Criticism of Onsager's reciprocal relations

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Abstract —
Onsager's second kind of "reciprocal relations" state that $\sigma(\vec{H}) = \sigma^T(-\vec{H})$ where σ is the 3×3 conductance matrix, $\vec{H}$ is an externally applied magnetic field, and T means matrix transpose. This is only supposed to hold for "linear" materials for which the current density $\vec{J}$ is related to the electric field $\vec{E}$ by $\langle\vec{J}\rangle = \sigma\vec{E}$. This is just one instance of a class of mathematically equivalent but physically different relations; e.g. the same relation is supposed to hold if σ is thermal conductivity and $\vec{H}$ is angular velocity for a rotating system. We demonstrate by two counterexamples that this relation (and its isomorphs) can be dramatically false. We also have counterexamples to the Onsager relations of the first kind (which are the special case $\vec{H} = \vec{0}$). There are two flaws in Onsager's reasoning and each counterexample exploits one of them. Both flaws had already been thought of but I feel that they are insufficiently appreciated.

If we instead define σ to be the 3×3 *differential conductance* (Jacobian) matrix $\sigma = \mathrm{d}\langle\vec{J}\rangle/\mathrm{d}\vec{E}$, then $\sigma_D(\vec{H}, \vec{E}) = \sigma_L(\vec{H}, \vec{E})$ where σ_D is for the original material, but σ_L is for a "reversed" material in which all spins and angular momenta (and consequently all magnetic dipoles), and the chirality (by a central inversion of 3-space) are reversed. In the limit $|\vec{E}| \to 0$ (the "zero voltage limit") $\sigma_D(\vec{H}) = \sigma_U^T(-\vec{H})$ where σ_U is for a "spin-reversed" material. Note that the U (or L) and D materials could be inequivalent – in which case Onsager's relation is not about one, but actually about two, materials, and hence is less useful.

Apparently there have been zero intentional experimental tests (so far) of any Onsager relation in a material inequivalent to its reversal; but I will argue that a 1996 experiment by Solin, Thio, et al. quite likely disproved Onsager's relations of the second kind.

Keywords — Onsager relation, galvanomagnetic effects, magnetoresistance, non-ohmic resistors, nonlinear electrical materials, chirality, errors in textbooks.

1 Introduction

1.1 The Onsager relations

Lars Onsager (1903-1976) discovered his "reciprocal relations" in 1931 [30]. Since then they have been rederived in many textbooks [1] [20] [22] [31] [32] [33] [47] and used in probably 100 papers. They have been said ([33] p.599) to "form the basis for the entire discipline of macroscopic irreversible thermodynamics." Onsager was awarded the 1968 Nobel prize in chemistry, solely for [30].

There are two types of Onsager relations. The first type ("Onsager$_1$") is typified by

$$\sigma = \sigma^T \tag{1}$$

where σ (defined by EQ 3) is the 3×3 conductance matrix for a "linear" electrical material and T means matrix transpose. In other words, σ is a symmetric matrix; Pathria ([31] p.480; also [20]) argues that indeed it must also be positive definite. This relation arises from considerations of time reversal $t \to -t$ invariance (among other things).

The second type ("Onsager$_2$") is exemplified by

$$\sigma(\vec{H}) = \sigma^T(-\vec{H}) \tag{2}$$

where $\vec{H}$ is an externally applied magnetic field. EQ (1) is the special case of EQ (2) arising when $\vec{H} = \vec{0}$. Note, σ can depend on composition, position, temperature, pressure, and on $\vec{H}$. Onsager's derivation had considered simultaneous time *and* $\vec{H}$ reversal.

It has been said the Onsager relations are a "general consequence of non-equilibrium thermodynamics," while Ashcroft & Mermin [1] view it as following from "the properties of the semiclassical equations of motion."

However, it is quite feasible to argue that those claims are both false. We shall construct two counterexample "gedanken-materials" which violate EQ (2), and a third violating EQ (1). The Onsager relations have also been called "the fourth law of thermodynamics" – a view which now also seems unjustified (§1.2).

Prigogine ([32] p.46) went so far as to call the Onsager$_1$ relation a "theorem," but most authors are not willing to go that far, including myself, Onsager, and Wannier ([47] p.502 top). Callen [9] and Birss [2], went even further by calling Onsager$_2$ a "theorem." In Callen's view (which is also Pathria's [31] view, except that Pathria does not use the word "theorem"), Onsager$_2$ must hold under the following three assumptions:

1. The material is linear, i.e. satisfies EQ (3). (This assumption seems necessary in order even to *define* σ or to *state* EQ (2). However, see below where we give a different definition allowing nonlinear materials.)

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2. The material is "near to thermal equilibrium" or equivalently near maximum entropy [31][1].

3. The laws of physics are invariant[2] under $t \to -t$, $\vec{H} \to -\vec{H}$, and reversal of all particle momenta.

But the counterexamples we shall exhibit do obey these three assumptions.

1.2 It's not thermodynamics

For a statement to be a "thermodynamical law," it should hold almost independently of what the laws of physics are and without need for careful examination of the precise microscopic physical scenario – as indeed (see Callen's 3 conditions at the end of §1.1) Onsager's relations were previously thought [9] to do. In my opinion it was the perception of this universal applicability which led to Onsager's Nobel prize. But on the contrary, we shall see that Onsager's relations are *not* thermodynamical since the question of whether they are applicable in a given material can only be decided after microscopic examination of every atom inside them – and even then the answer probably won't be apparent to those of us with limited computational resources.

And this is not merely a theorist's objection – as we shall see in §3.2, real materials appear to violate Onsager's relations.

1.3 More detailed look

Are Onsager's relations damaged beyond repair, or are they still true – one just has to be careful about how one applies them? Both views have merit.

First, it seems to be *wrong* to define σ (as in [47] EQ 23.52, [31] EQ 13.8(1), [20], etc.) by

$$\langle \vec{J} \rangle = \sigma \vec{E} \tag{3}$$

where the $\langle\rangle$ brackets denote thermal and time averaging. It is better to define σ to be the 3×3 *differential conductance* (Jacobian) matrix

$$\sigma = \frac{\mathrm{d}\langle \vec{J} \rangle}{\mathrm{d}\vec{E}}, \tag{4}$$

allowing arbitrary, possibly nonlinear, functional dependence (provided it is differentiable with nonsingular Jacobian) of $\langle \vec{J} \rangle$ on $\vec{E}$.

Onsager's relations appear to be valid *only* in the limit $|\vec{E}| \to 0$ in which the old and new definitions coincide (call this the "zero voltage limit") or in a chirally altered form (EQ 5) and only for the diagonal 3 elements of σ.

