Heat-current operator and transport entropy of vortices in type-II superconductors*

Chia-Ren Hu

Department of Physics, University of Southern California, Los Angeles, California 90007

(Received 23 June 1975)

The definition of a heat-current operator and the microscopic treatment of a temperature gradient in a magnetic conductor are revised in order to resolve a conflict with the third law of thermodynamics and Onsager's principle. Some new theoretical results on the transport entropy of vortices in type-II superconductors with magnetic and nonmagnetic impurities are reported to substantiate our new linear-transport analysis.

It has been noted in the recent literature[1-3] that the existing definition of a heat-current operator $\vec{j}^h$ and the microscopic treatment of a temperature gradient $\vec{\nabla}T$ in a *magnetic* conductor are unsatisfactory. As a result the microscopic calculation of the entropy S_D, transported by a unit segment of a moving vortex line in a type-II superconductor, violates either the third law of thermodynamics or the Onsager's reciprocity principle. The purpose of this paper is to present a resolution of this enigma and to report some new theoretical results on S_D in order to substantiate our present analysis.

For a type-II superconductor in the mixed state with a magnetic field in the z direction, the transverse thermal and electric linear transport properties are strongly coupled. If we ignore the small terms related to the Hall effect, then

$$j_x^h = K_s(-\nabla T)_x + \alpha \mathcal{E}_y,\\ j_y = \beta(\nabla T)_x + \sigma_s \mathcal{E}_y, \tag{1}$$

with $\vec{\mathcal{E}} \equiv \vec{E} - \vec{\nabla}\mu/e$, where $\vec{E}$ is the applied electric field, μ is the local chemical potential, and e is the electronic charge. For dirty type-II superconductors in the high-field limit (i.e., $B \simeq H_{c2}$), various authors have made microscopic calculations of the four linear transport coefficients: the thermal conductivity K_s by Caroli and Cyrot[4]; the flux-flow conductivity σ_s and the Ettinhausen coefficient α by Caroli and Maki (CM),[5] with σ_s later modified by Thompson[6]; and the Nernst coefficient β by Takayama and Ebisawa.[2] Physically $\alpha \neq 0$ here because moving vortices transport entropy. Putting $\vec{j}^h = n_v T S_D \vec{v}$ with vortex-line density $n_v = B/\phi_0$, ($\phi_0 = hc/2e$ being the flux quantum) and the flux-flow velocity $\vec{v}$ obeying $\vec{\mathcal{E}} = -\vec{v} \times \vec{B}$, one arrives at the relation $S_D = \alpha\phi_0/T$. The third law of thermodynamics requires that $S_D \to 0$ as $T \to 0$, but the CM result for α gives $S_D \propto T^{-1}$ at low temperatures. To clarify this difficulty, Maki[3] noted that the heat-current operator used by CM and others, $\vec{j}_0^h \equiv \vec{j}^E - (\mu/e)\vec{j}$, where $\vec{j}^E$ is defined in terms of the Hamiltonian density h via the continuity equation $\partial h/\partial t + \vec{\nabla}\cdot\vec{j}^E = 0$, is incomplete for magnetic conductors. Basing on the thermodynamic relation $\delta Q \equiv T\,\delta S = \delta E - \mu\,\delta N + H_{\text{ext}}\,\delta M$, where M is the average magnetization, he proposed the new heat-current operator $\vec{j}^h = \vec{j}_0^h + H_{\text{ext}}\vec{j}_M$. Assuming the continuity equation, $\partial M/\partial t + \vec{\nabla}\cdot\vec{j}_M = 0$, and a uniform steady flux flow, $\partial M/\partial t = -\vec{v}\cdot\vec{\nabla}M$, the magnetization current $\vec{j}_M$ was equated to $\vec{v}M$. This argument leads to the prescription

