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Thermodynamic analysis of interfacial transport and of the thermomagnetoelectric system

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We have applied the methods of nonequilibrium thermodynamics to study the transport of charge, heat, and nonequilibrium magnetization in discrete and continuous systems. The linear dynamic equations of thermoelectricity are extended to describe the interfacial thermoelectric effect, and to include the thermomagnetoelectric effect. A few ramifications of the equations are discussed, and they are applied, in the Appendix, to a detailed analysis of the transport of charge and nonequilibrium magnetization across a ferromagnetic-paramagnetic interface.

I. INTRODUCTION

The thermoelectric effect has served as a classic example of the application of nonequilibrium thermodynamics for more than a century. In the thermoelectric (TE) system, the flows of charge and heat are driven by an electric field and a gradient of temperature. Classically, the dynamic laws are derived for *continuous* systems, and the TE effects are described in terms of bulk properties of conductors, such as the absolute thermopower ϵ, the thermal conductivity κ, and the electrical conductivity σ. For example, if the ends of a conducting wire are held at different temperatures, a difference of voltage between them will develop. This is the Seebeck effect, and is a consequence of the above-mentioned bulk properties of the wire. Of course, one normally employs another wire, with a different absolute thermopower (ideally with vanishing thermopower, such as a superconductor) in order to measure this thermal voltage.

In the classical treatments of thermoelectric effects, the junctions between the two conductors are considered to be in complete thermal equilibrium; no temperature or potential difference appears across the junctions. This need not be the case, however, and the standard thermodynamic arguments may be applied to develop relations among the coefficients describing a number of transport effects specific to the behavior of a junction between two conductors. Note that the Seebeck and Peltier effects, though making frequent reference to the junctions between two metals, are related to differences in *bulk* properties of the two metals and are independent of the detailed nature of the junctions. We are concerned here with thermoelectric effects which are specific to the junction. Each conductor is considered to be a *discrete* subsystem, each in equilibrium with itself but out of equilibrium with the other, and the two subsystems are connected by a junction which sustains a difference of voltage and temperature, and through which charge and heat can flow.

Smith, Skocpol, and Tinkham[1] have discovered such a junction TE effect. Refer to Fig. 1. Two metals are separated by a tunnel (or other) junction, and the equilibrium electronic temperature on the left is greater than that on the right. No voltage is applied across the junction. If the probability of tunneling (or other transport process) is independent of energy, the current $I_{\mathrm{I}\rightarrow\mathrm{II}}$ equals $I_{\mathrm{II}\rightarrow\mathrm{I}}$, and no net current flows. However, if the probability of transport across the interface is a function of energy, there will be a nonzero current across the interface for zero applied voltage. Smith *et al.* demonstrated that a temperature difference across a tunnel junction drives a current in a closed circuit, or creates a voltage in an open circuit, and that the current or voltage depends on the nature of the junction.

Significant temperature differences may easily appear across metal to metal contacts of apparently negligible electrical resistance. The Wiedemann-Franz law implies that a metal-metal junction with a 0.1 Ω electrical resistance will have an electronic thermal resistance of 10^6 K/W at a temperature of 4 K. Usually this thermal resistance is shorted out by phonon thermal conductance. However, for small contact areas, or for lower temperatures, the phonon conductance will be limited by a Kapitza boundary resistance[2] and may also be less than or of order 10^6 K/W. With such a contact, the relatively modest heat flow of one microwatt will give a one Kelvin tem-

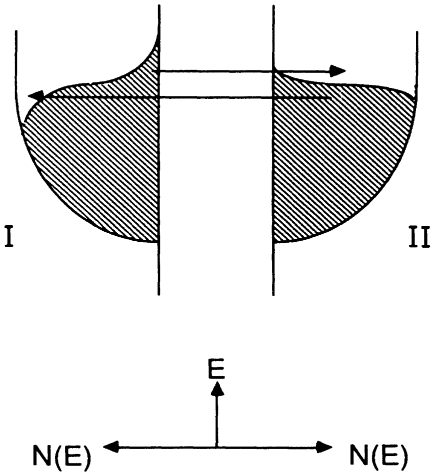

FIG. 1. Two free-electron metals are separated by a tunnel (or other) junction, and $T^{\mathrm{I}} > T^{\mathrm{II}}$.

perature drop across the junction. The resultant thermoelectric voltage, of origin proposed by Smith *et al.*, may be useful in probing nonequilibrium electron temperatures; it may also be a troublesome source of spurious effects. One purpose of this paper is to generalize the usual arguments developed for thermoelectric effects to describe these junction effects.

A second purpose is to include a treatment of magnetization transport; to generalize the discussion to include thermomagnetoelectric (TME) effects, both in the bulk and at junctions. The motivation for the development was the experiment of Ref. 3, which demonstrated that there can be coupling of charge and magnetization transport at a junction, in analogy with the coupling of heat and charge transport which is the basis of the TE effects.

Torrey[4] pioneered the study of the diffusion of nonequilibrium magnetization under the influence of an applied magnetic field gradient, using the particular system of a fluid of nuclear spins (of spin $\frac{1}{2}$). He showed that a current of nonequilibrium magnetization is given by

$$\mathbf{J}_M = -D\nabla(M - M_0) , \tag{1}$$

where D is the coefficient of self-diffusion, M is the magnetization (magnetic moment per unit volume), $M_0 = \chi_v H$ is the equilibrium magnetization, which is proportional[5] to the applied field H, and χ_v is the volume susceptibility. These ideas pertained to the flow of nonequilibrium magnetization in a continuous material. Flesner, Fredkin, and Schultz[6] extended this idea to study the transport of electronic nonequilibrium magnetization in a bimetal system. They pointed out that there is both the current of magnetization driven by a gradient of magnetization in a bulk metal, as discussed by Torrey, and in addition there is a flow of magnetization across a metal-metal interface in the presence of nonequilibrium magnetization on either side of the interface.

Aronov[7] was the first to propose a coupling between charge and spin. He considered a discrete system in which a ferromagnet is in interfacial contact with either a paramagnet or a semiconductor, and predicted that associated with an electric current driven through the ferromagnet into the paramagnet would be a current of magnetization. In the simplest, ideal case, in which a single-spin subband in the ferromagnet carries all the electric current, the magnetic current is just the product of the magnetic moment of each electron, the Bohr magneton β, and the number of carriers crossing the interface in unit time. The authors, in an experiment outlined below,[3] have demonstrated this effect and its converse:[8] nonequilibrium magnetization in a paramagnet that is in interfacial contact with a ferromagnet will induce a voltage across the interface. This, in a way analogous to that of the TE effect of Smith *et al.*, is a junction effect, where the current or voltage depend on the nature of the interface, as well as the properties of the materials.

Thermodynamics can be used to study both discrete and continuous systems, and we will find it useful to consider both cases. Conventionally, most processes of interest occur in continuous systems. Examples, which will be derived below, are the flow of heat Q, charge q, or magnetization M in a bar that has a continuous gradient of temperature T, voltage V, or *magnetization potential* $(M/\chi_v - H)$ (formally introduced below), respectively. The analogous processes in a discrete system are the flow of heat, charge or nonequilibrium magnetic moment from one homogeneous subsystem to another through an interface which supports a difference of temperature, voltage, or $(\mathcal{M}/\chi_s - H)$, respectively. Here $\mathcal{M}$ is the magnetic moment of a subsystem, and χ_s is the sample susceptibility.

Using the framework of thermodynamics, this paper will investigate the TME system, where charge, nonequilibrium magnetization, and heat simultaneously flow, for both continuous (bulk) and discrete (junction) systems. We will not concern ourselves with the myriad of TE effects that are particular to superconductors; rather we will confine our attention to normal metals. Also, the presence of large, externally applied magnetic fields affects TE transport in ways known as thermomagnetic, or thermo-galvano-magnetic effects. These effects are well known and well studied,[9] and arise from the Lorentz force of the applied field on the charge flow. These are *not* to be confused with the TME effects of interest to us, which arise from the flow of spins, driven by a magnetic field, in a way analogous to the flow of charge driven by a voltage. On a microscopic scale, our concern is with magnetization currents driven by terms such as βH in analogy with electric currents driven by eV.

In summary, our second goal is to develop the dynamical laws that describe the thermomagnetoelectric phenomenon associated with the the simultaneous flow of charge, heat, and nonequilibrium magnetization in both a continuous system and a discrete system. We will calculate the rate of entropy production in the system, and use a thermodynamic relationship to identify the relevant generalized forces. We will then use linear response formalism to write the dynamical laws, and employ an Onsager relationship to limit the number of independent coefficients. We will apply this derivation, in the Appendix, to an analysis of the flow of magnetization in a ferromagnetic-paramagnetic interfacial structure.