For nonlinear materials and nonzero voltages, I claim

$$\sigma_L(\vec{H}, \vec{E}) \ = \ \sigma_D(\vec{H}, \vec{E}) \tag{5}$$

where the L and D subscripts are for two chirally reversed (laevo and dextro; this chiral reversal is accomplished by a central inversion of 3-space, i.e. negation of x, y, z) and spin-reversed versions of the material. Notice that the diagonal elements of σ are unaffected by $\sigma \to \sigma^T$ (and the $\vec{H}$ and $\vec{E}$ fields are reversed by the central inversion of 3-space) hence this is an Onsagerian relation, *but* with a chirality switch and where equality is claimed only for the *diagonal* 3 entries of the 3×3 conductance matrix. EQ (5) is then just a consequence of the "parity invariance" of the relevant underlying physics. Our counterexample of §3 involves a chiral gedanken material disobeying EQ (2) if σ is defined by EQ (3). However, it obeys EQ (2) if σ is defined by "EQ (4) in the limit $|\vec{E}| \to 0$" (§3.3), and it obeys EQ (5). In the counterexample, EQ (3) holds, to within additive error $\pm\epsilon$, for all electric fields $\vec{E}$ obeying $|\vec{E}| < E_{\max}$ (for some large maximum allowed strength $E_{\max}$), where $\epsilon \to 0$ as the ratio of the macroscopic length scale to the microscopic one goes to ∞. This happens at any particular applied magnetic field $\vec{H}$ with $|\vec{H}| < H_{\max}$ (for some large maximum allowed strength $H_{\max}$), but within this $\vec{H}$-set, σ does *not* depend centro-symmetrically on $\vec{H}$, disobeying EQ (2).

Because real experiments are not, and cannot be, conducted in the zero voltage limit, EQ (2) can appear to be violated – and indeed there is reason to believe that such violations will always happen for *chiral* materials. In §3.2 we discuss an experiment by Solin, Thio, et al., in which just such a phenomenon was observed.

Our other counterexample (§2) to EQ (2) takes advantage of the fact that Onsager overlooked (cf. §1.6) that internal magnetic fields (and hence internal spins) *also* need to be reversed. The first to realize this flaw may have been M.Lax in the 1960's (cf. §6). The more correct, repaired way to state Onsager's EQ (2) is

$$\sigma_D(\vec{H}) = \sigma_U^T(-\vec{H}) \tag{6}$$

where the U is for a "spin-reversed" material in which all spins and angular momenta (and consequently all magnetic dipoles), and particle momenta are reversed[3].

[1] The merely qualitative nature of this "nearness" is a sore point. For example, consider sugar water. Most physicists up to now would have said it obeys Onsager's relations. (But sugar is chiral – see §3.) But clearly sugar water is not a maximum entropy state, a fact taken advantage of by yeast when converting the sugar into alcohol and CO_2. But even then we won't have maximum entropy, as we can see by considering various nuclear fusion reactions. Presumably these considerations are irrelevant, but no precise criterion for such irrelevance has ever been written.

[2] After Onsager and Callen, it was discovered that some laws of physics aren't time reversal invariant, e.g. certain kaon decay processes. The "final theory" of physics is thought to be CPT-invariant but not invariant under any subset of C, P, and T. But this quibble is irrelevant in all the situations Onsager's relations have been applied so far, since, e.g., the Maxwell-Lorentz equations are invariant under C,P, and T individually (if the fields are reinterpreted by appropriately changing their signs). It could be relevant in some future attempt to apply Onsager relations to the early universe. If the wording is changed to "the *relevant* laws of physics..." then this quibble is nullified.
For our purposes, it is more important to note that this reckoning neglected to mention that all angular momenta and spins *also* need to be reversed. This unfortunately is not what the Onsager derivation wanted and can also be viewed as its logical flaw.

[3] It has been suggested that Onsager *meant* by reversing $\vec{H}$, that spins also must be reversed. (The letter H is often used to denote the sum of externally generated and magnetization-generated fields.)

Our counterexample involves a material whose "reversed" version plainly is not equivalent[4] to the original one. It seems almost impossible to tell a priori whether such equivalence is going to happen and hence whether the more-usual form EQ (2) of Onsager's relations are applicable.

1.4 The flaws in Onsager's reasoning

There were two flaws in Onsager's reasoning, and each of our counterexamples exploits one of them.

Flaw #1, which became most clear for me after reading Pathria's discussion [31], involves Onsager's need to assume that the material is "close to thermodynamic equilibrium" (so that its entropy is near maximal and can be expanded as a certain Taylor series). *But* it is *not* necessarily the case that the probability distribution of states constituting "thermal equilibrium" with upward applied $\vec{H}$-field, is necessarily the same as the probability distribution of states constituting thermal equilibrium in a downward (i.e. negated) applied $\vec{H}$-field. In general, those two probability distributions will differ because each state will have different energies in the two fields, and/or the states themselves will differ. Hence the thermal state-occupation probabilities will differ. Hence simultaneous nearness to *both* thermal equilibria is *impossible.* In section 2 we will design a gedanken-material in which this effect does happen and is maximally dramatic.

Flaw #2, which had been pointed out earlier in Lax's careful treatment [22], involves Onsager's need to assume that the material is "linear," i.e. that EQ (3) holds. (Note well: Onsager's argument did *not* need to make any assumptions about linear dependence, nor about any other kind of dependence – not even continuity or differentiability is needed – of anything on $\vec{H}$.) Although EQ (3) is undoubtably macroscopically valid in a large and useful class of materials, it is *never* valid from the point of view of a single charge carrier at time scales smaller than the typical time between collisions/scatterings of the elementary charge-carriers inside the material. Indeed the very notion of σ is then not defined[5]. At such short time scales, charge carriers can behave, e.g., ballistically. For ballistic charge carriers, such as non-interacting electrons in vacuum, currents simply are not describable by a linear relation EQ (3), nor indeed by any functional relation at all. (E.g., the current would increase linearly with time in a constant applied electric field, since the electrons would accelerate.) It is possible to design materials with microstructure at size scales comparable to charge-carrier mean free paths, which maximally exploit this effect to violate EQ (2). That will be done in section 3.

I will not rederive the Onsager relations in this paper, since there are many such derivations available in the references, and since the flaws (and their corrections) are a relatively small part of them. Our counterexamples are verifiable without any knowledge about how Onsager relations were derived. None of my counterexamples to EQ (2) are counterexamples to EQ (5), or to EQ (6) with σ defined by EQ (4) in the limit $|\vec{E}| \to 0$.

It is these new relations which truly appear to follow from all the Onsager derivations in the references. Notice that the reversed material is *not* necessarily equivalent to the original one (§2) so EQ (6) in general relates the conductance matrices of *two different* materials, not one. (Similarly EQ 5 relates σ for two different materials.) Hence, unfortunately, the new corrected relations are comparatively useless[6].

Fortunately, most *simple* materials are equivalent to their reversals; for them the original Onsager relations are justified provided we define σ by EQ (4) in the limit $|\vec{E}| \to 0$.