$$\alpha = \alpha^0 + M, \quad S_D = S_D^0 + \phi_0 M/T, \tag{2}$$

where α^0 and S_D^0 denote the CM results. Near H_{c2} the so-predicted S_D indeed vanishes linearly as $T \to 0$, which is also supported by experimental measurements.[1] However, I find that Maki's argument can not be completely correct, since it is based on a thermodynamic relation with a wrong sign in the last term,[7] and there is no other compensating sign mistake. Another indication that Maki's argument is not satisfactory was found by Takayama and Ebisawa,[2] who pointed out that his argument does not give a corresponding correction term to β: Since a $\vec{\nabla}T$ in the absence of $\vec{\mathcal{E}}$ does not drive a flux flow, it can not possibly cause a magnetization current. The Onsager relation $\alpha = \beta T$, which is satisfied before $+M$ is added to α^0, must now be violated. Below I propose to resolve this dilemma with a new linear transport analysis. A new heat-current expression is derived which reduces to the prescription in Eq. (2) only for $B \simeq H_{c2}$. The Onsager relation is also retrieved near H_{c2} where β has been calculated, by discovering a new contribution to β.

Since I do not know of any heat-current expression which is not based on the assumption of local equilibrium, I begin by seeking a *local* thermodynamic relation between local density variables of a magnetic conductor: For a system of interacting charged particles at equilibrium (with spin paramagnetism ignored for simplicity), one may deduce from statistical mechanics that

$$T\,\delta S = \delta E - \mu \delta N + \int \vec{j}\cdot\delta\vec{A}\,d^3x\,,$$

where E is *defined* as the ensemble average of the total Hamiltonian without the electromagnetic field energy, and $\vec{b}=\vec{\nabla}\times\vec{A}$ is the local magnetic induction. Since $\vec{\nabla}\cdot\vec{j}=0$ at equilibrium, one may *define* a local magnetization density $\vec{m}$ via $\vec{\nabla}\times\vec{m}=\vec{j}$ and the boundary condition $\vec{m}=0$ at infinity. This converts $\int\vec{j}\cdot\delta\vec{A}$ to $\int\vec{m}\cdot\delta\vec{b}$. For a simply-connected sample, $\vec{m}$ may be chosen to vanish outside the sample.[8] It is then consistent to introduce the following *local* relation for the *equilibrium* entropy-density s:

$$T\,\delta s = \delta\epsilon - (\mu/e)\delta\rho + \vec{m}\cdot\delta\vec{b}\,, \tag{3}$$

where $\epsilon \equiv \langle h\rangle$, and ρ is the charge density. In order to assume the validity of Eq. (3) in a transport situation, however, we must still modify slightly the definition for $\vec{\epsilon}$ and $\vec{m}$: First, the total Hamiltonian density h_T now contains terms involving a scalar potential ϕ and a time-dependent vector potential in order to represent an electric field in a general gauge. We must put $\vec{\epsilon}\equiv\langle(h_T-\rho\phi)\rangle$, *so that* ϵ *and* $\vec{j}^E$ *can remain gauge invariant*. Secondly, we can no longer define $\vec{\nabla}\times\vec{m}$ as the total current $\vec{j}$ flowing *in* the sample, since the latter now includes a transport current $\vec{j}_t$ which does not close itself inside the sample. Had we known a unique way to separate $\vec{j}_t$ from $\vec{j}$, we could define $\vec{\nabla}\times\vec{m}=\vec{j}-\vec{j}_t$. But at the present stage there is no criterion for us to decide what is the unique correct way to define $\vec{j}_t$. We shall therefore proceed with our argument assuming that Eq. (3) is true for some generalization of the equilibrium $\vec{m}$, and postpone the task of defining $\vec{m}$ in a nonequilibrium situation until a later stage. We shall see that to calculate the linear transport coefficients we need only the definition of $\vec{m}$ at equilibrium. Then the linear transport equation for $\vec{j}$ automatically suggests to us how we should define $\vec{m}$ to first order in the thermodynamic affinities. It is likely that one could obtain the definition of $\vec{m}$ to higher order in the affinities by the same procedure, but this is beyond the scope of the present paper. The essential point is that a correct definition of $\vec{m}$ is actually *dictated* by our *assumption* of the local equilibrium condition Eq. (3). Of course this situation arises only because we did not *derive* Eq. (3) *for a nonequilibrium situation* from more fundamental physical principles in a microscopic level, but have merely assumed its validity.