II. DISCRETE SYSTEMS

The techniques of nonequilibrium thermodynamics are well established,[10,11] and we review them here for application, first, to the TE system. Consider an isolated system composed of two subsystems I and II, each in equilibrium with itself with entropy S^{I} and S^{II}, and separated by a semipermeable partition (refer to Fig. 2). Extensive vari-

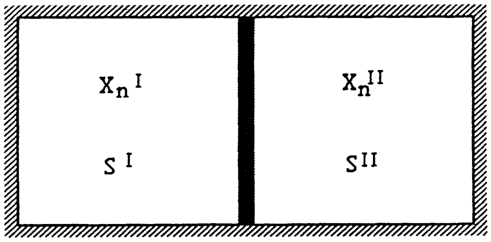

FIG. 2. An isolated thermodynamic system, composed of subsystems I and II separated by a porous partition.

able X_n will flow through the partition until the total entropy, $S^0=S^{\rm I}+S^{\rm II}$, is maximized. The change in entropy, at constant internal energy U, that results from the flow of dX_n is

$$dS^{\rm I}+dS^{\rm II}=\left[\frac{\partial S}{\partial X_n}\right]^{\rm I} dX_n^{\rm I}+\left[\frac{\partial S}{\partial X_n}\right]^{\rm II} dX_n^{\rm II} . \tag{2}$$

However, X_n is an extensive parameter, and the total amount in the system, $X_n^0=X_n^{\rm I}+X_n^{\rm II}$, is conserved. Then $dX_n^{\rm I}=-dX_n^{\rm II}$, and

$$dS^0=(F_n^{\rm II}-F_n^{\rm I})dX_n\equiv \mathbf{F}_n dX_n . \tag{3}$$

The difference, across the interface, of the intensive variable $F_n^i=\partial S^i/\partial X_n^i$ acts as a "pressure" that drives the flow of parameter X_n, and $\Delta F_n=\mathbf{F}_n$ is known as the *generalized force* or *affinity.* The response to the applied force is characterized by the rate of change of the parameter X_n, which is the flux $J_n=dX_n/dt$. Here, positive flow is defined to be from subsystem I to II, the direction of flow in response to a positive affinity $\mathbf{F}_n=F_n^{\rm II}-F_n^{\rm I}$ ($J>0$ for $\Delta X=X^{\rm II}-X^{\rm I}>0$; this sign convention will be convenient for the transformation to the continuum case, with the accompanying notation change $\Delta\rightarrow\nabla$). Of course, more than one extensive quantity may flow, and we wish to extend the ideas to include magnetization flow. Note that in general, the magnetization M (or equivalently the magnetic moment of the sample $\mathcal{M}$) is *not* conserved. Rather, it may be destroyed by spin-relaxation processes at a rate $1/T_1$. For this reason, we will see that generalization to the magnetic problem is not trivial.

When the affinity vanishes, the flux vanishes and the system is in equilibrium. The identification of the affinities in a particular system is frequently rendered more convenient by considering the rate of production of entropy. Differentiating the total entropy with respect to time,

$$\frac{dS^0}{dt}=\sum_n \frac{\partial S^0}{\partial X_n}\frac{dX_n}{dt} \tag{4}$$

gives

$$\dot S=\sum_n \mathbf{F}_n J_n . \tag{5}$$

We will use this approach to identify relevant affinities,[12] and we will also find this approach to be the most useful when we later move from discrete to continuous systems.

Each flux J_n can, in general, be driven by each of the generalized forces $\mathbf{F}_l$. In equilibrium, each flux vanishes as the affinities vanish, so that one can expand J_n in powers of the affinities, with no constant term,

$$J_n=\sum_m L_{mn}\mathbf{F}_m+\frac{1}{2!}\sum_{lm} L_{lmn}\mathbf{F}_l\mathbf{F}_m+\cdots . \tag{6}$$

The functions L_{mn} are called kinetic coefficients, and are determined empirically. If the system is close to equilibrium, quadratic and higher terms can be neglected and a linear relationship is valid,

$$J_n=\sum_m L_{mn}\mathbf{F}_m . \tag{7}$$

A. Junction thermoelectric effects

Let us first solve for the thermoelectric system, in which charge and heat are permitted to flow through a semipermeable partition from one subsystem to another. For example, each subsystem could be a metal, and the partition a finite resistance interface, such as a tunnel junction, or a thin oxide permeated by pinhole leaks. We suppose that the two subsystems are each internally in equilibrium, and that all of the irreversibility of the transport is confined to the *interface.* Each subsystem can deliver or receive thermodynamic quantities reversible to or from this interface. We place the boundaries between the subsystems and the interface, therefore, a few mean free paths into the bulk on either side of the physical junction, since the irreversibility is associated with thermalization of the excitation distribution within this region. Let the volume of the subsystems be fixed, and let dQ^i, dW^i, dq^i, and dS^i be the heat added to, the work done by, the charge added to, and the change of entropy of the ith subsystem.

Consider a steady-state process in which heat $dQ^{\rm I}$ and charge dq flow reversibly into the interface region at temperature $T^{\rm I}$ and voltage $V^{\rm I}$ from region I, in which there is irreversible heat flow and joule heating within the interface region, and in which heat $dQ^{\rm II}$ and charge dq flow reversibly into region II at temperature $T^{\rm II}$ and voltage $V^{\rm II}$. We suppose that $T^{\rm I}>T^{\rm II}$. The change in entropy of the full system is

$$dS=\frac{dQ^{\rm II}}{T^{\rm II}}-\frac{dQ^{\rm I}}{T^{I}} . \tag{8}$$

In steady state, the entropy of the interface cannot change, and the changes in subsystems I and II can be computed directly by the reversible heat flows to and from the interface. Applying the first law to the interface gives, in the steady state,

$$dU^{\rm interface}=dQ^{\rm I}-dQ^{\rm II}+(V^{\rm I}-V^{\rm II})dq=0 , \tag{9}$$

from which we derive the result

$$dQ^{\rm II}=dQ^{\rm I}+(V^{\rm I}-V^{\rm II})dq . \tag{10}$$

Treating the differences $dQ^{\rm II}-dQ^{\rm I}$, $V^{\rm I}-V^{\rm II}$, and $T^{\rm I}-T^{\rm II}$ as small quantities, recalling $\Delta X\equiv X^{\rm II}-X^{\rm I}$, and keeping only terms first order in the small quantities, the substitution of Eq. (10) into (9) gives

$$\begin{aligned} dS&=dQ^{\rm I}\left[\frac{1}{T^{\rm II}}-\frac{1}{T^{\rm I}}\right]+\frac{dq}{T^{\rm I}}(V^{\rm I}-V^{\rm II})\\ &=dQ\Delta\left[\frac{1}{T}\right]-dq\frac{1}{T}\Delta V+\text{second-order terms} . \end{aligned} \tag{11}$$

Considering the changes to have taken place in a time dt, and recalling the definition of the fluxes to be positive for a flow from I to II yields the following expression for the rate of entropy production in the interface due to irreversible processes:

$$\dot S_{\rm univ}=\Delta\left[\frac{1}{T}\right]I_Q-\frac{1}{T}\Delta V I_q , \tag{12}$$

where the I's refers to the rate of transport through the *interface*.

Comparison of Eqs. (12) and (5), after having adopted the arbitrary sign convention of Morse or Callen that $J_1 = -I_q$ and $J_2 = I_Q$, gives the equations analogous to Eq. (7) to be

$$\begin{aligned} -I_q &= \frac{L'_{11}}{T}\Delta V + L'_{12}\Delta\left[\frac{1}{T}\right] , \\ I_Q &= \frac{L'_{21}}{T}\Delta V + L'_{22}\Delta\left[\frac{1}{T}\right] . \end{aligned} \tag{13}$$

The relative magnitudes of the kinetic coefficients L'_{ij} in Eq. (13) may be estimated in terms of simple models. When there is no temperature difference across the interface, the ratio of current to voltage is defined as the conductance G. We thus make the trivial identification $L'_{11} = GT$. In a simple one-dimensional Drude model, in which a junction of area A is represented by a tunneling barrier with transmission probability $t \ll 1$, the conductance is [13]

$$\frac{G}{A} = \frac{e^2}{2} N(E_F) v_F t . \tag{14}$$

The cross coefficient L'_{12} may be identified with parameters discussed by Smith *et al.*, and we follow them[14] in calculating the voltage across an interface for a small temperature difference dT. As noted in the introduction, this coefficient is related to the energy dependence of the relative contributions of electrons of different energy to the tunneling current. The magnitude is conveniently estimated by writing the tunneling current in the form

$$I = \frac{G}{e}\int_{-\infty}^{\infty} P(E)[f^{\mathrm{I}}(E) - f^{\mathrm{II}}(E)]dE , \tag{15}$$

where E is measured from the Fermi level, $e = -|e|$ is the electron charge (a convention chosen throughout this paper), and f^i is the Fermi function for the ith subsystem at temperature T^i. Here, $P(E)$ is a relative measure of the contributions of electrons of energy E to the tunneling current. It is a *weak* function of energy, and can be expanded as

$$P(E) = 1 + c_1 E + \text{higher-order terms} . \tag{16}$$

In the second term, the constant c_1 is a parameter characteristic of the interface:

$$c_1 \equiv \frac{d}{dE}[\ln P(E)]_{E_F} . \tag{17}$$

If f^{I} and f^{II} differ only because of an applied voltage across the interface, then $f^{\mathrm{I}}(E) - f^{\mathrm{II}}(E) \approx eV(df/dE)$, and the integral gives $I = GV$. On the other hand, if there is no applied voltage, but if the electron temperatures on the two sides of the interface are different, there is a current which may be evaluated by noting that the first term integrates to zero by symmetry, and by using the Sommerfeld expansion[15] for the second term to give

$$I = G\frac{c_1\pi^2}{6e} k_B^2[(T^{\mathrm{I}})^2 - (T^{\mathrm{II}})^2] , \tag{18}$$

which, for small temperature differences dT across the interface, can be written as

$$I = G\frac{c_1\pi^2}{3e} k_B^2 T dT . \tag{19}$$

This result allows the identification

$$L'_{12} = -\frac{c_1\pi^2}{3e} k_B^2 G T^3 = -\frac{d}{dE}[\ln P(E)]_{E_F} \frac{\pi^2}{3e} k_B^2 G T^3 . \tag{20}$$

