly constrained media, where $q^2 \gg 1$, one can approximate

$$V_\alpha(x, q) \simeq \left(\frac{\alpha x}{2}\right)^2 q^2 + \frac{2^{4/\alpha}}{(-\alpha x)^{2+4/\alpha}} \qquad (44)$$

with the minimum at

$$x_m = -\frac{2}{\alpha}\left(\frac{2+\alpha}{4\alpha q^2}\right)^{\alpha/4(1+\alpha)} \qquad (45)$$

of value

$$\begin{aligned} V_m &\equiv V_\alpha(x_m, q) \\ &= 2q^2 \frac{1+\alpha}{2+\alpha}\left(\frac{2+\alpha}{4\alpha q^2}\right)^{\alpha/2(1+\alpha)} . \end{aligned} \qquad (46)$$

In the harmonic approximation,

$$V_\alpha(x, q) = V_m + \alpha(1+\alpha)q^2(x - x_m)^2 , \qquad (47)$$

the eigenvalues appropriate for $q^2 \gg 1$ are

$$\begin{aligned} \theta_{q\zeta} = {} & 2q^2 \frac{1+\alpha}{2+\alpha}\left(\frac{2+\alpha}{4\alpha q^2}\right)^{\alpha/2(1+\alpha)} \\ & + 2q[\alpha(1+\alpha)]^{1/2}(\zeta - \tfrac{1}{2}) . \end{aligned} \qquad (48)$$

Equation (48) remains useful even when $\alpha = 0+$, in that then $\theta_{q\zeta} = q^2$ in agreement with the exact result of (i).

The particle energies are now bunched with u values near the value corresponding to x_m, namely, $u_m = (-2/\alpha x_m)^{2/\alpha}$ by Eq. (32). Consequently, for $q \gg 1$, the effective particle-ensemble temperature T^* in the medium of temperature T is

$$\frac{T^*}{T} \simeq u_m = \left(\frac{4\alpha q^2}{2+\alpha}\right)^{1/2(1+\alpha)} > 1 . \qquad (49)$$

As in the case of diffusion cooling, the leading trapping rate $\kappa_{q1} \equiv \theta_{q1}\gamma_E$, Eq. (48), is always smaller than the general limiting value

$$\kappa_0 = [\Gamma(\tfrac{3}{2} - \alpha)/\Gamma(\tfrac{3}{2})]q^2\gamma_E \qquad (50)$$

corresponding to weakly constrained media ($q \ll 1$).

These examples illustrate that, except for $\alpha = 0$, constraints cause diffusion heating or cooling of the positron ensemble in restricted media. In either case, the rate of trapping at the walls is less than that expected for particles diffusing in thermal equilibrium with the medium. One can express this result by introducing an effective diffusion coefficient D_{eff} to which the trapping rate is proportional. This D_{eff} is, for $\alpha \neq 0$, a function of q and smaller than the thermal average $D_{\alpha T}$ (Appendix B).

IV. ADAPTATIONS FOR ANALYSIS OF EXPERIMENTS

In many measurements of positron-lifetime spectra, only one or two lifetime components can be resolved. As discussed in Ref. 19, the evolution of the positron lifetime spectrum is, except for the leading term in Eq. (28), usually submerged in the time resolution function of the measuring instrument. The components ($\nu > 1, \zeta > 1$) appear then as if initially deposited in the wall. We adapt Eq. (28) accordingly by writing, with $\sum_{\nu,\zeta=1}^{\infty} n_{\nu\zeta} = 1$,

$$p(t)=n_{11}(1-\Phi_{11})\,e^{-(\gamma_B+\kappa_{11})t}+[1-n_{11}(1-\Phi_{11})]e^{-\gamma_W t}\,. \qquad (51)$$