To proceed with our argument we note that the continuity equations $\partial\epsilon/\partial t+\vec{\nabla}\cdot\vec{j}^E=\vec{j}\cdot\vec{E}$ and $\partial\rho/\partial t+\vec{\nabla}\cdot\vec{j}=0$ follow simply from Heisenberg's equation of motion.[9] The Maxwell equation $\vec{\nabla}\times\vec{E}=-\partial\vec{b}/\partial t$ may be viewed as three continuity equations $\partial b_i/\partial t+\vec{\nabla}\cdot\vec{j}_{b_i}=0$ with $\vec{j}_{b_i}=\vec{E}\times\hat{e}_i+$ a pure curl, where $\hat{e}_i$ is the ith unit vector. The pure curl has no physical meaning but may be conveniently chosen as $\vec{\nabla}\times(-\mu\hat{e}_i/e)$. Then

$$\vec{j}_{b_i}=\vec{\mathcal{E}}\times\hat{e}_i\,. \tag{4}$$

Dividing Eq. (3) by δt and using the continuity equations, we obtain $\partial s/\partial t+\vec{\nabla}\cdot(\vec{j}^h/T)=w/T$, *where the heat-current density and the dissipation function are found to be*:

$$\vec{j}^h=\vec{j}^h_0+\sum_i m_i\vec{j}_{b_i}\,,$$
$$w=\vec{j}^E\cdot\vec{X}_T+\vec{j}\cdot\vec{X}_{\mathcal{E}}+\sum_i\vec{j}_{b_i}\cdot\vec{X}_{m_i}\,, \tag{5}$$

where

$$\vec{X}_T\equiv T\vec{\nabla}(1/T)\,,$$
$$\vec{X}_{\mathcal{E}}\equiv\vec{E}-T\vec{\nabla}(\mu/eT)=\vec{\mathcal{E}}-(\mu/e)\vec{X}_T\,,$$

and

$$\vec{X}_{m_i}\equiv T\vec{\nabla}(m_i/T)=\vec{\nabla}_{m_i}+m_i\vec{X}_T\,.$$

Now consider first the simpler case of a spatially uniform system. Then Eq. (5) suggests that the phenomenological linear-transport equations of a magnetic conductor should in general be (cf. Callen,[7] Chap. 16):

$$\vec{j}^E=\vec{L}_{11}\cdot\vec{X}_T+\vec{L}_{12}\cdot\vec{X}_{\mathcal{E}}+\sum_i\vec{L}^i_{13}\cdot\vec{X}_{m_i}\,, \tag{6a}$$

$$\vec{j}=\vec{L}_{21}\cdot\vec{X}_T+\vec{L}_{22}\cdot\vec{X}_{\mathcal{E}}+\sum_i\vec{L}^i_{23}\cdot\vec{X}_{m_i}\,, \tag{6b}$$

$$\vec{j}_{b_i}=\vec{L}^i_{31}\cdot\vec{X}_T+\vec{L}^i_{32}\circ\vec{X}_{\mathcal{E}}+\sum_j\vec{L}^{ij}_{33}\cdot\vec{X}_{m_j}\,. \tag{6c}$$

Some of the coefficients in these equations can immediately be deduced. Comparing Eq. (6c) with Eq. (4) we find $\vec{L}^{ij}_{33}=\vec{L}^i_{31}-(\mu/e)\vec{L}^i_{32}=0$ and $L^{z,xy}_{32}=+1$, etc. Also $\vec{L}^i_{13}-(\mu/e)\vec{L}^i_{23}=0$, since the second law of thermodynamics would be violated if a $\vec{\nabla}m_i$ could drive a heat current in any direction; and $L^{z,xy}_{23}=-1$, etc., since one expects $\vec{\nabla}\times\vec{m}=\vec{j}$ when $\vec{\nabla}T=\vec{\mathcal{E}}=0$. If we now use the first part of Eq. (5) to eliminate $\vec{j}^E$ in favor of $\vec{j}^h$, and further assume $\vec{m}$ and $\vec{b}$ to be constant vectors in the z direction, then Eqs. (6a) and (6b) reduce to Eq. (1) with $K_s=K^0_s$, $\alpha=\alpha^0+m$, $\beta=\beta^0+m/T$, and $\sigma_s=\sigma^0_s$, where the superscript 0 are now used to mark all quantities that can be calculated with the existing method involving the operators $\vec{j}^h_0$ and $\vec{j}$. We thus find $\alpha=\beta T$ if only $\alpha^0=\beta^0 T$. The new contribution found for β is seen to result from the fact that a $\vec{\nabla}T$ does not merely act through the two thermodynamic affinities $\vec{X}_T$ and $\vec{X}_{\mathcal{E}}$, but also through the new affinities $\vec{X}_{m_i}$ which occur in magnetic systems.