For a tunnel barrier of height ϕ (measured from E_F) and thickness s, the transmission probability as a function of energy E (measured from E_F) is of the form $P(E) \propto \exp(-\kappa s\sqrt{\phi - E})$. Then we find $c_1 = \kappa s/2\sqrt{\phi} \approx 3.1\ \text{eV}^{-1}$ for the parameters of the junctions of Smith *et al.* For a uniformly insulating barrier with pinhole leaks, the current across the interface, and thus $P(E)$ (now measure E from the bottom of the band), is proportional to the component of velocity normal to the interface. Then the order of magnitude of c_1 will be given by

$$\begin{aligned} c_1 &= \frac{d}{dE}[\ln(v_{\text{perp}})]_{E_F} = \frac{1}{2}\frac{d}{dE}[\ln(E)]_{E_F} \\ &= \frac{1}{2E_F} = O(0.1\ \text{eV}^{-1}) . \end{aligned} \tag{21}$$

Using $c_1 = O$ (1 eV^{-1}), and asking for the open circuit voltage that would be associated with an electron temperature difference across the interface gives a value of 10^{-7} volts/kelvin at a temperature of 4 K. This is a small coefficient, but it is measurable, as demonstrated in Ref. 1 for the case of a superconducting film, and as recently reported in Ref. 16 for a point contact geometry.

Finally, to estimate L'_{22}, one must find the electronic contribution to the heat transported across the interface. The solution is in the same spirit as the standard Wiedemann-Franz calculation, and is readily conceptualized with the aid of Fig. 1. A particle of energy E above E_F transports this much energy from I to II when it tunnels across the interface. Thus, the heat current from particles tunneling left to right is

$$I_{Q_{\mathrm{I}\to\mathrm{II}}} = \frac{G}{e^2}\int_{-\infty}^{\infty} EP(E)\{f^{\mathrm{I}}(E)[1 - f^{\mathrm{II}}(E)]\}dE . \tag{22}$$

We write a similar term for particles tunneling from II to I (leaving a hole which is filled at cost of energy $-E$), sum the two terms, use Eq. (16) for $P(E)$ (keeping only the first term this time), and use the Sommerfeld expansion again to find

$$I_Q = -\frac{G}{e^2}\frac{\pi^2}{3} k_B^2 T dT \tag{23}$$

for small temperature differences dT across the interface. Note that in Fig. 1 the temperature is greater on the left ($T^{\mathrm{I}} > T^{\mathrm{II}}$), and recall our previously defined sign conventions.

Defining $\kappa'(T)$ to be the phonon contribution to the conductance of the junction, L'_{22} is given by

$$L'_{22}=\left[\frac{\pi^2}{3}\frac{k_B^2T^3G}{e^2}+T^2\kappa'(T)\right] . \tag{24}$$

We can now write the dynamical equations for the junction thermoelectric effect as

$$I_q=-G\Delta V+\frac{\pi^2}{3}\frac{c_1}{e}k_B^2T^3G\Delta\left[\frac{1}{T}\right] , \tag{25a}$$

$$I_Q=-\frac{\pi^2}{3}\frac{c_1}{e}k_B^2T^2G\Delta V+T^2\left[\frac{\pi^2}{3}\frac{k_B^2TG}{e^2}+\kappa'(T)\right]\Delta\left[\frac{1}{T}\right] . \tag{25b}$$

Here we have used the Onsager relation $L'_{12}=L'_{21}$ to determine the heat current driven by a voltage drop in absence of temperature difference.

Note that these equations predict an inverse of the Smith *et al.* thermal emf: an electric current driven through an interface between metals at different temperatures will carry a reversible heat. Consider the case where the junction is thermally isolated (for example by superconducting leads) so that $I_Q=0$, but an electric current is allowed to flow, $I_q\neq 0$. Then, from Eq. (25b),

$$\frac{L'_{21}}{T}\Delta V=-L'_{22}\Delta\left[\frac{1}{T}\right]=\frac{L'_{22}}{T^2}\Delta T ,$$

which is to say

$$\Delta T=c_1eT\Delta V .$$

To obtain this result we have assumed a low enough temperature that the electronic thermal conductance of the junction dominates, i.e., $\pi^2k_B^2TG/3e^2\gg\kappa'(T)$. Using a typical value for c_1 of 3 eV^{-1}, one finds at $T=4$ K that $\Delta T/\Delta V\sim 10$ K per volt. Note that this is a reversible effect, and changes sign as the polarity of the current is reversed, whereas joule heating at the junction is irreversible, and does *not* change sign as the current is reversed. The joule heating may be minimized by maximizing the resistance of the junction, but the full ΔT is obtained only as long as the electron thermal conductance dominates that of the phonons.

The magnitude of this reversible junction heat will depend on the metals involved and the junction itself, and may be of the same order as the Peltier heat that reversibly evolves, at the junction, due to the difference of thermopowers of the two metals. The simplest method to discriminate against the Peltier heat is to use the same metal on both sides of the junction, in which case there is no Peltier heat. Even with different metals, careful attention to the thermal impedance of the measuring thermometers will allow discrimination between the generation of heat at the junction, characteristic of the Peltier and joule heats, and the establishment of a temperature difference across the junction, characteristic of the newly predicted junction TE effect.

B. Thermomagnetoelectric discrete system

Let's now generalize the TE system to one which includes the transport of nonequilibrium magnetization. The motivation for this has been an experiment, described in a previous paper[3] and illustrated in Fig. 3, in which the junction magnetoelectric effect is demonstrated. Magnetic dipole moments are injected into a paramagnetic metal by driving an electric current through a ferromagnetic film (called an injector) that is in interfacial contact with the paramagnet. In the idealized model proposed first by Aronov, all of the current in the ferromagnet is carried by a single-spin subband, and the current of magnetic dipole moments is simply given by $I_M=(\beta/e)I_q$. In reality, both spin subbands in the ferromagnet are likely to contribute to current conduction. We can write an expression like Eq. (14) for each subband, where the density of states at the Fermi surface, the Fermi velocity, and the interfacial transmission probability may be different for each subband. Then the fraction of spin polarized current will be determined by a phenomenological parameter $|\eta|<1$ defined by

$$\eta\equiv\frac{I_{\text{maj}}-I_{\text{min}}}{I_{\text{maj}}+I_{\text{min}}}=\frac{G_{\text{maj}}-G_{\text{min}}}{G_{\text{maj}}+G_{\text{min}}} , \tag{26}$$

where maj refers to the majority spin subband and min refers to the minority spin subband. Notice that η is defined as positive for dipole current polarized in the direction of the equilibrium magnetization of the ferromagnet. The resulting current of magnetization across the interface is

$$I_M=\frac{\eta\beta}{e}I_q . \tag{27}$$

An injected spin diffuses on average a distance of a spin depth $\delta_s=\sqrt{2DT_1}$ (D is the diffusion constant) in a relaxation time T_1 before its spin orientation is randomized by a collision, and a nonequilibrium magnetization $M=I_MT_1/\delta_sA_{\text{bar}}$ develops in the paramagnet (of cross section A_{bar}) in the volume $A_{\text{bar}}\delta_s$. We can equally state that the sample volume develops a net magnetic moment $\mathcal{M}=I_MT_1$, and can equivalently think of this (in the absence of applied field[17]) as a number of nonequilibrium spins, $\Delta N=\mathcal{M}/\beta$, or nonequilibrium spin concentration

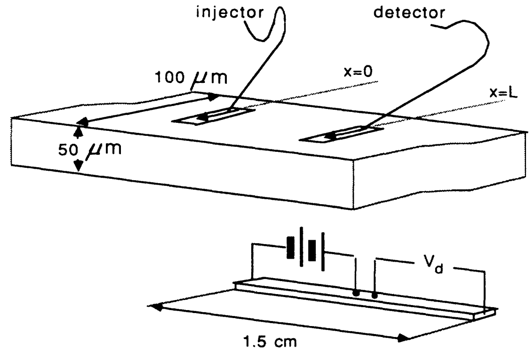

FIG. 3. The geometry of the spin injection experiment.

$\Delta n = M/\beta$. The net magnetic moment $\mathcal{M}$ is an extensive parameter, and is the proper thermodynamic variable for the discrete case. When we consider a continuous system we will use the magnetization M, an intensive variable.

The nonequilibrium magnetization described above can be detected as a voltage V_d by a second ferromagnetic film (called a detector) that is in interfacial contact with the paramagnet and located within δ_s of the injector. The expression for the voltage V_d is derived for a specific model in a previous paper, and for the general case below.