Following Eq. (26), we set

$$\Phi_{11}=\Phi=\kappa/(\kappa+\gamma_B-\gamma_W)$$

by abbreviating $\kappa_{11}=\kappa$ and $n_{11}=n$, and retrieve the new lifetime spectrum in the familiar form[6]

$$p(t)=I_1e^{-\Gamma_1 t}+I_2e^{-\Gamma_2 t}\,, \qquad (52)$$

where now

$$I_1=1-I_2=n(\gamma_B-\Gamma_2)/(\Gamma_1-\Gamma_2)\,, \qquad (53)$$

$$\Gamma_1=\gamma_B+\kappa,\quad \Gamma_2=\gamma_W\,. \qquad (54)$$

This formulation incorporates two new aspects of positron trapping resulting from the developments presented in Secs. II and III. First, the factor n is the experimentally resolvable leading coefficient in the bulk lifetime spectrum Eq. (22)

$$p_B(t)=ne^{-(\gamma_B+\kappa)t}\,. \qquad (55)$$

Although all positrons are considered to reside initially in the medium, the fraction $(1-n)$ escapes so rapidly, through higher modes of the diffusion equation in (ρ,u) space as given by Eqs. (20)–(22), that it cannot be identified as a bulk component by an instrument with finite resolution time. Instead, such positrons appear as if they were residing in the wall at $t=0$, so that the wall-lifetime spectrum, Eq. (25), in practice is analyzed as

$$p_W(t)=n\Phi(e^{-\gamma_W t}-e^{-(\gamma_B+\kappa)t})+(1-n)e^{-\gamma_W t}\,. \qquad (56)$$

The sum $p(t)=p_B(t)+p_W(t)$ is equal to Eq. (52). When $q\ll 1$, $n\simeq 1$ and we retrieve the formulation given earlier.[6] When $q\sim 1$, n begins to decline and approaches zero as q becomes large.

Second, diffusion heating or cooling always cause the escape rate κ to be smaller than the value appropriate for positrons with a Boltzmann distribution, which it in any case approaches in the limit $q\to 0$, i.e., in weakly constrained media. The values of κ as tabulated for sinks of various geometries in Table I of Ref. 19 may still be applied for all q values, if a q-dependent effective diffusion constant $D_{\rm eff}$ is introduced according to Appendix B.

It is useful to collate a number of relations between measured quantities and the theoretical counterparts as deduced from the lifetime spectrum Eqs. (51)–(54). For dense media, in particular, experimental values of the quantities in the first column of Table II are often reported. The first four quantities can be culled from measurements that resolve two lifetime components. The fifth is the result of the determination of one mean lifetime τ, (when Γ_1 and Γ_2 are too close to be resolved) so that

$$\tau\simeq\int_0^\infty t\,\frac{dp}{dt}\,dt\,. \qquad (57)$$

In theory this quantity agrees, of course, with formula (b). The symbol P in the second formula (e) refers to a measured parameter, such as the width or the height of a 2γ angular-correlation curve, or the S parameter in Doppler-shift measurements. The limiting values P_B and P_W refer to P values under conditions where all positrons annihilate, respectively, in the bulk or in the absorbing walls. The formula relates these quantities to F_B, Eq. (23), and F_W, Eq. (27), under the assumption that the shape of the curves pertaining to annihilations in the bulk and in the walls are well defined and independent of q, so that[7]

$$F_W=1-F_B=(P-P_B)/(P_W-P_B)\,.$$

In formula (f), F_B is the fraction annihilating in the bulk as it appears in the analysis of angular-correlation and Doppler-shift measurements.

The second column of Table II gives the limiting values for $q\to 0$, as they have been derived in the past under the assumption that the particle-energy distribution can be adequately represented by the mean thermal energy, independent of constraints.[6] The last column gives new formulas which differ from the previous ones through the constraint-dependent quantities n and κ. We discuss these results in relation to recent experiments in the following.

A. Positronium diffusion in gases

In a series of experiments by Spektor and Paul,[4] lifetime spectra of positrons were measured in seven gases at room temperature as a function of gas pressure in a multiplate gas chamber. Changes in the lifetime spectra as a function of gas pressure were attributed to changes in the trapping rate κ (labeled λ_W in Ref. 4) of ortho positronium by the cell walls. Using diffusion theory, a universal relation between κ and $N\sigma$, in a medium of atomic density N, was found to be born out by all data when an appropriate choice of the positronium-atom collision cross section σ was made for each gas. For He, the empirical value, $\sigma_{\rm emp}=0.017\ \pi a_0^2$, so determined is some three orders of magnitude smaller than predicted by theory[23] ($\sigma_{\rm th}\simeq 7.7\ \pi a_0^2$).