For type-II superconductors where $\vec{m}$ varies in space, the demonstration of $\alpha=\beta T$ is more difficult in general. But near H_{c2} when the order parameter is small, and $\vec{X}_T$, $\vec{\mathcal{E}}$, and $\vec{j}_{b_i}$ are space independent to the order of interest, one may first average Eq. (5) over a unit cell of the vortex lattice and then argue as above to retrieve Eq. (2) and $\alpha=\beta T$. I emphasize that since Maki's argument is logically inconsistent, the present argument is the only existing justification of Eq. (2). In order to further establish the validity of this equation for $B\simeq H_{c2}$, I apply it below to calculate S_D for a gapless superconductor with arbitrary amount of magnetic and nonmagnetic impurities. For the same system we have previously calculated the flux-flow resistivity for both the high- and the low-field limits.[10] We therefore follow closely the notations introduced there. The method for calculating S_D^0 near H_{c2} follows closely the work of Houghton and Maki[11] and therefore requires no detailed description. I only remark that (i) only the fluctuation diagrams contribute in the vector gauge, (ii) contributions from the anomalous frequency regime[6] are found to be important except in the dirty limit. The result is

$$\frac{\phi_0}{T}M=-\frac{4\pi^2\sigma}{e^2}\frac{\langle|\Delta|^2\rangle}{(4\pi T)^2}L_M(T),\quad S_D=\frac{4\pi^2\sigma}{e^2}\frac{\langle|\Delta|^2\rangle}{(4\pi T)^2}L_S(T)\,, \tag{7}$$

$$L_M(T)=\frac{\rho_1}{(\rho_1-\rho_s)^2}\left[\psi(\tfrac{1}{2}+\rho_s)-\psi(\tfrac{1}{2}+\rho_1)\right]+\frac{\rho_1}{\rho_1-\rho_s}\psi^{(1)}(\tfrac{1}{2}+\rho_s)\,, \tag{8}$$

$$L_S(T)=\left(1+\frac{\rho_1\rho_s}{(\rho_1-\rho_s)^2}\right)\psi^{(1)}(\tfrac{1}{2}+\rho_s)-\frac{\rho_1\rho_s}{(\rho_1-\rho_s)^2}\psi^{(1)}(\tfrac{1}{2}+\rho_1)+\frac{\rho_1\rho_s}{\rho_1-\rho_s}\psi^{(2)}(\tfrac{1}{2}+\rho_s)\,, \tag{9}$$

$$\frac{\langle|\Delta|^2\rangle}{(4\pi T)^2}=-\frac{\ln(T_c/T)+\psi(\frac{1}{2}+\rho_sT/T_c)-\psi(\frac{1}{2}+\rho_s)}{\psi^{(2)}(\frac{1}{2}+\rho_s)+\frac{1}{3}\rho_s\psi^{(3)}(\frac{1}{2}+\rho_s)}\,\frac{2\kappa^2}{1.16(2\kappa^2-1)+1}\left(1-\frac{B}{H_{c2}}\right)\,, \tag{10}$$