This experiment demonstrated a new concept which is analogous to the junction thermoelectric effect. We will call it the magnetoelectric effect: the transport of charge and of nonequilibrium magnetization across a ferromagnetic-paramagnetic metal interface are *each* driven by differences both of voltage and of magnetization potential across the interface. This section will examine this concept by a process which requires embedding the magneto-electric effect in the more general formalism developed above.

Let us reconsider our thermodynamic system, assumed to have spin-up–spin-down symmetry, in which charge and heat flow in a steady state from one homogeneous subsystem to another. Each charge carries a magnetic moment β, but in equilibrium the magnetic moments are randomly oriented (there is an equal number of up and down moments). We wish to consider now a system in which the spin-up–spin-down symmetry is broken. In a system comprised of a ferromagnetic metal in interfacial contact with a paramagnetic metal, some fraction η of the charges which compose the current I_q crossing the interface are spin polarized (there is a nonequal number of up and down spins). Thus, in addition to the flow of charge and heat there is also a flow of magnetic moment I_M. For the discrete (one-dimensional) system, I_M is a vector that points in the direction of the magnetization. We will let the axis of polarization be fixed along some arbitrary direction, and treat I_M as a scalar.

In contrast to the development of the TE effect, in which the charge q is conserved, for the TME problem the magnetic moment $\mathcal{M}$ is generally *not* conserved, but can be destroyed by, for example, spin relaxation events characterized by a time T_1. Similarly, it can be created by, for example, scattering events (characterized by a time T_{1f}) in a ferromagnet that scatter an unpolarized electron into a polarized band. The change in magnetic moment, $d\mathcal{M}$, of a system may refer either to such a T_1 process, which we will refer to as internal processes $d\mathcal{M}_i$, or to the transfer of magnetization into the system from the outside, an external transfer $d\mathcal{M}_e$. Then we can write

$$d\mathcal{M} = d\mathcal{M}_i + d\mathcal{M}_e \ . \tag{28}$$

Nonequilibrium magnetization is only conserved when $T_1 \rightarrow \infty$, $d\mathcal{M}_i = 0$.

We wish to consider the system in the presence of an applied field H, and adopt the convention[18] that the magnetic field energy represented by the bilinear term $M\,H$ is considered to be outside of the system under consideration. With this convention, the magnetic work done by the system under both a change in H and an internally induced change in $\mathcal{M}$ is $\mathcal{M}dH$. Adopting this convention, the term in the internal energy involving the external field is the "spectroscopic energy"

$$U_H = -H\left[\sum_i \mu_i\right] = -H\mathcal{M} \ , \tag{29}$$

where μ_i are the individual atomic or electronic moments of the system.

In a ferromagnet there exists a large magnetic moment $\mathcal{M}_0$ (later, magnetization M_0), but it is in equilibrium, and there is an associated effective internal field which can be quite large. We wish to expand several thermodynamic functions in deviations $\tilde{\mathcal{M}}$ of the magnetic moment (later, deviations $\tilde{M}$ of the magnetization) from a reference state. We take the reference state to be one of zero applied field H. For a paramagnetic metal $\tilde{\mathcal{M}}$ is just the magnetic moment. For a ferromagnetic metal, there is a large magnetic moment $\mathcal{M}_0$ in zero field, and we define

$$\tilde{\mathcal{M}} = \mathcal{M} - \mathcal{M}_0 \ . \tag{30}$$

To further simplify the discussion, our ferromagnets will always be considered to be ideal, thin film single domains where the equilibrium magnetization is well defined, and we will take H to be parallel to the plane of the film so that we can ignore demagnetizing fields. Similarly, in paramagnetic materials we will assume that demagnetizing fields can be ignored.

We will work at fixed volume, let dQ^i, dW^i, dq^i, and dS^i be the heat added to, the work done by, the charge added to, and the change of entropy in the ith subsystem, and let $d\mathcal{M}^i$ be the change in magnetic moment. In order to identify the generalized force to be coupled to the magnetization current, we need to develop an expression for the rate of entropy production in the presence of a magnetization current for comparison with Eq. (5). From the first law we know that

$$dU = dQ - dW \ . \tag{31}$$

Here, dW is the sum of two contributions, $dW = dW_1 + dW_2$, where dW_1 is the electric work and dW_2 is the magnetic work. As in the usual development of the thermoelectric effects, we have $dW_1 = -Vdq$. For the magnetic work we must distinguish between changes in $\mathcal{M}$ due to internal relaxation processes $d\mathcal{M}_i$, for which there is no analog in the electrical problem, and changes due to transfer of magnetization, $d\mathcal{M}_e$ into or out of the system. With our definition of the internal energy, i.e., it is not to include the contribution to the magnetic field energy which is proportional to $\mathcal{M}H$, there is no magnetic work associated with change in $\mathcal{M}$ due to internal processes, but there is a term $\mathcal{M}dH$ associated with a change in the applied field. For transfer of magnetic moment $d\mathcal{M}$ into the system there is a term, analogous to the electrical Vdq, which we shall denote as $-H^* d\mathcal{M}_e$, where $-H^*$ is a *magnetization potential* which we must determine. The first law may then be written as

$$dU = dQ - \mathcal{M}dH - H^* d\mathcal{M}_e + Vdq \ , \tag{32}$$

which gives the change of free energy $F = U - TS$ to be

$$dF = dQ - TdS - SdT - \mathcal{M}dH - H^* d\mathcal{M}_e + Vdq \ . \tag{33}$$

This is the change in free energy associated with an arbitrary process in which any of the parameters can vary. If the process is reversible, then $dQ = TdS$ and we have

$$dF_{\text{reversible}} = -SdT - \mathcal{M}dH - H^* dM_e + Vdq \ . \tag{34}$$

We can identify the magnetization potential $-H^*$ as follows. For a small deviation of magnetic moment from equilibrium, we can Taylor expand the free energy in powers of the magnetic moment:

$$F(T,H,\tilde{\mathcal{M}},q,V) = F_0(T,q,V,\mathcal{M}_0) + a\tilde{\mathcal{M}} + \frac{b}{2}\tilde{\mathcal{M}}^2 + \cdots \ , \tag{35}$$

where a and b may be functions of H and T. Recall that in a ferromagnet the expansion is in powers of $\tilde{\mathcal{M}} = \mathcal{M} - \mathcal{M}_0$, i.e., in powers of a small deviation $\tilde{\mathcal{M}}$ from the equilibrium magnetic moment in zero applied field. At equilibrium, for fixed T, H, q, and V, the free energy F is a minimum with respect to a variation of $\tilde{\mathcal{M}}$:

$$\frac{\delta F}{\delta \tilde{\mathcal{M}}} = a + b\tilde{\mathcal{M}}_{\text{eq}} = 0 \ , \tag{36}$$

which determines that $\tilde{\mathcal{M}}_{\text{eq}} = -a/b$. Equation (29) requires that a include a term linear in $-H$, $a = a' - H$, and the definition $\tilde{\mathcal{M}}_{\text{eq}} = 0$ at $H = 0$ demands that $a' = 0$. Finally, b must be given by $b = 1/\chi_s$, the isothermal sample susceptibility (the ratio of net sample moment to applied field), and we conclude that

$$F(T,H,\tilde{\mathcal{M}},q,V) = F_0(T,q,V,M_0) - H\tilde{\mathcal{M}} + \frac{\tilde{\mathcal{M}}^2}{2\chi_s} \tag{37}$$

is the proper form of the free energy at and near equilibrium. It follows that, under an arbitrary change in T,$\tilde{\mathcal{M}}$, and H,

$$dF = \frac{dF_0}{dT}(T,q,V,\mathcal{M}_0)dT - \tilde{\mathcal{M}}\,dH + \left[\frac{\tilde{\mathcal{M}}}{\chi_s} - H\right]d\tilde{\mathcal{M}} . \tag{38}$$

We wish to deduce the H^* appearing in Eq. (34) by comparison of that equation with Eq. (38). The validity of the comparison requires that the changes in Eq. (38) be reversible. Since we are interested in situations in which there may be magnetic moment transport associated with the presence of nonequilibrium magnetization, changes in magnetic moment from T_1 relaxation processes will be irreversible and must be excluded. We can use the analogy with thermoelectric phenomena to study the magnetization transport if we briefly impose a conservation of magnetic moment restriction by requiring an infinite T_1 relaxation time; i.e., we require $d\mathcal{M}_i = 0$ and set $d\mathcal{M} = d\mathcal{M}_e$. Then Eq. (38), under the restriction of reversibility, becomes

$$dF_{\text{rever}} = \frac{dF_0}{dT}(T,q,V,\mathcal{M}_0)dT + \tilde{\mathcal{M}}\,dH + \left[\frac{\tilde{\mathcal{M}}}{\chi_s} - H\right]d\tilde{\mathcal{M}}_e \ . \tag{39}$$

Finally, for a reversible change of magnetic moment carried out under the constraints of fixed T and H, comparison of Eqs. (39) and (33) permits the identification

$$-H^* \equiv \left[\frac{\tilde{\mathcal{M}}}{\chi} - H\right] . \tag{40}$$

Recall that other authors[4,6,19] have previously introduced H^* as a driving term for currents of magnetization. We are here extending this idea to make a formal identification as a thermodynamic variable.