If the results are corrected to account for the effects discussed in this paper, the cross sections become even smaller than the values quoted. Thus

TABLE II. Experimentally accessible quantities that can be deduced from lifetime spectra of the form Eqs. (52)–(54). The first column lists the quantities, the second gives the interpretation given heretofore, and the third collates the results of this work. [a]

Quantity	Previous values	Present results
(a) $\Gamma = I_1\Gamma_1 + I_2\Gamma_2$	$\gamma_B = 1/\tau_B$	$\gamma_B - (1-n)(\gamma_B - \gamma_W)$
(b) $\tau = \dfrac{I_1}{\Gamma_1} + \dfrac{I_2}{\Gamma_2}$	$\tau_B \dfrac{1+\kappa_0\tau_W}{1+\kappa_0\tau_B}$	$\tau_B \dfrac{1+\kappa\tau_W}{1+\kappa\tau_B} + (1-n)\dfrac{\tau_W - \tau_B}{1+\kappa\tau_B}$
(c) $I_2(\Gamma_1 - \Gamma_2)$	κ_0	$\kappa + (1-n)(\gamma_B - \gamma_W)$
(d) I_2/I_1	$\dfrac{\kappa_0}{\gamma_B - \gamma_W}$	$\dfrac{\kappa}{n(\gamma_B - \gamma_W)} + \dfrac{1-n}{n}$
(e) $\dfrac{\tau - \tau_B}{\tau_W - \tau}$, $\dfrac{P - P_B}{P_W - P} = \dfrac{F_W}{F_B}$	$\kappa_0\tau_B$	$\dfrac{1}{n}(\kappa\tau_B + 1) - 1$
(f) $F_B = 1 - F_W$	$\dfrac{1}{1+\kappa_0\tau_B}$	$\dfrac{n}{1+\kappa\tau_B}$

[a] The trapping rate κ_0 in the second column corresponds to the small-q limit, and is proportional to q^2, as given by Eq. (50) for the model $\omega^* = u^{1+\alpha}$. Values of κ_0 for different constraint geometries are listed in Table I of Ref. 19 in terms of the diffusion coefficient. The trapping rate $\kappa \equiv \theta\gamma_E$ in the third column is calculated for arbitrary constraints on the medium as described in the text. It approaches κ_0 when $q \ll 1$.

diffusion heating or cooling phenomena cannot be invoked to explain the discrepancy between this experiment and theory.

B. Positron trapping by thermal vacancies in metals

Recent measurements of positron-lifetime spectra in Pb (Ref. 14) and Al (Ref. 15) as a function of T were decomposed according to Eq. (52) into I_1 and I_2, with disappearance rates Γ_1 and Γ_2, and the activation energy E_V for vacancy formation ($E_V = 0.62$ eV for Pb, $E_V = 0.66$ for Al) extracted. Contrary to expectations based on column 2 of Table II, namely, that formula (a), $\Gamma = I_1\Gamma_1 + I_2\Gamma_2$, is equal to γ_B for all vacancy concentrations, Γ dropped dramatically to values $\Gamma \sim \Gamma_2$ when T exceeded 200 °C for Pb and 300 °C for Al. In addition, the Al data of $I_2(\Gamma_1 - \Gamma_2)$, formula (c), which were expected to yield κ_0, proportional to the vacancy concentration, and, hence, to give a straight line in an Arrhenius plot, actually fall lower when $T \gtrsim 300$ °C.

We attribute these new trends to discernible diffusion cooling of positrons at the highest vacancy concentrations investigated. For a demonstration we refer to formula (a) in Table II, and replot the data of Γ in the form

$$n = (\Gamma - \gamma_W)/(\gamma_B - \gamma_W) \tag{58}$$

vs T, as shown in Fig. 2. For comparison we calculate n for the model parameters $\alpha = -1$ and $\alpha = \frac{1}{2}$, remembering that for $\alpha = 0$, $n = 1$ for all T. The constraints in the medium appear through the value of q. For vacancies or voids of trapping radius r_V, at the concentration C_V, or density NC_V, corresponding to a mean spacing expressed by R defined as $\frac{4}{3}\pi R^3 NC_V = 1$, q is given by

$$q^2 = 3r_V\Lambda_E^2/R^3 = 4\pi r_V NC_V\Lambda_E^2 \tag{59}$$

according to Appendix A. Compared to the thermal vacancy production,

$$C_V = C_{V0}\exp(-E_V/kT), \tag{60}$$

Λ_E^2 varies only weakly with T, Eq. (3), so that one may set $q^2 \simeq q_0^2\exp(-E_V/kT)$ and treat q_0^2 as a material constant related to Λ_E and to the nature of the defects. Expressions to be compared with Eq. (58) are given in Table III. The results, shown as curves in Fig. 2, were adjusted through q_0 so that the asymptotic expressions for $\alpha = \frac{1}{2}$ and $\alpha = -1$ cross when $n = 0.5$, at $T = 280$°C for Pb and $T = 400$ °C for Al. In this manner, our theory accounts for the changes in $\Gamma = I_1\Gamma_1 + I_2\Gamma_2$ with temperature as observed by Sharma *et al.*[14] on Pb and Fluss *et al.*[15] on Al.