and $\rho_s=(2\pi\tau_sT)^{-1}$, $\rho_1=(4\pi\tau_1T)^{-1}$ with τ_1 and τ_s being the total- and exchange-scattering lifetimes, respectively. In the dirty limit when $\rho_1\gg\rho_s$ and 1, this result agrees with that of Baba and Maki,[12] but the result is more interesting when the ratio τ_1/τ_s is left arbitrary: Taking the limit $\rho_1,\rho_s\to\infty$, corresponding to high concentrations of magnetic impurities, so that absolute zero temperature falls into the gapless region, Eq. (9) becomes $L_s=(1/6\rho_s^3)(1+2\tau_1/\tau_s+2\tau_1^2/\tau_s^2)\propto T^3$, so that again $S_D\propto T$, but this time a rather nontrivial cancellation of T^{-1} divergences between S_D^0 and ϕ_0M/T happens for *arbitrary* values of τ_1/τ_s. This is clearly a strong support for Eq. (2) as a correct prescription near H_{c2}. Less directly it is also a confidence vote to our new linear transport analysis for magnetic conductors.

Next we note that if Eq. (4) is substituted into the first part of Eq. (5), we obtain

$$\vec{j}^h=\vec{j}_0^h+\vec{\mathcal{E}}\times\vec{m}\,. \tag{11}$$

Since both $\vec{\mathcal{E}}$ and $\vec{m}$ become space dependent for fields well below H_{c2}, we expect $\langle\vec{\mathcal{E}}\times\vec{m}\rangle\neq\langle\vec{\mathcal{E}}\rangle\times\vec{M}$, and therefore Eq. (11) is no longer equivalent to Eq. (2). This is indeed verified by an extension of the above calculation to the low-field limit $B\simeq 0$[13]: First an expression for $\vec{j}_0^h$ in terms of f, $\vec{Q}$, u_1, ψ_6, and ϕ is derived using the same method previously used[10] to derive a complete set of dynamic equations for the same system. The part of $\langle\vec{j}_0^h\rangle$ which makes S_D^0 divergent at low T is then identified and shown *exactly* cancelled by the $\langle\vec{\mathcal{E}}\times\vec{m}\rangle$ term, where $m\equiv(4\pi)^{-1}(b-H_{c1})$. Since even at equilibrium there is no exact solution for an isolated vortex line, the cancellation is achieved by repeatedly transforming one expression using the dynamic equations derived previously,[10] until it becomes exactly the negative of the other expression. As a result of this cancellation we find again $S_D\propto T$ at low temperatures for all values of τ_1/τ_s. This finding leaves essentially no further ground for doubting that Eq. (11) is the correct heat-current expression for magnetic conductors. The details of this calculation will be reported elsewhere.

Let us now return to the definition of $\vec{m}$ for a transport situation. First we note that Eqs. (2) and (11) require only the equilibrium $\vec{m}$ for the purpose of calculating *linear* heat-current responses. But if one wishes to eliminate $\vec{m}$ from our dissipation function w of Eq. (5), then one needs an expression for $\vec{m}$ that is valid to first order in the affinities. The clue is already contained in Eq. (6b), which says that indeed $\vec{\nabla}\times\vec{m}=\vec{j}-\vec{j}_t$, if only one identifies $\vec{j}_t$ as

$$\left(\overleftrightarrow{L}_{21}-(\mu/e)\overleftrightarrow{L}_{22}+\sum_i m_i\overleftrightarrow{L}_{23}^i\right)\cdot\vec{X}_T+\overleftrightarrow{L}_{22}\cdot\vec{\mathcal{E}}\,.$$

Then w may also be written as

$$w=\vec{j}^h\cdot\vec{X}_T+\vec{j}_t\cdot\vec{\mathcal{E}}\,, \tag{12}$$

which should be compared with the usual expression for nonmagnetic conductors, which is just Eq. (12) with $\vec{j}_t$ replaced by $\vec{j}$. Equation (12) has the appealing feature that only transport current dissipates, although in so far as the *total* dissipation is concerned, the two expressions differ in a steady state only by a surface integral $\int_{\partial V} \vec{m} \times \vec{\mathcal{E}} \cdot d^2\vec{S}$, which usually vanishes. It would be very interesting if an actual case could be found where the two expressions could predict different total dissipations, but this possibility has not yet been fully explored at the present time.