We have chosen this particular sign convention so that H^* has the same sign as H in the limit of vanishing $\tilde{\mathcal{M}}$. The magnetization potential H^* has units of magnetic field. It is not to be confused with magnetic potential ϕ, which describes the response of a test monopole, nor vector potential **A**. Because it describes the response of magnetization, we have called it the *magnetization potential.* In the formalism of statistical mechanics, it would enter as a term in the *magneto-electro-chemical potential.* Both of these are equally descriptive titles.

Having made the identification of H^*, we may examine the result of a finite T_1 in which an internal, irreversible change of magnetic moment $d\mathcal{M}_i$ may occur. Comparison of Eqs. (33) and (38) for fixed T, H, V, and q, and with $dQ = dM_e = 0$ (no magnetization transport, and thermal isolation from the external world) gives

$$-TdS = \left[\frac{\tilde{\mathcal{M}}}{\chi} - H\right]d\tilde{\mathcal{M}}_i \ . \tag{41}$$

The change of entropy is

$$dS = -\frac{1}{T}\left[\frac{\tilde{\mathcal{M}}}{\chi} - H\right]d\tilde{\mathcal{M}}_i \ . \tag{42}$$

This represents the change in entropy associated with the approach of the magnetization to equilibrium and, under the assumption $dM_i/dt = -(\tilde{\mathcal{M}} - \chi H)/T_1$, the entropy production dS/dt is clearly positive, as it must be for an irreversible relaxation process.

Next, as before, consider two subsystems separated by an interfacial region which acts as a partition. Each subsystem can deliver or receive thermodynamic quantities reversibly to or from the *interface.* Irreversible processes are confined to be within the interface. That is to say, each subsystem is in equilibrium with itself, and irreversibility associated with the transport of magnetization is confined to within the interface. Consider a process in which, in addition to a flow of heat and of charge, there is a transfer of magnetic moment $d\mathcal{M}$, reversibly from I to the interface, irreversibly within the interface, and reversibly from the interface to II. In this development we neglect the possibility of spin relaxation within the interface by taking $-d\mathcal{M}_e^{\text{I}} = d\mathcal{M}_e^{\text{II}} = d\mathcal{M}_e$. Generalization of the argument to include interfacial relaxation is straightforward but cumbersome, and it seems to play no important role in many of the bilayer spin-resonant experiments. The irreversible magnetization flow within the interface is associated with a difference ΔH^*, just as irreversible charge flow (joule heating) is associated with an interfacial voltage drop ΔV. We find that the change of entropy in the universe, generated by the irreversible transport of dQ, $d\tilde{\mathcal{M}}_e$, and dq, is

$$dS_{\text{univ}}=\Delta\left[\frac{1}{T}\right]dQ-\frac{1}{T}\Delta(-H^*)d\tilde{\mathcal{M}}_e-\frac{1}{T}\Delta V dq\ , \tag{43}$$

where T is the temperature of the interface. Again, the irreversible entropy generation within the interface has been expressed in terms of the reversible transfers at the boundaries of I and II, and the affinities. It follows that the rate of entropy production, for the discrete system, is

$$\dot{S}_{\text{univ}}=\Delta\left[\frac{1}{T}\right]I_Q-\frac{1}{T}\Delta(-H^*)I_M-\frac{1}{T}\Delta V I_q\ , \tag{44}$$

where the I's refer to the rate of transfer of quantities through the interface.

As before, from Eq. (44) we can identify the generalized forces by comparison with Eq. (5), and write the linear expansion[10,11]

$$\begin{aligned}-I_q&=\frac{L'_{11}}{T}\Delta V+L'_{12}\Delta\left[\frac{1}{T}\right]+\frac{L'_{13}}{T}\Delta(-H^*)\ ,\\ I_Q&=\frac{L'_{21}}{T}\Delta V+L'_{22}\Delta\left[\frac{1}{T}\right]+\frac{L'_{23}}{T}\Delta(-H^*)\ ,\\ -I_M&=\frac{L'_{31}}{T}\Delta V+L'_{32}\Delta\left[\frac{1}{T}\right]+\frac{L'_{33}}{T}\Delta(-H^*)\ .\end{aligned} \tag{45}$$

This generalization of Eqs. (13) involves three new, independent coefficients. These are phenomenological coefficients to be determined empirically. However, it is of interest to estimate their magnitudes. Aronov's postulate, Eq. (27), suggests writing

$$L'_{31}=L'_{13}=\eta\frac{\beta}{e}GT\ , \tag{46}$$

where η is the phenomenological parameter previously discussed whose modulus is less than one, and e is the electron charge.

In order to estimate the magnitude of L'_{33}, a simple free-electron model calculation may be performed, in analogy to the calculation of the conductance of a tunnel junction. We find

$$L'_{33}=\xi\frac{\beta^2}{e^2}GT\ , \tag{47}$$

where ξ is a phenomenological parameter (typically of magnitude unity) introduced in the same spirit that η was introduced. This result is valid for a limited class of junction models, but it should give the proper magnitude of the *magnetic conductance* of a junction if the electrical conductance is known.

Finally, to find $L'_{23}=L'_{32}$, we make a postulate similar to Aronov's. Assume that, when $\Delta V=\Delta H^*=0$, some fraction η' of the electrons in the thermoelectric current will be spin polarized. Then we have $L'_{23}=\eta'(\beta/e)L'_{12}$, or

$$L'_{23}=-\eta'\beta\frac{\pi^2}{3}\frac{c_1}{e^2}k_B^2GT^3\ . \tag{48}$$

The parameter η' is not necessarily the same as η, though it is likely to be of the same order of magnitude. In a simple model, the majority and minority spin subbands are treated independently. Each has its own conductance G and energy-dependent transport parameter c_1. Then we expect η' to be given by

$$\eta'=\frac{c_{1,\text{maj}}G_{\text{maj}}-c_{1,\text{min}}G_{\text{min}}}{c_{1,\text{maj}}G_{\text{maj}}+c_{1,\text{min}}G_{\text{min}}}\ , \tag{49}$$

and $\eta'=\eta$ only for the case

$$c_{1,\text{maj}}=\frac{d}{dE}\ln[P_{\text{maj}}(E)]=\frac{d}{dE}\ln[P_{\text{min}}(E)]=c_{1,\text{min}}\ .$$

Using these estimates for the transport coefficients, we can write the linear, dynamic transport equations. Let $1/\varepsilon\equiv\pi^2c_1/3$, so that ε has units of energy. We write Eq. (24) as

$$L'_{22}=a\frac{k_B^2T^3G}{e^2}\ ,$$

where $a=\pi^2/3$ for a Sommerfeld model. Here we have neglected the phonon contribution to thermal conduction, which is valid for small area contacts at low temperatures. Then electronic transport across an interface is given by the following equations:

$$\begin{bmatrix}I_q\\ I_Q\\ I_M\end{bmatrix}=-G\begin{bmatrix}1 & \dfrac{k_B^2T}{e\varepsilon} & \dfrac{\eta\beta}{e}\\ \dfrac{k_B^2T^2}{e\varepsilon} & \dfrac{ak_B^2T}{e^2} & \eta'\dfrac{\beta}{\varepsilon}\left[\dfrac{k_bT}{e}\right]^2\\ \dfrac{\eta\beta}{e} & \eta'\dfrac{\beta T}{\varepsilon}\left[\dfrac{k_B}{e}\right]^2 & \xi\dfrac{\beta^2}{e^2}\end{bmatrix}\begin{bmatrix}\Delta V\\ \Delta T\\ \Delta(-H^*)\end{bmatrix}\ . \tag{50}$$

Let us analyze some of the ramifications of these equations. We can now offer a very simple explanation of the spin injection experiment, which was presented in Ref. 3, and briefly described at the beginning of this section. Suppose there is no temperature difference across a ferromagnetic-paramagnetic metal interface. Equation (50) implies that, even when there is no difference of magnetization potential across the junction, we can drive a magnetization current (i.e., a current of magnetic dipoles) by biasing the junction with a voltage difference ΔV. This describes how the injector in Fig. 3 functions. The injected magnetic current creates a nonequilibrium magnetization (a magnetic dipole moment) in the sample within a spin depth of the injector. The operation of the detector is also described by Eq. (50). The ferromagnetic film and bulk paramagnetic sample are externally connected by a high-impedance voltmeter, so that $J_q=0$. To achieve zero electric current and to thwart the tendency of the nonequilibrium magnetization to drive an electric current via the cross-coefficient L'_{21}, a voltage must develop across the junction:

$$V_f - V_p = -\frac{\eta\beta}{e}(H_f^* - H_p^*) \ , \tag{51}$$

where $V_f - V_p$ is the voltage measured by the external voltmeter, connected to both metals far from the junction. If the relaxation processes in the ferromagnet are sufficiently rapid (see the Appendix), then the ferromagnetic magnetization is essentially in equilibrium, $-H_f^*=0$, and we derive the detector voltage V_d to be

$$V_d \equiv V_f - V_p = \frac{\eta\beta}{e}\left[\left(\frac{\tilde{M}}{\chi}\right) - H\right]_p \ . \tag{52}$$

The generalization of the junction thermoelectric effects to magnetic systems suggests other possible experiments as well. For example, Eq. (50) suggests that a temperature drop across an interface will drive a magnetization current determined by the coefficient L'_{32} through the interface. To our knowledge, such a thermomagnetic effect has not been experimentally observed. A simple model is easily described with the aid of Fig. 4. On the left side of the junction, a ferromagnet whose spin subbands are in substantial imbalance is at a higher temperature than a paramagnet on the right side. If the tunneling probability is energy dependent, as in the Smith *et al.* model, then a net current will result. One expects a larger contribution to this current from one of the spin subbands than the other, which is the same (in the absence of interfacial relaxation) as an associated current of magnetization, and which in principle could be detected by a spin detector film. Furthermore, the converse effect should also be possible: a current of magnetization across the interface should, under suitable boundary conditions, create a temperature difference.