My guesses about which real materials seem likeliest to most-violate EQ (2), are listed in section 4.

Notice, also, that the form of the corrected relation suggests that even the type-1 special case EQ (1) of EQ (2) might be false. Indeed, it is false: either of the two counterexamples to EQ (2) may be used as building blocks to construct counterexamples to EQ (1). I'll do that in §7.

1.5 Impact

The impact of this on Onsager's reputation and on non-equilibrium thermodynamics is not as severe as one might worry from the plaudits in §1.1. Nevertheless, papers are still being produced up to the present day which depend integrally on Onsager relations, and hence whose conclusions may be false. Specifically, Baker and Heremans [3]'s abstract states: "This work reports theorems on.. geometrical magnetoresistance... in [2D or 3D]. We... assume that the current/voltage relations are linear. It is shown that the resistance of any two-wire device must be an even function of the [applied] magnetic field." This is false, as both our counterexamples demonstrate. I believe that the fault lies not in Baker and Heremans's reasoning itself (that seems valid), but merely in their unskeptical acceptance of Onsager$_2$. The "theorem" of [3] unfortunately must be regarded as a non-theorem, or if it is a theorem, then it is one

However this suggestion contradicts [9] "Onsager's theorem states that $L_{ij}(H) = L_{ji}(-H)$ where H is the *applied* magnetic field (or Coriolis field). If no magnetic field is *applied* then $L_{ij} = L_{ji}$." (My italics.) Also: saying a sum is negated is not the same as saying the summands are, and H is generally used to denote a macroscopically smoothed field combination anyhow, whereas for this interpretation to hold water it would have to denote the microscopic unsmoothed field. On the other hand if we agree with this interpretation, then we have to admit it is experimentally useless, since $\vec{H}$ would then not be experimentally accessible. Also, the spin reversed material need not be equivalent to the original material so the relation would then concern two inequivalent materials just as does EQ (6).

[4] See §6.1 for what "inequivalent" means.

[5] Indeed, it is a little schizophrenic to, on the one hand, pretend σ is a function of position defined at single points because doing so often is mathematically convenient, while on the other hand, we realize that physically, σ is undefined except at large enough length scales. Fortunately, Onsager's arguments were supposed to go through if σ were defined at *any* length scale significantly smaller than the experimenter, so such details had not been thought to be very relevant.

[6] The main uses of Onsager relations are to use the symmetry of σ to cut down on the number of measurements needed to determine σ (or to reduce the noise in those measurements), and to prove theorems that depend on the symmetry of σ. Both these applications are no longer a possibility.

valid only for materials equivalent to their reversals, and is presumably false for most other materials. (See also §3.2.)

1.6 Interpretations

One interpretation of my results is that EQ (2) is simply unjustified; it is almost never going to be exactly true, in almost any[7] real material. Also, the same logical flaws also pertain to the numerous mathematically parallel, but physically totally different, alternate versions of EQ (2). Hence these isomorphs are also unjustified (§5).

Another interpretation is that EQ (2) is perfectly valid, provided we agree that one simply is not allowed to apply it in materials for which logical flaws 1 & 2 pertain. For example, EQ (2) is valid if we agree to apply it only in the zero-voltage limit $|\vec{E}| \to 0$ and only for materials completely free of internal magnetism; or only to materials equivalent to their (chiral and magnetic) "reversals" and only for the diagonal entries of σ.

There presently is no known algorithm for deciding a priori, given an atomic description of a material inequivalent to its reversal, how severe the discrepancy is going to be. In other words, as a *theoretical tool* for application to *general* materials, EQ (2) is entirely useless. As a *practical* tool, though, it might still be quite useful, because empirical experience might at some future point verify that in some class of materials, EQ (2) always seems to hold to considerable accuracy; plus, many simple materials are known to be equivalent to their reversals.

Which of these two interpretations is correct? That is somewhat subjective. Onsager seemed to have awareness of flaw #2, e.g. [30] p. 419 realizes the importance of the nonzero mean free path, but he then says that it "can be neglected in all cases... likely to be studied," which I think is doubtful and unjustified. Onsager's derivation ([30] p. 2278-2279) of EQ (2) seemed to be unaware of flaw #1.

1.7 Experimental status

There have been an extreme paucity of experimental tests of Onsager type-2 relations to date. The type-1 relations EQ (1) seem experimentally well supported[8] both via checks of the symmetry of the thermal conductivity tensor in anisotropic materials, and by osmotic measurements of "cross effects" in simultaneous diffusion of several chemical solutes; *but* I have been unable to find *any* experimental tests of Onsager_1 in chiral materials or materials clearly inequivalent to their spin reversals. None of the books or papers I've referenced, including the 118-page [16], cited any Onsager_2 experiments, nor did numerous other survey papers and books I haven't referenced, nor did Onsager's 1968 Nobel lecture, which one might have expected to have surveyed any such tests that happened during the 37 years after [30].

A computer aided literature search turned up *one* experimental Onsager_2 test [26]. It confirmed EQ (2) for thermal diffusion (actually for the "Dufour effect" – temperature gradient due to diffusion) in an N_2-Ar equimolar gas mixture at room temperature, in the presence of a magnetic field. This confirmation does not affect my faith that EQ (2) is generally incorrect, because the materials involved were achiral.

See §3.2 for discussion of an experiment suggesting Onsager_2 is false.

2 First Counterexample

Figure 1 depicts a 1D array of marbles, each containing a permanent bar magnet, linked by electrically conductive links. The two hemispheres of each marble are made of ohmic materials with different resistivities. The marbles are free to rotate but cannot translate. If you prefer, you can instead consider 2D marble arrays with links now going in 4 directions in a plane; or 3D marble arrays. Also, the permanent magnets could be replaced by superconducting loops (with an insulating coating) in which persistent currents circulate. I say this to make it clear that it does not matter what is going on inside the magnets to make them magnetic – they could also just be some elementary particle with a magnetic dipole moment.

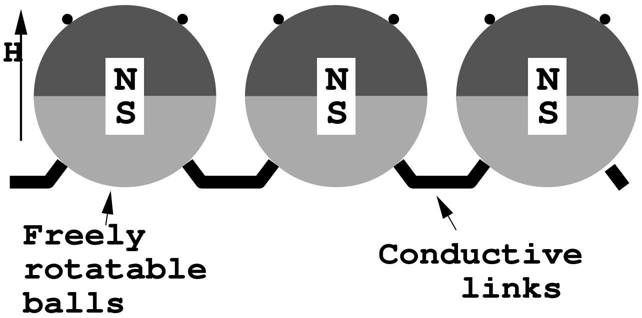

Figure 1: Marbles.