One of the central objectives in performing these measurements is the determination of the vacancy formation energy E_V. This is usually done through a best fit of experimental quantities given in formulas (c)–(f) of Table II to an Arrhenius plot of the form $\kappa_0 = \kappa_\infty\exp(-E_V/kT)$ as suggested by col-

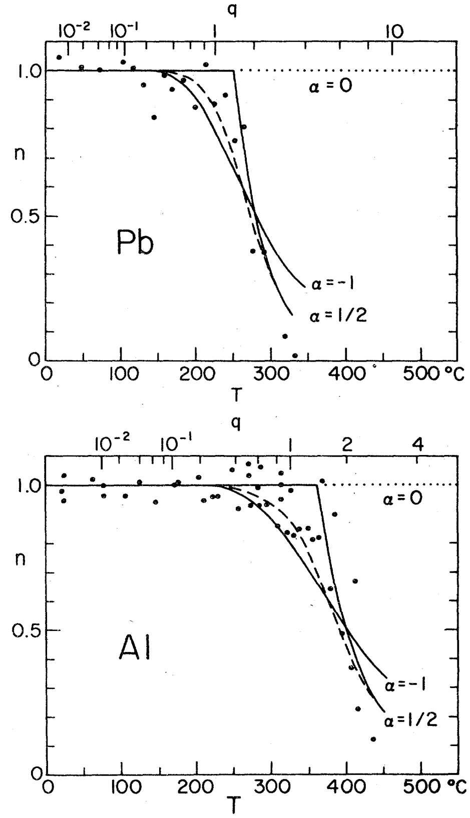

FIG. 2. Fraction n in the first decay mode of a positron-lifetime spectrum, Eqs. (52)–(56), as a function of q (upper scales), which is a measure of the positron-thermalization length in units of the distance between vacancies in metals. It is thus related to the thermal vacancy concentration in Pb and in Al at temperature T (lower scales). The curves are calculated for sample α values in Eq. (29) corresponding to the Boltzmann distribution ($\alpha = 0$), to diffusion heating ($\alpha = \frac{1}{2}$), and to diffusion cooling ($\alpha = -1$) of the positrons in the medium. The graphs signify that, for both diffusion heating and cooling in finite media, a positron fraction $(1-n)$ escapes so rapidly from the volume that it appears as if deposited initially at the vacancies. The solid curve for $\alpha = -1$ and the dotted line for $\alpha = 0$ represent exact results. The solid curve for $\alpha = \frac{1}{2}$ combines the asymptotic limits for $q \ll 1$ and $q \gg 1$; the dashed curve is an interpolation between these limits. The data represent Eq. (58) based on measurements on lead (Ref. 14) and aluminum (Ref. 15).

umn 2. According to the new results listed in column 3, deviations from this form should occur when $q \gtrsim 1$, because then $\kappa < \kappa_0$. This effect sets in when n, Table III and Fig. 2, begins to drop below the value 1. We have calculated formula (c) for Al with the n values shown in Fig. 2 and for $\alpha = -1, 0, \frac{1}{2}$. The result is displayed in the form of an Arrhenius plot in Fig. 3(a), together with the data reported by Fluss *et al.*[15] Formula (d)

TABLE III. Expressions of $\theta(q) \equiv \kappa(q)\tau_E$ and $n(q)$ used in the comparison of experiments (Figs. 2 and 3), with the simple scattering model Eq. (29), for $\alpha = -1, 0, \frac{1}{2}$. The constraints are expressed through q, Eq. (59), or $\beta \equiv (q^2 + \frac{1}{4})^{1/2}$. [a]