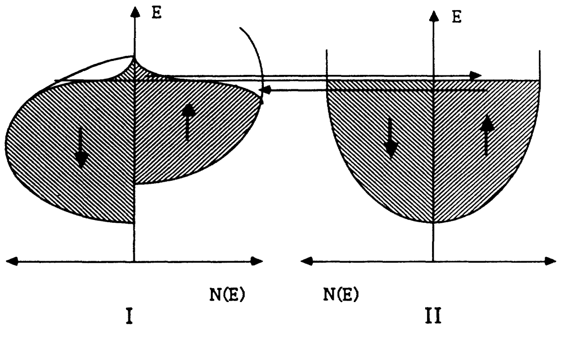

FIG. 4. The thermomagnetic effect. The conductance between spin down subbands is less than the spin up subband conductance (depicted by arrows).

III. CONTINUOUS SYSTEMS

The dynamical laws for a continuous system are developed in the same way as in the preceding section, with a few conceptual changes. First, let the extensive quantities of interest X_n^i become intensive by dividing each by the volume of the ith subsystem. Second, model the continuous system by a sequence of partitions of the sort described in conjunction with Fig. 2, in which the irreversible processes occur; the interfaces are interleaved between thin layers which are taken to be in local internal equilibrium with well-defined thermodynamic variables. The derivation of the equations of thermoelectricity is standard, and the reader can find details in standard texts such as Refs. 10 and 11.

For the TME system, the calculation of the rate of entropy production associated with the flow of heat, charge, and magnetization proceeds identically to the argument leading up to Eq. (44). One should everywhere replace "magnetic moment" $\mathcal{M}$ with "magnetization" M. We find

$$\dot{S}_{\rm univ} = \nabla\left(\frac{1}{T}\right)\cdot\mathbf{J}_Q - \frac{1}{T}\nabla(-H^*)\cdot\mathbf{J}_M - \frac{1}{T}\nabla V\cdot\mathbf{J}_q \ , \tag{53}$$

where $\mathbf{J}_M$ is the flux of magnetic moments per unit area per sec, $\mathbf{J}_q$ is the flux of charge per unit area per sec, and $\mathbf{J}_Q$ is the flux of heat per unit area per sec. From Eq. (53) we can identify the generalized forces and write a linear expansion for the fluxes $-\mathbf{J}_q$, $-\mathbf{J}_M$, and $\mathbf{J}_Q$,

$$\begin{aligned} -\mathbf{J}_q &= \frac{L_{11}}{T}\nabla V + L_{12}\nabla\left(\frac{1}{T}\right) + \frac{L_{13}}{T}\nabla(-H^*) \ , \\ \mathbf{J}_Q &= \frac{L_{21}}{T}\nabla V + L_{22}\nabla\left(\frac{1}{T}\right) + \frac{L_{23}}{T}\nabla(-H^*) \ , \\ -\mathbf{J}_M &= \frac{L_{31}}{T}\nabla V + L_{32}\nabla\left(\frac{1}{T}\right) + \frac{L_{33}}{T}\nabla(-H^*) \ . \end{aligned} \tag{54}$$

Note that if $L_{3j}=0=L_{i3}$, the familiar dynamic equations of the thermoelectric effect result. Once again, Onsager's symmetry theorem tells us that $L_{ij}=L_{ji}$, so that there are six independent coefficients. We can immediately write down three of them from the conventional thermoelectric equations:[20]

$$\begin{aligned} &L_{11} = T\sigma, \quad L_{12} = L_{21} = -T^2\sigma\epsilon \ , \\ &L_{22} = T^3\sigma\epsilon^2 + T^2\kappa \ , \end{aligned} \tag{55}$$

where σ is the electrical conductivity of the material, ϵ its thermopower, and κ the electronic thermal conductivity. The term in $\sigma\epsilon^2$ appears because κ is defined under conditions of zero electric current flow while the L_{22} defines the heat flow under conditions of zero voltage gradient. We will neglect it as small compared to the term linear in κ. Also note that we have neglected the phonon contribution to thermal conduction; this is valid for a bulk material as long as the electrons have reasonable mobility.

The new coefficients involving the magnetization are to be experimentally measured. However, as in the case of the junction effects, their expected magnitudes can be estimated from a simple free electron model. In a homogeneous material, let p be the degree of spin polarization of the electric current. Then, by Aronov's postulate, there is an associated current of nonequilibrium magnetization $\overleftrightarrow{\mathbf{J}}_M$ given by

$$\overleftrightarrow{\mathbf{J}}_M = \frac{\mathbf{p}\beta}{e}\mathbf{J}_e \ . \tag{56}$$

Most generally $\overleftrightarrow{\mathbf{J}}_M$ is a second-rank tensor which specifies both the direction of flow and the orientation of the magnetization. We shall impose the simplifying constraint that the nonequilibrium magnetization is measured along an arbitrary direction, for example the direction of equilibrium magnetization $\mathbf{M}_0$ in the ferromagnetic injector or detector. Then we can treat $\mathbf{J}_M$ as a vector. At fixed T and H^*, we deduce that

$$L_{31} = \frac{p\beta\sigma T}{e} \ . \tag{57}$$

For a ferromagnetic metal, p might be expected to be of order one, and will be determined by things such as the densities of states at E_F, the Fermi velocities, and relaxation times for each spin subband. For a Pauli metal p would be effectively zero and the coupling between charge and magnetization currents would be negligible.

From the work of Torrey,[4] Flesner *et al.*,[6] and Monod,[21] we know that a current of magnetization will be driven by a gradient of magnetization, and the proportionality constant is the coefficient of diffusion of the moments: $\mathbf{J}_M = -D\nabla\tilde{M}$. It follows that $L_{33} = T\chi D$, which can be rewritten, in a simple free-electron model using an Einstein relation, in terms of the conductivity σ as

$$L_{33} = \zeta\frac{\beta^2}{e^2}\sigma T \ , \tag{58}$$

which is analogous to Eq. (47). Here, ζ is a phenomenological parameter analogous to ξ. With the assumption $\zeta = 1$, Eq. (58) would give a plausible estimate for the kinetic coefficient in a nearly free electron, nonmagnetic metal, and would likely overestimate the coefficient in a ferromagnetic metal in which the spin polarization is dominantly in the d band, but where the conductivity is dominated by s band electrons.

Finally, consider coefficients $L_{23} = L_{32}$. If we follow Aronov's logic and assume that a fraction p' of the thermoelectric current is polarized, we find that an estimate for L_{23} is given by

$$L_{23} = L_{32} = -\frac{p'\beta}{e}\sigma T^2\epsilon \ . \tag{59}$$

As in the junction case, p' is likely to be of the same order of magnitude as p, but generally $p \neq p'$. In the spirit of the free-electron model we can write the thermopower ϵ as $a''k_B^2T/eE_F$, where $a'' \approx \pi^2/2$. Finally, with our assumption that electron thermal transport dominates over the phonon contribution, we use the Wiedemann-Franz law to estimate the thermal conductivity κ as $a'k_B^2/e^2T\sigma$, with $a' = \pi^2/3$. Using these estimates for the magnitudes of the transport coefficients, and omitting terms higher than first order in the off-diagonal components, the linear dynamical laws for the flow of heat, charge, and nonequilibrium magnetization in a continuous medium are, to rough order of magnitude

$$\begin{bmatrix} \mathbf{J}_q \\ \mathbf{J}_Q \\ \mathbf{J}_M \end{bmatrix} = -\sigma \begin{bmatrix} 1 & \dfrac{a''k_B^2T}{eE_F} & p\dfrac{\beta}{e} \\ \dfrac{a''k_B^2T^2}{eE_F} & \dfrac{a'k_B^2T}{e^2} & p'\dfrac{\beta}{E_F}\left[\dfrac{k_BT}{e}\right]^2 \\ p\dfrac{\beta}{2} & p'\dfrac{\beta T}{E_F}\left[\dfrac{k_B}{e}\right]^2 & \zeta\dfrac{\beta^2}{e^2} \end{bmatrix} \begin{bmatrix} \nabla V \\ \nabla T \\ \nabla(-H^*) \end{bmatrix} . \tag{60}$$

One may ask whether these terms involving the transport of magnetization induced by gradients in a magnetization potential, electric field, or temperature gradient have been observed, or are of a magnitude to be observable. The diagonal term I_{33}, as already noted, was proposed by Torrey in the context of nuclear magnetic resonance in 1956. It is an essential term in the interpretation of transmission electron spin resonance and in the spin-injection experiment of Ref. 3. In the context of conduction spin transport the magnitude has been confirmed to be that expected with $\zeta \approx 1$. In systems containing localized magnetic moments, however, there is reduction of the coefficient from that predicted by the free electron theory by the factor $\chi_c/(\chi_c + \chi_l)$, where χ_c and χ_l are the contributions of the conduction electrons and the local moments, respectively, to the total susceptibility. Similarly, in strongly exchange enhanced systems there should be a reduction of the magnetization transport relative to charge transport by a factor of the exchange enhancement of the susceptibility.