For maximal clarity and drama choose the bar magnets's magnetic moments μ, the strength B of the applied traverse magnetic field (pointing either up or down in the plane of the figure), the temperature T, and the lengths L of the conductive links, so that

$$\mu^2 \mu_0 L^{-3} \ll k_B T \ll \mu B \tag{7}$$

where $k_B \approx 1.38 \times 10^{-23}$Joules/Kelvin is Boltzmann's constant, and $\mu_0 \approx 1.26 \times 10^{-6}$Henry/meter is the permittivity of free space. This causes our material to be a "saturated paramagnet." Finally, assume that the magnetic field is not strong enough to cause "Hall effects" to have any significant effect on resistivities.

Regard the whole array as an artificial "material" and view it from the perspective of somebody much larger than a marble or a link. In that case, in an upward magnetic

[7] "Almost any" in the sense that almost all reasonably complicated molecular structures are chiral and have some magnetism inside them.

[8] Although [7] might have naively seemed – just from reading the title and abstract – to be refuting Onsager_1, they actually are in favor of Onsager_1 and instead are attacking the Kedem-Katchalsky membrane transport model. The story of a different attack on Onsager_1 has been recounted in [42].

field, the marbles will all line up pointing upward (aside from small thermal fluctuations in their angular orientations). In the negated magnetic field, the marbles will orient themselves the other way, and we will get *arbitrarily different* macroscopic conductivity values $\sigma(-\vec{H})$, clearly contradicting EQ (2). By design, this material obeys the linearity condition EQ (3) perfectly.

The fact that this material is a "gedanken material" not actually available at your local chemist's, in no way affects the logical validity of our refutation of EQ (2). There is no reason that effects of this nature could not actually occur (perhaps in a less obvious form) in a genuine material.

Also, this material could, of course, be built from macroscopic marbles. Certain proteins in magnetotactic bacteria are known [5] to be attached to small (40nm diam) oriented crystals of "magnetite" (Fe_3O_4) or "greigite"(Fe_3S_4), which serve as tiny magnetic "compasses." Horse spleen ferritin [13] is another protein attached to small magnetic particles ($\leq$ 8nm diam). (But: these particles, at least in their natural incarnations, are "soft" magnetic materials, not permananet magnets.) Also, arrays of rotatable nanoscale magnets have been made by entirely non-biological methods [17]. Hence, it seems likely that by "genetic engineering" one could make a nanostructured material dramatically disobeying EQ (2). Also, tiny (submicron) plastic balls made of two hemispheres of different-colored plastics with different electrical properties have been made for use in experimental devices for displaying two-color images.

Finally, I believe that Onsager_2 violations are routinely experimentally observed at low temperatures ($\lesssim$ 10Kelvin) in "spin glass" materials. Onsager defenders could argue that these materials might not be "close to thermal equilibrium" (the vagueness inherent in this phrase was always a focal point of worries about Onsager's relation) and hence Onsager's relations were never applicable to them anyway. I agree with that argument, but think it probably is not the full explanation.

3 Second Counterexample

Figure 2 depicts another gedanken-material made of vacuum (white areas) and an ohmic material such as amorphous carbon (gray areas). The vacuum areas form long narrow curved "channels."

Imagine that the temperature is high enough so that thermionic emission from the carbon-vacuum surface is common enough, so that the electrical conductivity of the material is dominated by (or at least, in large part due to) electrons flowing in the vacuum areas.

Now, the channels are shaped in such a way that electrons emitted in a narrow range of angles (pointing along the channel) will travel unimpeded to the opposite end of that channel, *following the curve*, due to the effect of the applied magnetic field. Assuming also the presence of an electric field accelerating these electrons along those channels, very high electron velocities can be reached for arbitrarily long channels, which will enable large currents to be transmitted along the channels despite the narrow angular range in which such long transits are possible.

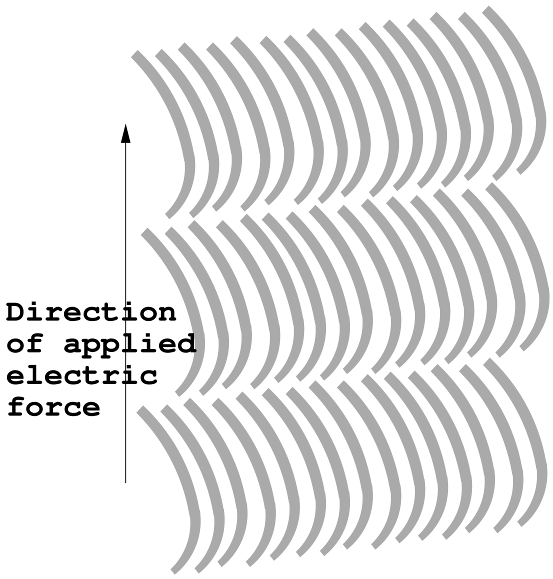

Figure 2: Chiral microstructure.

Such long transits will *only* be possible, though, if the magnetic and electric fields are just the right value. If the magnetic field is of any wrong value (including zero, or even worse of the wrong sign) then no long trajectories are possible and all electrons will be continually "banging their heads against the wall." In this connection, it is important to realize that the curves of the channels are not circular arcs; they instead have curvatures which decrease as the electric potential energy drops (because electrons will have a larger radius of curvature in a constant magnetic field when they move faster). In order to cause $\sigma(\vec{H}) = \sigma^T(-\vec{H})$, it would be nice if an electron following this curve would, were its velocity and the magnetic field and the electric field reversed, retrace its trajectory. But in fact, that won't happen, because the curvature is increasing. Such retracing will only occur if the velocity and magnetic field are reversed and the electric field is *not* reversed. In that case these reversed trajectories would be *unphysical* – electrons deaccelerating from initially far super-thermal speeds – and hence irrelevant as far as conductivity is concerned, hence there is no basis for concluding either $\sigma(\vec{H}, \vec{E}) = \sigma^T(-\vec{H}, -\vec{E})$ or $\sigma(\vec{H}, \vec{E}) = \sigma^T(-\vec{H}, \vec{E})$.

The material will clearly be macroscopically linear EQ (3) if the applied electric field $\vec{E}$ is so weak that $k_B T \ll eE\Lambda$ where Λ is free path length for electrons. (Because: the effect of the accelerating E-field on the trajectories will then be a small perturbation.) However – and I admit this is a bit of a cheat – if we are at precisely the right $\vec{H}$ and $\vec{E}$ values, for electrons moving in precisely the right angular range of directions, Λ will be much longer than usual. Hence, our material will look like a linear resistive material normally, except that at a particular $\vec{H}$ and for a particular current direction and strength, our resistor will act as though it is in parallel with a *nonlinear* resistor shunting some of the current[9].

By controlling the lengths, widths, and shapes of the channels and the resistivity and surface emissivity (both as functions of position) of the "carbon," it is clearly possible in principle to get a macroscopic unidirectional resistance (viewed from the perspective of somebody much larger in size than a channel) which is minimized at (or at least, has a "blip" at) a particular *nonzero* value of the applied magnetic field, and *not* at its negation, again clearly violating EQ (2), probably arbitrarily severely.