α	$\theta = \kappa\tau_E$	n
-1	$\frac{3}{4}(2\beta - 1)$	$\left(\frac{2^{3/2}\beta^{1/2}}{1+2\beta}\right)^3$
0	q^2	1
$\frac{1}{2}$	$\frac{q^2}{(1+q)^{1/3}}$	$\begin{cases} 1 & \text{for } q^2 \ll 1, \\ (4/q)\exp(-q^{2/3}) & \text{for } q^2 \gg 1 . \end{cases}$

[a] The expressions for $n = n_{11}$ are derived from Eq. (21) with A_{11} values calculated according to Eq. (20) with the assumption $\hat{f}_0 = \exp(-u)$ at time $t = 0$.

was calculated in the same way, and is compared with the data of McKee *et al.*[24] in Fig. 3(b). Clearly the high-temperature data in Fig. 3(a) fall below the straight $\alpha = 0$ line by amounts consistent with values $\alpha \neq 0$. The data as plotted in Fig. 3(b) appear to support α values between 0 and -1. One should be cautious in drawing conclusions from these model comparisons about the dominant scattering mechanism. But we can note that if phonon-positron interaction is the diffusion-limiting scattering mode in solids, the collision frequency becomes

$$\omega_{ph} = akTE^{1/2} = \omega_0 u^{1/2} , \tag{61}$$

where a is a material constant[25] and $\omega_0 = a(kT)^{3/2}$. That is, by Eq. (29) $\omega_{ph}^* = u^{1/2}$ implies that $\alpha = -\frac{1}{2}$ for this process, which is consistent with the trend of the data in Fig. 3.

Apparently, the value of E_V should be deduced from the slope in a vacancy-concentration range limited so that $q^2 \ll 1$. If, instead, one determines a "best" straight line through experimental points that include a wider vacancy-concentration range, one would obtain from the upper plot in Fig. 3 according to Table II (c) an effective $E^*_{V(c)} \leq E_V$. By contrast, the reverse is true for the lower plot according to Table II (d), i.e., $E^*_{V(d)} \geq E_V$. If the data are plotted according to Table II (e), one should also find $E^*_{V(e)} \geq E_V$ and, in general, $E^*_{V(e)} \leq E^*_{V(d)}$. In fact, recent analyses gave for Al the values $E^*_{V(c)} = 0.66 \pm 0.01$ eV,[15] $E^*_{V(d)} = 0.71$ eV (Ref. 24) or 0.74 ± 0.01 eV,[15] and $E^*_{V(e)} = 0.67 \pm 0.03$ eV,[15] while for Pb the values[14] $E^*_{V(c)} = 0.645 \pm 0.028$ eV and $E^*_{V(d)} = 0.737 \pm 0.019$ eV.

The relation between n and q used here was calculated with the simplest assumption of a canonical initial distribution, viz., $\hat{f}_0 = \exp(-u)$, at time $t = 0$. A more comprehensive treatment would start with an initial distribution far from the ther-

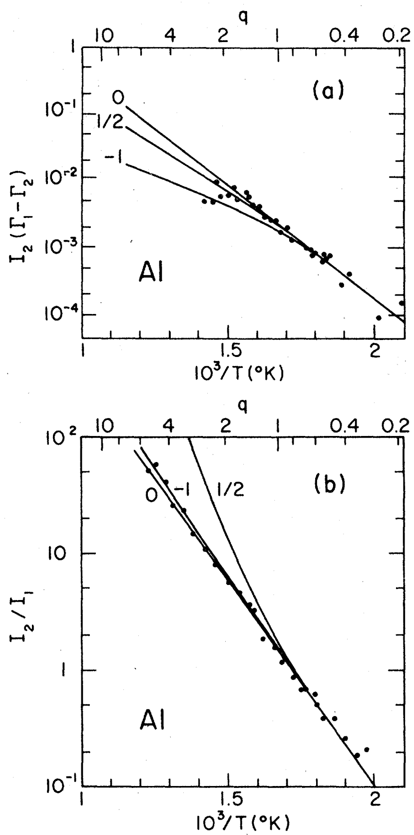

FIG. 3. Arrhenius plots of Al data according to formula (c) in Table II (upper graph a, Ref. 15) and according to formula (d) in Table II (lower graph b, Ref. 24) for the determination of the thermal vacancy formation energy E_V, Eq. (60). The curves are calculated according to the corresponding formulas in the third column of Table II, with the n values given in Table III and displayed in Fig. 2 for $\alpha=-1, 0, \frac{1}{2}$.

mal equilibrium. We have performed additional sample calculations, for $\alpha=-1$, by assuming uniform initial distributions ranging from zero to some maximum energy value,[3,17] $E_0 \gg kT$, below which electronic excitation processes do not dominate the slowing down of positrons. The drop of the n values, then, depends on this additional parameter E_0. It commences at lower values of q than those found for the canonical distribution, so that the q scale in Fig. 2 moves to the right relative to the T scale.