The off-diagonal components have not, to our knowledge, been observed. The coefficient L_{13} could, in principle, be contributing to the injection signal in the spin-injection experiment. To argue this in detail requires combining the implications of both the bulk and the interface TME effects for the spin-injection experiment, and this is done in the Appendix. Suppose that the interfacial charge-spin coupling is zero, but that there is a large coupling p in the ferromagnet. There is then a large J_M in the ferromagnet, but no J_M across the interface associated with the J_q flowing through the interface. As a consequence, a large nonequilibrium M must develop in the ferromagnet at the interface in order to drive a back diffusion current to make the total J_M at the interface small compared with the J_M in the bulk ferromagnet. But then there *can* be a magnetization transport across the interface due to the *diagonal* L_{33} term in the interfacial coupling. To decide unambiguously the relative contribution of the two mechanisms requires rather complete characterization of the interface and the magnetization transport within the ferromagnet. The problem is discussed in more detail in the Appendix.

The thermomagnetic coupling L_{23} is of sufficient magnitude to give rise to effects of observable magnitude and predicts, for example, that an open circuit ferromagnetic wire will develop an extra magnetic moment in proportion to a temperature difference between its ends. However, there would arise ambiguities of interpretation similar to those discussed in the preceding paragraph in disentangling the bulk and interfacial contributions to any specific experiment.

Finally, we note in passing that an analytic tool for the thermoelectric system is the calculation of the current of entropy in a continuous medium (wire) that carries current $\mathbf{J}_q$ along a temperature gradient ΔT. From Eqs. (54) we can algebraically eliminate the variable ∇V, and write $\mathbf{J}_Q[\nabla(1/T),\mathbf{J}_q]$. The current of entropy is $\mathbf{J}_S=\mathbf{J}_Q/T$, and is found to be

$$\mathbf{J}_S=\kappa T\nabla(1/T)+\epsilon\mathbf{J}_q \ . \tag{61}$$

The first term is the entropy current that is independent of any electronic current. The second term implies that each electron carries with it an entropy ϵe. We can analyze the TME system by the same procedure; we algebraically eliminate ∇V and ∇H^*, and solve for $\mathbf{J}_Q[\mathbf{J}_q,\mathbf{J}_M,\nabla(1/T)]$. For a free-electron model, we find

$$J_S=\left[\frac{\zeta+pp'}{\zeta-p^2}\right]\epsilon J_q-\frac{p+p'}{\zeta-p^2}\frac{e}{\beta}\epsilon J_M$$
$$+T\kappa\nabla\left[\frac{1}{T}\right]+\text{terms of order } \epsilon^2 \ . \tag{62}$$

Note that this reduces to the form Eq. (61) for $p=0$, as it must. If we take $p\approx p'$, we discover that the entropy transported per electron (in a metal for which $p\neq0$) is *reduced* from what it would be for $p=0$ if $p>0$, i.e., if the polarized current is in the majority band, and is *increased* if $p<0$, i.e., if the polarized current is in the minority band. Knowing $J_M(x)$ (which is calculated in the Appendix), $J_S(x)$, and $-H^*(x)$, one can calculate the rate of entropy production, and the associated heating (or cooling), in various regions of the ferromagnetic-paramagnetic system.

IV. CONCLUSIONS

In order to better understand the spin-injection experiment of Ref. 3, we have applied the methods of nonequilibrium thermodynamics to study transport processes at interfaces. After a brief review of formalism, we first examined effects, associated with the transport of charge and heat, specific to junctions. We then generalized to include the transport of nonequilibrium magnetization. Finally, we extended the study of charge, heat and magnetization flow to a continuous system. In each case, our method was to calculate the rate of entropy production, identify the *generalized forces,* and use linear response theory to write the thermodynamic equations of motion. We briefly discussed some of the ramifications of these equations, and, in the Appendix, we apply them to a detailed analysis of the spin-injection experiment.

We have noted that there may be a significant departure from thermodynamic equilibrium across a small area contact of moderately high conductance; this junction nonequilibrium can lead to unexpected sources of heat generation and of thermally induced voltages which are distinct from the usual thermoelectric effects. If one of the two metals is ferromagnetic there is, in addition, the possibility of electrically and thermally induced magnetization currents and of magnetically induced thermal and electrical currents at the junction. In a similar fashion, electric and thermal potential gradients in a bulk ferromagnetic metal will drive a magnetization current. Rough magnitudes of the various possible effects are estimated.

V. ACKNOWLEDGMENTS

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APPENDIX

As a specific application of the formalism developed in the paper, we use Eqs. (50) and (60) to model the isothermal flow of magnetization from the ferromagnet into the paramagnet at the injector junction in the experiment described briefly in the main body of the text.[3] The one dimensional model used is depicted in Fig. 5. For simplicity we assume the area of the interface to be unity. An electric current J_q is imposed and we ask for the resultant magnetization current J_M injected from the ferromagnet into the paramagnet.

Consider first the steady-state flows within each metal. We use Eq. (60), assuming the temperature everywhere the same, to relate the currents to the potential gradients. The conservation of charge requires that $J_q(x)$ is indepen-

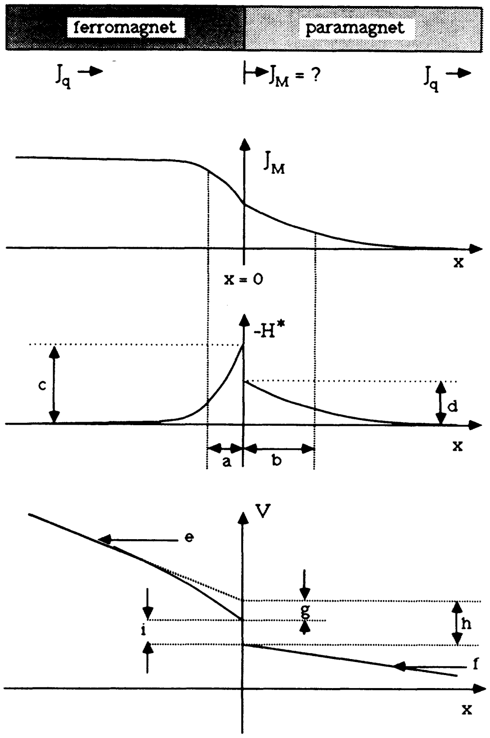

FIG. 5. One-dimensional model of a ferromagnet and a paramagnet in interfacial contact, to study magnetization flow in the spin-injection experiment. (a) The spin depth δ_f in the ferromagnet; (b) The spin depth δ_s in the paramagnet; (c) $-H^*_{0,f}$; (d) $-H^*_{0,p}$; (e) The slope is $1/\sigma_f$; (f) The slope is $1/\sigma_p$; (g) $(\beta/e)p_f H^*_{0,f}$; (h) $V_{0,f}-V_{0,p}=J_q\times$(the apparent junction resistance); (i) ΔV.

dent of x, hence that within either metal the magnetization and electric potentials are related simply by

$$\nabla V_i=\frac{p_i\beta}{e}\nabla H_i^*-\frac{1}{\sigma}J_q \ , \tag{A1}$$

where the subscript $i=f,p$ denotes respectively the ferromagnet and the paramagnet. The magnetization need not be conserved in the presence of spin relaxation at a rate $1/T_{1i}$. We have, then, from the continuity equation for magnetization,

$$\begin{aligned}\nabla\cdot J_{Mi}&=-\frac{\tilde{M}_i-\chi_i H}{T_{1i}}=\frac{\chi_i}{T_{1i}}H_i^*\\ &=-\nabla\cdot\left[\frac{\sigma_i p_i\beta}{e}\nabla V_i+\zeta_i\sigma_i\frac{\beta^2}{e^2}\nabla H_i^*\right]\\ &=-[p_i^2-\zeta_i]\frac{\sigma_i\beta^2}{e^2}\nabla^2 H_i^* \ ,\end{aligned} \tag{A2}$$

where we have used Eqs. (A1) and (60). This may be solved for the spatial dependence of H_i^*:

$$H_i^*=H_{0i}^*e^{\pm x/\delta_i} \ , \tag{A3}$$

where the upper sign is for $i=f$, and the lower sign for $i=p$. The spin diffusion length δ_i is defined by

$$\delta_i\equiv\left[\frac{(\zeta_i-p_i^2)\sigma_i\beta^2T_{1i}}{e^2\chi_i}\right]^{1/2} . \tag{A4}$$

This is essentially the definition $\delta\equiv\sqrt{DT_1}$ with the diffusion constant D given by an Einstein relation $D=\beta^2\sigma/e^2\chi$, modified by the factor ζ_i which allows for differences in the charge and spin diffusion constants, and the term p_i^2 which arises from the coupling between the charge and spin currents. Equation (A1) may then be integrated to give

$$V_i(x)=\frac{p_i\beta}{e}H_{0i}^*e^{\pm x/\delta_i}-\frac{x}{\sigma_i}J_q+V_{0i} \ . \tag{A5}$$

From these solutions the magnetization current at the interface may be evaluated for either metal as

$$J_{Mi}(x=0)=\pm\frac{(\zeta_i-p_i^2)\sigma_i\beta^2}{e^2\delta_i}H_{0i}^*+\frac{p_i\beta}{e}J_q \ . \tag{A6}$$

Note that the second term on the right is the magnetization current carried in the bulk associated with the cross coupling to the electric current. It is present in the ferromagnet, but not in the paramagnet ($p_p=0$).