3.1 Linearity can be faked

At this point the reader is free to object that, since the I-V curve (for current I flowing in the magic direction) will have a "blip" at a particular magic value of $\vec{H}$ and the voltage V (solid curve in figure 3), the material cannot truly be claimed to be "linear" (despite its linearity in every other direction, $\vec{H}$, and voltage combination) and hence I cannot truly claim to have violated Onsager$_2$.

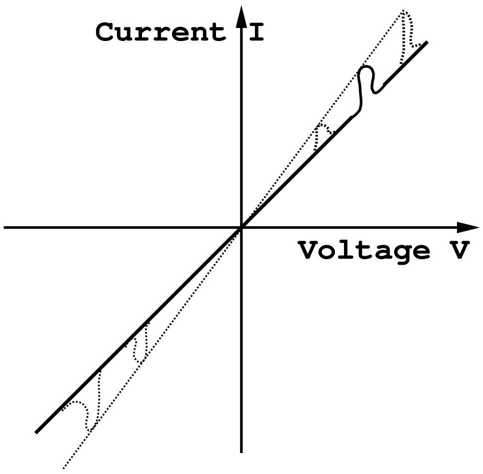

Figure 3: Trick to make exactly linear I-V curve.

But it is possible to overcome that objection and make the I-V curve, even in the magic direction, exactly linear at all sufficiently large length scales. The trick is to put in channels of different shapes, acting as resistors in parallel or in series (we can freely choose which). Each channel contributes a blip in the I-V curve at its own individual magic V. By choosing the proportions of the different channels correctly, we can make the sum of all the blips be a blip-free straight line (at least out to some high voltage, higher than we ever plan to encounter – after all, all materials are non-ohmic at *very* high voltages). This is shown dashed in figure 3[10].

All these channels will be designed to function only at a single common magic $\vec{H}$ value, so the resistance still will exhibit a blip only at that $\vec{H}$.

In this example, it is not necessary that the "vacuum" actually be vacuum. It could be any material with a large electron mean free path (comparable to the channel length); meanwhile electrons in the "carbon" have a very short mean free path.

If the "vacuum" is actually a metal, then I suspect this counterexample will not work very well because the electron energies due to acceleration in the applied electric field, will tend to be much smaller than the "Fermi energies" they have anyway. I would expect the counterexample to work much better if the "vacuum" is a semiconductor with non-negative "gap;" in that case occupancy of Fermi "sea" states will be very sparse and drift velocities will be much larger in comparison to the thermal velocities they perturb.

Other geometries are possible; for example the channels could be shaped roughly like helices with axis in the electric field direction (which now also will be the magnetic field direction).

I remark that magnetoresistance coefficients in resistors made of such a composite material seem capable of being arbitrarily vastly higher than the so-called "Corbino limit" in either component material. Solin, Thio et al. [40] had earlier shown experimentally that it was possible to exceed the Corbino limit, but they did not exceed it by nearly as large a factor as it should be possible in principle to exceed it by.

3.2 A material investigated by Solin, Thio, et al

In this section, I am going to argue that it is plausible that semiconductive films that have already been experimentally investigated by Solin, Thio, et al., [39][40][41] violate Onsager$_2$ via a mechanism of action similar in spirit to the counterexample just described in §3.

Quick summary: Their films exhibited apparently Ohmic resistance which depended on the applied magnetic field in a manner clearly disobeying EQ (2).

I will now treat the Solin-Thio experiment in much greater detail. It will be necessary for me to critique [39][40][41] fairly extensively, since (1) those papers contain errors and misleading statements, as well as good discoveries, and (2) their experimental investigations were aimed at answering different questions than the one we are interested in. I think the evidence is fairly convincing, but future investigations of the same nature, but directed specifically to answering the Onsager$_2$ question, should (if undertaken) yield a conclusion with considerably more confidence attached to it[11].

The Solin-Thio materials are non-magnetic, undoped, unannealed, "dirty," zero-gap semiconductors of composi-

[9] Incidentally, any fears that the trajectory curvature induced by the magnetic field will be nullified by the buildup of "countercharges," may be eliminated by making the "carbon" be extremely conductive (anisotropically) in the direction perpendicular to the channels and by macroscopically shaping the material as an annular "Corbino" geometry [21]. Indeed by choosing the resistivity matrix as a function of position in the "carbon," one has enough control to "sculpt" the steady state charge distribution and electric field inside the material to be most anything one wants.

[10] Even then, although the resistance would be exactly ohmic in any particular direction, the conductance still would not be linear, at the critical $\vec{H}$, in the matrix sense of EQ (3). (EQ 3 implies, but is not implied by, Ohm's law.) But even this objection can be overcome with additional blip superposition tricks of the same nature, but now in different directions rather than at different voltages.

[11] Solin, Thio, and Hines told me they plan a future investigation of intentionally created "chiral spiral" inhomogeneities.

tion $Hg_{1-x}Cd_xTe$ with $x = .10 \pm .015$. The main discovery of [39] was that annular-shaped samples of films of this material can exhibit magnetoresistive "bias." (The diameter of the annulus was $\approx$ 1cm, the film thickness was $\approx$ 5 microns on top of an intrinsic Si substrate, and its room temperature resistance was $\approx 5\Omega$.)

That is, in an applied magnetic field $\vec{H}$ perpendicular to the plane of the annulus, the graph of the resistance as a function of $\vec{H}$ was roughly parabolic with a minimum at $H_0 \neq 0$. This bias was believed by Solin and Thio to have something to do with microstructural inhomogeneities in the material (as in our §3). They confirmed that hypothesis [39] experimentally by intentionally scratching a sample and finding this increased H_0 by a factor of ≈ 2.

The free path length Λ_e for electrons is estimable from the measured [34][41] electron mobility $\mu_e \approx 3\,\text{meter}^2\text{volt}^{-1}\text{sec}^{-1}$ by assuming Maxwell-Boltzmann statistics [1]: $\Lambda_e \approx 2(\mu_e/q_e)\sqrt{3k_BTm_e}$, which in this case yields $\Lambda_e \approx 4$ microns (the hole mobility and estimated path length are almost 200 times smaller and hence of no great relevance as far as the conductivity is concerned). There is reason to believe [15][10] that the "effective mass" of each electron was only (0.01-0.02)m_e, though, in which case we would get $\Lambda_e = .4$-$.6$ microns. (Presumably the effective mass is the correct one to use for this purpose, but either way, the same conclusions follow.) These length scale estimates seem compatible with my idea that ballistic effects caused by inhomogeneities smaller than the free path caused an Onsager_2 violation (e.g. microscopy showed the inhomogeneities of [35][36] had diameters 100-400nm and were separated by 1-3 microns; Solin & Thio [39] estimated indirectly that their inhomogeneities had sizes somewhere between 31 and 218nm, but [15] any such inhomogeneities were invisible using optical and some types of electron microscopy.).