Further analysis is required to ascertain to what extent the scaling of q vs T can contribute to the understanding of a problem of long standing, viz., the approach of swift positrons to thermal equilibrium in dense media.

The appearance of diffusion heating or cooling in the positron annihilation characteristics conveys new information on the dynamics of positrons. Specifically it permits an estimate of the thermal relaxation time τ_E and the associated thermal relaxation length Λ_E from lifetime measurements in the context of thermal vacancy production. From formula (e), Table II, it is clear that at the temperature T_B where $\tau=\frac{1}{2}(\tau_B+\tau_W)$, one has $\kappa_B = \kappa_\infty \exp(-E_V/kT_B) \simeq \gamma_B$. At the temperature T_E where $n=0.5$ and, thus, according to formula (a), $\Gamma \simeq \frac{1}{2}(\gamma_B+\gamma_W)$ one has $\kappa_E=\kappa_\infty \exp(-E_V/kT) \simeq \gamma_E$, so that

$$\frac{\tau_E}{\tau_B}=\frac{\kappa_B}{\kappa_E} \simeq \frac{e^{-E_V/kT_B}}{e^{-E_V/kT_E}}\,. \tag{62}$$

We estimate for Pb with $T_B=200\,°C$, $T_E=280\,°C$, $E_V=0.62$ eV, and $\tau_B=200$ psec, that $\tau_E=30$ psec; and for Al with $T_B=345\,°C$, $T_E=400\,°C$, $E_V=0.66$ eV, and $\tau_B=166$ psec, that $\tau_E=60$ psec. For a diffusion constant $D_+ \sim 0.1$ cm^2/sec one obtains $\Lambda_E=(D_+\tau_E)^{1/2} \simeq 200$ Å. These values appear to agree with theoretical estimates.[3]

V. DISCUSSION

Consider a positron with velocity $v=v_1$ at time $t=t_1$, in a medium of temperature T. The velocity probability density is then $\delta(v-v_1)$. In time, the velocity distribution broadens as prescribed by a Fokker-Planck equation, and approaches asymptotically the canonical Maxwell-Boltzmann probability distribution. The characteristic time τ_E for these processes is normally short compared to the lifetime of positrons in the bulk, τ_B, that annihilate with an electron into γ quanta. When the mean scattering time τ_{sc} is short, $\tau_{sc}(v) \ll \tau_E$, the spatial motion of the positron is governed by a velocity-dependent diffusion coefficient $D(v)$ which, over times $t>\tau_E$, averages to the usual temperature-dependent diffusion constant D_T of an ensemble of particles in thermal equilibrium with the medium. A parameter $q \propto \Lambda_E/L$ gauges the mean relaxation length $\Lambda_E \equiv (D_T\tau_E)^{1/2}$ relative to the dimension L of the constraints on the medium.

When the medium is constrained so tightly ($q>1$) that the positrons reach an absorbing wall in times that are short compared with τ_E, the medium is depleted preferentially of the particles that diffuse the most rapidly, and the positron velocities in the medium can no longer be described by the canonical distribution. For example, if scattering conditions are such that $D(v) \propto v^{-2\alpha}$, the fastest positrons are trapped preferentially if $\alpha<0$. The result is the diffusion cooling of the steady-state positron population in the medium. If, on the other hand, $\alpha>0$, the slowest particles are trapped first. The result is diffusion heating. Such effects will change the Doppler shift and the width of the angular correlation of the annihilation γ quanta emanating from the bulk of the medium.

An important consequence of these effects is that the trapping rate κ becomes smaller than it would be if the positrons could establish complete thermal equilibrium with the medium before becoming trapped. If one nevertheless analyzes data in terms of the thermal-averaged D_T, one extracts values of the concentration of sinks that are too low. It follows that the influence of diffusion heating or cooling on the determination of the thermal-vacancy formation enthalpy E_V can be neglected only as long as the vacancy concentration is so low that $q^2 \ll 1$. Otherwise, effective E_V^* values are extracted which may turn out to be larger or smaller than E_V depending on the way in which the analysis is conducted.