In our approximation of no spin relaxation in the interfacial region, the two currents J_{Mf} and J_{Mp} given by Eqs. (A6) must be equal. Further, they must equal the current through the interface given by Eq. (50),

$$J_M=-G\left[\frac{\eta\beta}{e}\Delta V-\zeta\frac{\beta^2}{e^2}\Delta H^*\right] , \tag{A7}$$

subject to the condition on ΔV and ΔH^* that the electric current must equal J_q, or

$$J_q=-G\left[\Delta V-\frac{\eta\beta}{e}\Delta H^*\right] , \tag{A8}$$

with ΔV and ΔH^* determined from Eqs. (A3) and (A5) by

$$\begin{aligned}\Delta V&=V_p(0)-V_f(0)=(V_{0p}-V_{0f})+\frac{\beta}{e}p_fH_{0f}^* \ ,\\ \Delta H^*&=H_{0p}^*-H_{0f}^* \ .\end{aligned} \tag{A9}$$

The conservation of current across the interface gives the two independent equations

$$J_{Mf}=J_M=J_{Mp} \ ,$$

which, together with the condition of Eq. (A8), determine the three unknowns H_{0f}^*, H_{0p}^*, and ΔV in terms of J_q and the bulk and interfacial transport coefficients. Equation (A9) may then be used to determine the junction resistance

$$R\equiv\frac{V_{0f}-V_{0p}}{J_q} \ . \tag{A10}$$

After the appropriate algebraic manipulations, we find the following expression for the magnetic current:

$$J_M=\frac{\eta\beta}{e}J_q\left[\frac{1+G(p_f/\eta)(\delta_f/\sigma_f)(\xi-\eta^2)/(\zeta_f-p_f^2)}{1+G(\xi-\eta^2)[(\delta_p/\sigma_p)(1/\zeta_p)+(\delta_f/\sigma_f)1/(\zeta_f-p_f^2)]}\right]$$
$$\equiv\eta^*\frac{\beta}{e}J_q\ . \tag{A11}$$

The interpretation of Eq. (A11) depends critically upon the products $G(\delta_i/\sigma_i)$. The ratio σ_i/δ_i is an effective conductance of the ith metal from the interface to the bulk of the metal via the combined effects of spin diffusion and relaxation. If $G(\delta_i/\sigma_i)\ll 1$, then the spin distributions are little disturbed on either side of the interface as a consequence of magnetization transport across the interface and it is the interfacial transport parameter η which entirely determines the ratio of magnetic to electric current:

$$J_M=\frac{\eta\beta}{e}J_q\ . \tag{A12}$$

On the other hand, if the interfacial conductance is large compared with the diffusive spin conductance of the ferromagnet, $G(\delta_f/\sigma_f)\gg 1$ (and the dimensionless parameters p, ζ, etc. are of order unity), then the magnetization current is given by

$$J_M=p_f\frac{\beta}{e}J_q\left[\frac{1}{1+(\delta_p/\sigma_p)(\sigma_f/\delta_f)(\zeta_f-p_f^2)/\zeta_p}\right]\ . \tag{A13}$$

In this limit the injection efficiency is proportional to the bulk transport properties of the two metals and independent of the interface. If spin diffusion and relaxation are rapid in the paramagnet compared with the ferromagnet, then the injector efficiency,

$$\eta^*=p_f\ , \tag{A14}$$

is just the cross coupling of electric and magnetic currents in the ferromagnet; all of the magnetization current carried in the bulk of the ferromagnet is carried into the paramagnet and is relaxed there. With a low diffusion and long relaxation in the paramagnet, nonequilibrium magnetization builds up in the paramagnet and J_M is reduced by the factor in the denominator of Eq. (A13). This same "pile up" is reflected in the apparent or measured junction resistance, the ratio of the voltage difference $(V_{0f}-V_{0p})$ of Eq. (A9) to J_q, which may deviate from the nominal value of G^{-1} as a consequence of the bottlenecking of the magnetization transport in the paramagnet. The relevant algebra is straightforward, messy, and not particularly revealing.

Finally, we note that the detector junction in the spin-injection experiment may be modeled in a similar fashion with the result

$$V_d=\eta^*(-H_p^*)\frac{\beta}{e}=\eta^*\frac{\beta}{e}\left[\frac{\tilde{M}}{\chi}-H\right]\ , \tag{A15}$$

with η^* given by Eq. (A11).

It should be noted that the model geometry used in this appendix is rather far from the actual experimental geometry. Without attempting a quantitative argument, one may simply remark that the effect of the real geometry is to increase the effective spin diffusion conductance σ_i/δ_i on either side of the junction and to make it probable that the experiments of Ref. 3 were carried out in the weak coupling, $G(\delta_i/\sigma_i)\ll 1$, regime.

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[1] A. D. Smith, M. Tinkham, and W. J. Skocpol, Phys. Rev. B **22**, 4346 (1980).

[2] R. E. Peterson and A. I. Anderson, J. Low Temp. Phys. **11**, 639 (1973).

[3] M. Johnson and R. H. Silsbee, Phys. Rev. Lett. **55**, 1790 (1985).

[4] H. C. Torrey, Phys. Rev. **104**, 563 (1956).

[5] More properly, suppose coordinate axes are chosen with arbitrary orientation to the applied field. Let the moments be quantized along the $\hat{x}$ axis. Then the diffusion current of the x component of magnetization is given by $J_{M_x}=-D\nabla(M_x-M_{0x})$, where M_{0x} is the x component of the equilibrium magnetization, $M_{0x}=(n\beta^2/kT)H_x$.

[6] L. D. Flesner, D. R. Fedkin, and S. Schultz, Solid State Commun. **18**, 207 (1976).

[7] A. G. Aronov, Pis'ma Zh. Eksp. Teor. Fiz. **24**, 37 (1976) [JETP Lett. **24**, 32 (1976)].

[8] R. H. Silsbee, Bull. Magn. Reson. **2**, 284 (1980).

[9] H. B. Callen, *Thermodynamics* (Wiley, New York, 1960), Sec. 17.6.

[10] See H. B. Callen, *Thermodynamics*, Ref. 9, Chaps. 16 and 17.

[11] P. M. Morse, *Thermal Physics* (Benjamin, New York, 1969), Chap. 8 and particularly the discussion beginning on p. 107.

[12] See H. B. Callen, *Thermodynamics*, Ref. 9, p. 286.

[13] This formula is equally valid for interfacial conductance dominated by pinhole leaks through an insulating barrier, where the pinhole diameter is in the Knudsen limit. Then the transmission probability t is interpreted as the ratio of the area of the pinhole to the area of the interface. Equation (14) can be generalized to three dimensions as $G/A=(e^2/2)N(E_F)\langle v_\perp\rangle\langle t\rangle$, where $\langle v_\perp\rangle$ and $\langle t\rangle$ are suitably defined averages. See M. Johnson, Ph.D. thesis, Cornell University, 1986.

[14] See Ref. 1, Eq. (7).

[15] F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, New York, 1965), p. 396.

[16] O. I. Shklyareskii, A. G. M. Jansen, J. G. H. Hermsen, and P. Wyder, Phys. Rev. Lett. **57**, 1374 (1986).

[17] In the more general case of an applied, external field H, there will be an equilibrium magnetization $\chi_v H$, and an equilibrium

magnetic moment $\chi_s H$, where χ_v and χ_s are the volume and sample susceptibilities. The nonequilibrium moment will be the difference $\mathcal{M}-\chi_s H$, where $\mathcal{M}$ is the total magnetic moment, and similarly the nonequilibrium magnetization will be $M-\chi_v H$. This nonequilibrium magnetization can still be thought of as a nonequilibrium density of aligned spins, and can be created with external field H and a saturating microwave field tuned to resonance.

[18] C. Kittel, *Elementary Statistical Physics,* (Wiley, New York, 1958).

[19] R. Magno and J. H. Pifer, Phys. Rev. B **10**, 3727 (1974).

[20] See Ref. 11, Eq. (8.48).

[21] P. Monod (private communication); R. H. Silsbee, A. Janossy, and P. Monod, Phys. Rev. B **19**, 4382 (1979).