Due to [3], the nonzero bias immediately proves Onsager_2 must have been violated, *except* for various considerations (labeled A,B,C,D) which we'll now discuss.

A. There is the question of whether this bias actually existed at all. By itself, [39] is unconvincing to a skeptical reader. This is because each parabola in the graph ([39] fig. 1) of resistance versus $\vec{H}$ clearly exhibits hysteresis of magnitude about 1% (vertically). (1) The authors claimed [39] this was "due to induction; it becomes smaller as the sweep rate is lowered." But with a properly designed sample and leads (which they may or may not have had), induction should have been impossible due to symmetry. (2) Thio [15] told me this hysteresis was actually due to "lag in the magnetometer." (3) One can also speculate that it was due to genuine hysteresis in the sample itself (e.g. due to lag in re-adjusting to thermal equilibrium in the magnetic field as it swept[12]), or finally that (4) it was due to stray magnetic hysteretic materials nearby. No attempt was made to determine which of these 4 hypotheses was correct, nor to calibrate out and correct for known biases of form (1), (2), or (4). Since a horizontal shift of the parabolas by their $H_0 \approx .014$ Tesla would have resulted in approximately the same vertical shift as was due to the hysteresis, it remained plausible that H_0 was actually 0 and all results of [39] were illusory[13]. Fortunately, according to Thio [15], other samples have since been measured with much larger $H_0 = .16$ Tesla. The remanent magnetic field in her chamber is $\approx .002$ Tesla, by contrast. In combination with the factor-2 change in H_0 caused by scratching, this seems convincing.

B. Onsager's relations are only supposed to hold for *linear* materials, i.e. those obeying EQ (3). Hence we may regard this as a violation of Onsager_2 only if this material is known to be linear. But: comprehensive experiments addressing the question of whether this material is ohmic, have not yet been made. Nevertheless, I believe the material *was* ohmic, for reasons I'll now explain.

An incomplete set of measurements were made, which support ohmicity (both of the material and interfaces to the contacts): [40] page 5-6; [44] p. 12240; and also [15] "the four-probe I-V characteristic is quite linear" up to 10milliamps, which exceeds the maximum current used in their resistance measurements.

Solin had speculated to me their material might not be ohmic and hence that the bias might have nothing to do with a violation of Onsager_2, instead being somehow caused by nonlinear effects involving "Schottky diodes." But I believe this hypothesis can be ruled out by two different arguments. First, recall "Schottky's diode equation" [43] relating the current I to the voltage V across an (idealized) PN or Schottky diode:

$$I = \left[\exp(\frac{qV}{k_BT}) - 1\right] I_0 \tag{8}$$

where I_0 is a constant, T is temperature, k_B is Boltzmann's constant, and q is the magnitude of a charge. Notice that this I-V relation becomes *linear* to better and better approximation for small $|V|$, or small $|I|$, or large T. (If $|V| \ll k_BT/q$, we will be in the linear regime; with $q = q_e \approx 1.6 \times 10^{-19}$Coulomb, i.e. one elementary charge, and $T = 300$ Kelvin, we have $k_BT/q = .026$ Volts.) Hence, if Solin's hypothesis were true, we would expect $|H_0|$ to decrease toward 0 for resistance measurements made at constant voltage as T is increased[14]. But in fact (figs. 2 and 3 of [39]) as T was increased, H_0 *increased* and by sample-dependent amounts. This finding is incompatible with any Schottky diode hypothesis, but is not incompatible with a geometry based hypothesis such as in our own §3.

A different datum incompatible with the hypothesis of small Schottky diodes causing nonlinearities at the inhomogeneities is, e.g. the fact that, even for an 10-micron inhomogeneity (much larger than we believe they actually were), assuming 50 millivolts across 1cm of sample (larger

[12] If this hysteresis really exists, that suggests that logical flaw #1 might *also* be active in this material.

[13] Their observation that H_0 "changes sign when the sample is inverted in the magnetic field" has no logical impact since it could be compatible with all 4 hypotheses.

[14] And since, as Thio remarked to me [15], the I-V characteristic was quite linear, the question of whether constant voltage or constant current, or varying, was employed, does not matter much.

than the voltages used), the total voltage across the inhomogeneity would be 5 microvolts. This is *very* much in the linear regime for semiconductive diodes at room temperature. Thio [15] measured the resistance using low frequency AC with maximum current of either 10 or 1 milliamp, she could not recall which. (The papers [39][40][41] gave no indication of the currents and voltages employed.) However, Thio expressed confidence that either way, the results would have been the same and the I-V curve very linear. At 1 milliamp full scale, notice the total voltage across the *entire sample* would have been only 5 millivolts, quite in the linear regime for semiconductor diodes; whereas, at 10 milliamps full scale (50 millivolts), any diode nonlinearities should have been noticed, but weren't ([40] page 5-6). The evidence seems convincing that nonlinearities due to such diodes were not a factor.

C. A conclusion of Onsager$_2$ violation can, strictly speaking, only be drawn from [3] for 2-electrode resistance measurements. But (despite some misleading appearances such as figure 3 in [40]) [40][39] based their work on 4-probe measurements instead [15]. As [39] explains, they used a "4-ring Corbino geometry" ([44], fig.1b) meaning 4 concentric plated-on metal rings (metal electrodes), the innermost and outermost being current sources, and the other two rings attached to a voltage measuring device. The diameters of the rings were of order 1 cm, their widths were of order 1 mm, and the radial gap between the two voltage rings was ≈ 3 mm. The film thickness was ≈ 5 microns. The current was low frequency AC to allow use of a "lock-in amplifier." (For some discussion of such issues of experimental technique, see [21][46][48].) They still have not performed comprehensive 2-probe measurements (although they plan to).

It is likely that 4 probes versus 2 did not actually make any real difference. That is (1) because of the above evidence supporting ohmicity, and (2) because in this geometry, there is no way for material between the two voltage sensor rings, which (being metal) are equipotentials, to "know" about the two current probes. From the point of view of this material, this *is* a 2-probe measurement. The only way in which it isn't, would be if the voltage rings were not equipotentials, or were somehow separated from the film. That seems unlikely. (Visual inspection and intentional pull-off tests [15] showed no metal peel-off.) Hence for practical purposes I cannot see how the fact that the measurement was 4 probes rather than two, could have made a detectable difference.

In some 4-probe geometries it would be possible to mix Hall voltage and resistive voltage (one of which changes in sign when H or the current direction are reversed, the other of which does not) and thus reach an erroneous conclusion of Onsager$_2$ violation. However, the 4-ring geometry is designed to avoid that trap.