In conclusion, the following remarks are in order: (i) So far, $\vec{m}$ is defined only up to an arbitrary gradient term if only it vanishes outside the sample, but this ambiguity can likely be settled by the reasonable requirement that $\vec{\nabla} \times \vec{j}^h = 0$, since circular flow of heat apparently violates the second law of thermodynamics. (ii) While Maki's derivation of $\vec{j}_M$ relies heavily on a *uniform* flux flow, our Eq. (4) for $\vec{j}_{b_t}$ is valid even for a static $\vec{m}$. *Thus the heat-current expression and the new contributions to α and β predicted here should also apply to normal magnetic metals and plasmas in a magnetic field.* (iii) The explicit demonstration of $\alpha = \beta T$ for $B \ll H_{c2}$ remains to be done. But from the above discussion it should be clear that to calculate β correctly in this limit, one must include the effect of the affinities $\vec{X}_{m_t} = m_t \vec{X}_T$ and realize that $\langle m_t \vec{X}_T \rangle \neq M_t \langle \vec{X}_T \rangle$. Thus it is necessary to find the local temperature distribution around an isolated vortex line.

The author wishes to thank K. Maki for a careful reading of the manuscript and for several useful comments.

*Work supported in part by the National Science Foundation.

[1] F. Vidal, Phys. Rev. B 8, 1982 (1975), particularly see Ref. 5 therein.

[2] H. Takayama and H. Ebisawa, Prog. Theor. Phys. 44, 1450 (1970). See, in particular, the discussion section of this article.

[3] K. Maki, Phys. Rev. Lett. 21, 1755 (1968); J. Low Temp. Phys. 1, 45 (1969).

[4] C. Caroli and M. Cyrot, Phys. Kondens. Mater. 4, 285 (1965).

[5] C. Caroli and K. Maki, Phys. Rev. 164, 591 (1967).

[6] R. S. Thompson, Phys. Rev. B 1, 327 (1970).

[7] See, for example, P. M. Morse, *Thermal Physics* (Benjamin, New York, 1969), Eq. (6-5); or H. B. Callen, *Thermodynamics* (Wiley, New York, 1960), Eq. (14.19).

[8] See L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Addison-Wesley, Reading, Mass., 1960), pp. 113 and 114. Note that its Eq. (27.5) may be applied to simply connected metals in the absence of transport currents.

[9] J. M. Luttinger [Phys. Rev. 135, A1505 (1964)] mistakenly identified ϵ as the ensemble average of the total Hamiltonian density $\langle h_T \rangle$, and obtained a continuity equation $\partial\epsilon/\partial t + \vec{\nabla} \cdot \vec{j}^{ET} = \rho\, \partial\phi/\partial t$, which has an undesired source term. The total energy current $\vec{j}^{ET}$ obtained in this way should not be used in the definition for $\vec{j}^h$, as may be seen already from the gauge-invariance requirement on $\vec{j}^E$ and $\vec{j}^h$. Aside from this point, however, this work of his and a sequel to it [Phys. Rev. 136, A1481 (1964)] have served as a very useful guide to our present analysis.

[10] C.-R. Hu and R. S. Thompson, Phys. Rev. Lett. 31, 217 (1973). We note some misprints in this article: In Eq. (3), C_1 should be C_2. In Eq. (20), $2\kappa^2 - 2$ should be $2\kappa^2 - 1$. In Ref. 6, Kapnin should be Kopnin.

[11] A. Houghton and K. Maki, Phys. Rev. B 3, 1625 (1971).

[12] Y. Baba and K. Maki, Prog. Theor. Phys. 44, 1431 (1970).

[13] There are two attempts to calculate S_D for $B \ll H_{c2}$ previous to this work, but both of them considered only the part S_D^0: O. L. de Lange [J. Phys. F 4, 1222 (1974)] studied the limit $\rho_s \to 0$ of the system studied here, and used a thermodynamic argument to find $\vec{j}_0^h$, which is generally incorrect since it can not take into account the anomalous contributions. N. B. Kopnin [Zh. Eksp. Teor. Fiz. 69, 364 (1975)] considered dirty superconductors with no magnetic impurities. Both of these calculations are restricted to the vicinity of T_c and can not be checked of their consistency with the third law of thermodynamics.