Even if all positrons are deposited initially in the bulk, diffusion effects in tightly constrained media can cause an accumulation of positrons in sinks so rapidly, compared to the instrument resolution time, that measurements identify only a fraction $n(q) < 1$ as having been deposited in the medium, and the remainder $1 - n(q)$ as having been deposited in sinks at $t = 0$.[26]

In fitting the Brandeis data[14] on Pb to an initial sink fraction, Warburton and Shulman[27] extracted parameters labeled $t_0 \sim 10$–20 psec and $\mu'/\mu \sim 2$–5, for which we have now provided a theoretical basis. Indeed, the two parameters correspond to the thermal relaxation time τ_E and to a mean value of the relative trapping rates $\kappa_{\nu\xi}/\kappa_{11}$, $(\nu, \xi) > 1$, respectively. These rates are associated with the higher-mode solutions of the diffusion equation and cause the escape of positrons from the medium in times that are short compared with the resolution time. In consequence, the mean positron disappearance rate $\Gamma = I_1\Gamma_1 + I_2\Gamma_2$ as deduced from experiment is equal to γ_B only when $q < 1$ and $n(q) \simeq 1$. Conversely when $\Gamma < \gamma_B$, as has now been found for Pb (Ref. 14) and Al (Ref. 15) at high temperatures, the constraints are so severe that $q \gtrsim 1$ and $n(q) < 1$. When this occurs, the experimental data should be treated in terms of the theory as presented in Sec. IV.

It would be desirable to extend measurements systematically to other constrained media, because our model of positron trapping in the expanded form developed in this paper gives, for the first time, a method to extract information not only about annihilation rates and sink concentrations, but now also about the positron-energy relaxation time τ_E and relaxation length Λ_E. The magnitude of these quantities in different media should elucidate the dominant processes governing the dynamics of positrons in matter.

ACKNOWLEDGMENT

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APPENDIX A: SPATIAL CONSTRAINTS

In order to illustrate the parametric dependence of the diffusion equations on spatial constraints through the variable q used in the text, we recall here the solutions of Eq. (7) for spherical symmetry,

$$R(\rho) = (q\rho)^{-1}\sin(q\rho - \phi)\,, \tag{A1}$$

with arbitrary phase ϕ. The values of q and ϕ are determined by the boundary conditions. For instance in the case of absorbing voids of radius r_V, distributed in a solid with density $NC_V = 3/4\pi R_V^3$, these conditions are

$$R(\rho) = 0 \quad \text{for } \rho = r_V/\Lambda_E\,, \tag{A2}$$

$$\frac{dR}{d\rho} = 0 \quad \text{for } \rho = \frac{R_V}{\Lambda_E}\,, \tag{A3}$$

which give, respectively,

$$\phi = q r_V/\Lambda_E\,, \tag{A4}$$

$$qR_V/\Lambda_E = \tan[q(R_V - r_V)/\Lambda_E]\,. \tag{A5}$$

The solutions q_ν to Eq. (A5) may be approximated for $r_V \ll R_V$ as follows:

$$q_1 = (3r_V/R_V)^{1/2}(\Lambda_E/R_V) \quad \text{for } \nu = 1\,, \tag{A6}$$

$$q_\nu \cong (2\nu - 1)(\pi\Lambda_E/2R_V) \quad \text{for } \nu = 2, 3, \ldots\,. \tag{A7}$$

Another example of interest is that of a foil of thickness L, bounded by absorbing surfaces, for which

$$q_\nu = \pi\nu\Lambda_E/L\,, \quad \nu = 1, 2, 3, \ldots\,. \tag{A8}$$

The values of q_1 in other geometries as a function of Λ_E and the dimensions of the medium can easily be obtained from the corresponding escape rates κ_0 given in Table I of Ref. 19, by using the relation $q_1^2 = \Lambda_E^2\kappa_0/D$. Applied to small solids with absorbing surfaces, this treatment pertains to the diffusion of positrons in metal grains[28] and to the escape of positronium[5,29] or muonium[30] from insulators.

APPENDIX B: TRAPPING RATE IN WEAKLY CONSTRAINED MEDIA ($\Lambda_E/L \ll 1$)

Let us consider the solution of Eq. (9) for the first mode $q = q_1$, $\theta = \theta_{11}$, $F(u) = F_{11}(u)$, in the limit of receding constraints, i.e., $q \to 0$.