Büttiker [8] argued theoretically (and all his claims were confirmed experimentally [6] by measurements on submicron-sized objects made of ultrapure silver and gold at .04 Kelvin) that 4-probe resistance measurements $R_{12,34}$ can exhibit $R_{12,34}(H) \neq R_{12,34}(-H)$, *despite* validity of Onsager's $R_{12}(H) = R_{21}(-H)$ for any 2-probe measurement, *provided* that the measurement length scales are smaller than or comparable to the electron "dephasing length." Even then, Büttiker claimed, the *sum* $R_{12,34} + R_{34,12}$ of two resistance measurements with the current and voltage probes switched, ought to be invariant under negation of H. Büttiker also argued ([8], final paragraph) that, if Onsager's relations held, then it ought to be *impossible* for $R_{12,34}(H) \neq R_{12,34}(-H)$ if "the length of the conductor exceeds the localization [dephasing] length."

At least if we take this Büttiker quote at face value[15], considering the Solin-Thio samples had centimeter length scales whereas the dephasing and collision length scales were microns or less, we would be forced to conclude the Solin-Thio 4-probe measurement did disprove Onsager$_2$.

Suppose we instead disregard this Büttiker quote; can we than believe that Büttiker's phase-coherent 4-point mesoscopic effects somehow managed to affect a macroscopic 4-probe measurement? That belief is undermined by the *increase* in the asymmetry seen by Solin and Thio [39] with increasing temperature. Since the dephasing length decreases (and so does the mobility and the free path [34]) with increasing temperature in the measured range, we would have intuitively expected Büttiker-like effects to decrease as it gets hotter, not increase.

D. A theoretical explanation for $H_0 \neq 0$ was proposed in [39]. One can see immediately that this explanation is invalid. The reason I say that, is that it nowhere involves nonlinear resistivity effects anywhere in it; it goes through purely assuming conventional ohmic resistivities everywhere. And [3] proves that in that case, assuming Onsager$_2$, no matter how the resistivities depend on position, H_0 *must* be zero. The analysis of [39] reached the opposite conclusion (and certainly [15] neither it, nor their cite [14], were intended to be denying Onsager$_2$) and is therefore incorrect.

Actually, though, [39]'s explanation could be correct, provided you deny Onsager$_2$, as I do. In that case [39]'s "V_{Hall}" term resulting from "inhomogeneity geometry" becomes acceptable, [3] becomes invalid, and nonzero H_0 becomes possible and indeed probable.

3.3 Is this counterexample "legitimate?"

The material whose construction was sketched in figures 2 and 3 had a nearly-linear I-V curve, within some fixed range of voltages $-V_{\max} < V < V_{\max}$. Indeed, this curve everywhere lies within ϵ of the perfect line segment, where $\epsilon \to 0$ in the limit as the ratio of macroscopic/microscopic length scales $\to \infty$.

And, sure enough, the slope of this line segment (the conductance) depends on the applied magnetic field H in an asymmetric way, violating EQ (2).

[15] I am unsure that one should, though, since I am unsure whether Büttiker has considered carefully enough how incoherent conduction works. It would be best, to eliminate all possibility of confusion, if the Solin-Thio measurements were redone with measurement of symmetrized 4-probe resistance sums, and/or 2-probe measurements.

But, it has been remarked [50] that in the *different limit* in which we take $V_{\max} \to 0^+$ while keeping the macroscopic and microscopic length scales *fixed*, we will *not* get a violation of EQ (2). (In other words, redefine σ by EQ 3 *but* in the limit $|\vec{E}| \to 0$.)

This is because our construction depended on a plenitude of microscopic nonlinear electrical elements, whose net effect was macroscopically linear. In the zero-voltage limit, the microscopic nonlinearity vanishes. Indeed, in some sense my construction is "pathological" and "not playing fair" because I have taken a situation which "really" is microscopically nonlinear (unfair!) but by using the fact that, e.g., a sum of nonlinear functions can be linear, made it macroscopically linear[16].

Furthermore, it can be argued that in the zero-voltage limit, all microscopic pieces of the material *must* be both electrically linear, and their quantum "transmission coefficients" reifying this linearity must exhibit time-H reversibility properties. Hence, any macroscopic assembly of such microscopic transmissive elements (assumed to be transmitting one electron at a time) interspersed with thermalizing reservoirs *must* obey EQ (2) in this limit.

Moral: Onsager_2 apparently really *is* valid (in any material free of internal magnetism and viewable as an collection of microscopic transmissive elements transmitting 1 electron at a time and interspersed with thermalizing reservoirs) provided we agree to operate only in this zero-voltage limit.

But I would counter-argue that the macro/micro length scale limit I adopted can be the one more relevant to experiment. Indeed, one can imagine cases in which it might be experimentally infeasible to strive for the zero-voltage limit, due to the fact that the measurements would then be swamped by noise (and possibly in practice this "noise" would contain asymmetry, leading to apparent Onsager_2 violations anyhow). Furthermore, the fact that chirality appears naturally in EQ (5) suggests that maybe there is something very legitimate about this chiral counterexample to (EQ 2).

4 Guesses about which materials most violate Onsager_2

Which kinds of materials should be looked at experimentally to try to see large discrepancies from EQ (2)?

Only materials inequivalent to their spin and/or chiral reversals seem capable of violating EQ (2).

We have already mentioned possible future "designer materials," containing tiny magnets, in §2; and the "dirty semiconductor" ($Hg_{1-y}Cd_yTe$, $y \approx .1$) materials of Solin and Thio (which may already violate EQ 2) in §3.2.

The quaternary system $Hg_{1-x-y}Cd_yMn_xTe$ is known to allow both zero gap and magnetism simultaneously (this should occur for, e.g., $x \approx .02$, $y \approx .09$), and hence might be even better. Also, using Zn instead of Cd may have advantages: Zn is cheaper and less toxic than Cd, and $Hg_{1-x}Zn_xTe$ is harder and more stable with respect to Hg retention than $Hg_{1-y}Cd_yTe$, and it also allows zero gap ($x \approx .06$).

Another interesting class of semiconductor materials – GaAs containing 100-400nm Mn-rich ferromagnetic inclusions – are described in [35][36][37]. By combining this ferromagnetic inclusion idea with the idea of Solin and Thio [39][40] of striving for small bandgaps, it may be possible to get far larger "giant" magnetoresistances than have yet been achieved.

It is also possible to introduce tiny inhomogeneities into materials by exposing them to radiation. The result is "damage tracks." It is known that radiation damage can cause substantial increase in anistropy of electron mobility in semiconductors. Also, in some materials, such as SiO_2, damage tracks are much more susceptible than bulk material to etchants (e.g. HF). One might even be able to produce "chiral curved tunnel" damage tracks of the same sort as in §3 by exposure to a high energy electron beam in an intense magnetic field.

Another approach would be, by methods of organic synthesis, to try to make chiral conductive substances. Many organic semiconductors have been made (e.g. pentacene, poly-thiophenes) but I have not yet heard of one which is chiral, although there is no reason it should be difficult to make one.