It is convenient to write Eq. (9) as

$$\frac{d}{du}\left[u^{3/2}\omega^*\left(F + \frac{dF}{du}\right)\right] + (\theta u^{1/2} - q^2u^{3/2}/\omega^*)F = 0\,, \tag{B1}$$

and to integrate over u from 0 to ∞. In situations of physical interest the contribution from the first term vanishes, which leaves

$$\theta \int_0^\infty du\, u^{1/2} F(u) = q^2 \int_0^\infty du\, \frac{u^{3/2} F(u)}{\omega^*(u)} . \quad \text{(B2)}$$

In the limit $q \to 0$ the positrons approach thermal equilibrium with the medium, $F(u) \cong e^{-u}$, and we obtain

$$\theta \cong \frac{q^2}{\Gamma(\frac{3}{2})} \int_0^\infty du\, \frac{e^{-u} u^{3/2}}{\omega^*(u)} . \quad \text{(B3)}$$

This exhibits the general proportionality between the escape rate $\kappa \equiv \theta\gamma_E$ and q^2 for $q \ll 1$. In particular, the model $\omega^* = u^{1+\alpha}$ gives the result

$$\theta \cong q^2 \Gamma(\tfrac{3}{2} - \alpha)/\Gamma(\tfrac{3}{2}) . \quad \text{(B4)}$$

The factor $\Gamma(\frac{3}{2} - \alpha)/\Gamma(\frac{3}{2})$ accounts for the appropriate diffusion coefficient $D_{\alpha T}$ of Eq. (31). The escape rate is proportional to $D_{\alpha T}$ when $q \ll 1$ [see Eq. (50)]. In the more general situation in which $\omega^*(u)$ is not a simple power function, Eq. (B3) incorporates into the expression for the trapping rate $\kappa = \theta\gamma_E$ the diffusion coefficient

$$D_T = \frac{1}{3} \left\langle \frac{v^2}{\omega} \right\rangle_T \cong D_{0T} \frac{2}{\sqrt{\pi}} \int_0^\infty du\, \frac{u^{3/2} e^{-u}}{\omega^*(u)} , \quad \text{(B5)}$$

where $D_{0T} = \Lambda_E^2/\tau_E = \frac{2}{3} kT/m_+\omega_0$, Eq. (4).

Thus, in the limit of weakly constrained media we retrieve the results of Ref. 19, provided that in the expressions for the escape rates the appropriate thermal average of the diffusion coefficient, Eq. (B5), is used.

When the constraints are important and q is not small, the escape rate κ may still be written in the same fashion as that resulting from elementary diffusion theory, if an effective diffusion coefficient is defined by

$$D_{\text{eff}} = D_{0T}\theta/q^2 , \quad \text{(B6)}$$

where θ/q^2 is given by Eq. (B2). For instance,

$$\kappa(\text{foil}) = \frac{\pi^2}{L^2} D_{\text{eff}} , \quad \kappa(\text{voids}) = \frac{3\gamma_V}{R_V^3} D_{\text{eff}} . \quad \text{(B7)}$$

The value of D_{eff} defined in this way depends on q, and is always smaller than the diffusion coefficient for an infinite medium, i.e., $D_{\text{eff}} < D_T$. For example in the model $\omega^* = u^{1+\alpha}$, $\alpha \neq 0$, $D_{\alpha T}$ is the diffusion coefficient appropriate for the infinite medium. It is related to D_{eff} as

$$D_{\text{eff}} = \frac{\Gamma(\frac{3}{2})}{\Gamma(\frac{3}{2} - \alpha)} \frac{\theta}{q^2} D_{\alpha T} . \quad \text{(B8)}$$

The ratio $D_{\text{eff}}/D_{\alpha T}$ was shown to be <1 in Sec. III. When $q^2 \ll 1$, D_{eff} approaches D_T for all $\omega^*(u)$.

As an illustration, we quote the exact result for $\alpha = -1$. With the θ value given by Eq. (42), Eq. (B8) becomes

$$\frac{D_{\text{eff}}}{D_{-1T}} = [(1+4q^2)^{1/2} - 1]/2q^2 \to \begin{cases} 1 - q^2, & \text{for } q \ll 1 , \\ 1/q, & \text{for } q \gg 1 . \end{cases} \quad \text{(B9)}$$

The parameter q is related to the constraints of the medium as discussed in Appendix A.

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