For example, one could adjoin chiral groups to "copper phthalocyanine," a well known, very stable, organic semiconductor manufactured in 10,000-ton quantity every year for use as a blue pigment. Thousands of derivatives are known [45][23].

The "helicenes" [19][24][25][27][28][29][49] are interesting chiral organic materials made of benzene rings fused in a spiral. Helicenes have been synthesized with every number up to 14 of benzene rings [25][27] and in many derivative forms. They are known to exhibit nonlinear optical behaviors and very large optical rotations, indeed one helicene derivative (a red, translucent wax [29]) holds the world record: 1400 degrees/mm. Some of the higher helicenes may be electrically conductive (perhaps when doped with, e.g., potassium), and they might exhibit violations of EQ (2) when the electrical current flows along the helix axis and the magnetic field is also oriented (either way) along that axis.

Something like the counterexample in §7 (for either thermal or electrical conductivity) might be realizable as an antiferromagnetic crystal.

Any or all of these ideas might lead to materials with bigger and/or more reproducible Onsager violations and/or bigger magnetoresistance, which might be technologically important. (An application would be making a 2-pin resistive sensor for 2-state bits stored as $\pm H$.)

To present guesses of a less specific nature, let "$<$" be an ordering in which if $A < B$, then materials of type B seem more likely to include examples showing more-visible Onsager_2 violations. Here are my guesses:

[16] I could counterargue, though, that *all* materials are microscopically nonlinear, so it is impossible to play fair. But really, in a statistically and thermally averaged sense, materials *can* be microscopically linear.

1. gases$<$liquids$<$amorphous solids$\ll$liquid and solid crystals
2. materials with chiral molecular structure or microstructure$\gg$non-chiral materials.
3. metals$\ll$semiconductors
4. materials with smaller charge-carrier mean free path$<$ materials with larger charge-carrier mean free path.
5. simpler materials$<$materials with more complicated and less symmetric structures.
6. materials without unpaired electrons$\ll$materials with them.

5 Isomorphs

There are numerous [9] mathematically isomorphic (but physically different) versions of Onsager type-2 relations. For example, EQ (2) is also supposed to apply when σ is thermal rather than electrical conductivity, and the role of the applied magnetic field $\vec{H}$ is replaced by angular velocity (for a rotating system). All of these other isomorphs are also logically unjustified for logically isomorphic reasons.

Also, one can devise specific counterexamples. Consider my marble arrays from §2, but now with different heat conductivities in each hemisphere (not electric conductivities). The result is a material disobeying Onsager's second kind of relations for heat conductivity and magnetic field.

Consider the chiral tunnel examples of §3 but now for a rotating material. Coriolis forces will now play the role formerly assumed by the magnetic field, and we'll have a counterexample to Onsager's second kind of relations for electric conductivity and angular velocity.

6 Related work by Lax, and the corrected Onsager relations

Both of the logical flaws that I have pointed out, had also been pointed out by Melvin Lax in his book [22] (his sections 10.5). (See also [11][12][18].) Lax's treatment is the most careful one I have seen, and he has an excellent way to state all the Onsager-isomorphs at once by using "ϵ's" to denote the signs of certain symmetry effects.

I came to my conclusions before I was aware of Lax.

Lax only mentioned these flaws in 1 sentence each (one cryptic and in a footnote) did not state the corrected relations EQ (6) and EQ (5), and did not point out that it might be practical to exploit these flaws to get large discrepancies from EQ (2) in real materials.

6.1 *Lax's footnote re Ferromagnets*

The purpose of Lax's footnote ([22], p.288, #10) had been to make the claim that Onsager$_2$ is valid in ferromagnets if stated as

$$\sigma(\vec{H}, \text{spin majority} \uparrow) = \sigma(-\vec{H}, \text{spin majority} \downarrow); \quad (9)$$

Lax wanted to warn the reader away from

$$\sigma(\vec{H}, \text{spin mjrty} \uparrow) = \sigma(-\vec{H}, \text{spin mjrty} \uparrow) \quad \text{(WRONG)}. \quad (10)$$

Lax's point is that if $|\vec{H}|$ is small enough, it can be possible to reverse $\vec{H} \to -\vec{H}$ *without* causing the majority of spins in the ferromagnet to flip ("hysteresis"), in which case we will have a stable thermodynamically inequivalent "material" and should not expect EQ (10) to hold. But if $\vec{H}$ is reversed "hard enough" then the spin majority will flip and this ambiguity won't pertain. Similar reasoning could yield EQ (6); but flaw #2, which I exploited in §3, still would remain active.

But really – *my* point – EQ (9) is *only* valid in those ferromagnets for which the "reversed" material is equivalent to the original one. Our marbles material doesn't have that kind of symmetry. The problem here is not an $\uparrow\downarrow$ ambiguity of two stable "phases" – that issue is irrelevant for the marbles material since it is a paramagnet, not a ferromagnet, if EQ (7) holds[17] – the problem is outright falsity.

Let me further reinforce the difference between our marbles material from §2 and ferromagnets. Ferromagnets can be reversed by applying a strong enough magnetic field. But the marbles material cannot be converted to its reversal by the application of any magnetic field, no matter how strong. This is because when one tries to reverse the applied field, the marbles will rotate, at which point any strengthening of the reversed field would merely magnetize the bar magnets harder in the direction they are already magnetized. Any attempt to reverse the applied field so quickly that the marbles do not have time to rotate can be defeated either by

1. Assuming that the thermal relaxation time for the bar magnets to remagnetize themselves, is longer than the thermal relaxation time for the marbles to rotate.
2. Assuming that the melting point of our material is low enough, that too rapid and strong a magnetic field reversal will induce (via Faraday's law of induction) a large enough electric current to melt, or vaporize, the material.

More generally, *no* macroscopic physical operation whatever will convert our material into its reversed version, so in a very real physical sense the material and its reverse are different materials.

6.2 *Lax's sentence about small length scales*

In Lax's other sentence (the final one, p.289 in his "macroscopic derivation") he cites Zwanzig [52]. Zwanzig was interested in extending Onsager$_1$ relations to hold in materials with history-dependent conductivity – which Onsager's original linearity assumption EQ (3) had not permitted. Zwanzig did not discuss type-2 Onsager relations, and again had not suggested my idea of practically exploiting ballistic effects to get dramatic Onsager violations. Zwanzig's

[17] And even without this assumption, it still would be an antiferromagnet.

formalism *is* in principle capable of at least starting to consider such effects, however, because all such effects at small length scales may be viewed, at least approximately, as alterations to the conductance matrix which occur only at high AC frequencies.

7 Counterexamples to Onsager relations of the first kind

There are many ways to combine my Onsager_2 counterexamples to construct counterexamples to the Onsager relations of the *first* kind EQ (1). A counterexample simple enough to plausibly occur in nature may even be obtained by using materials which *obey* Onsager_2; see figure 4.

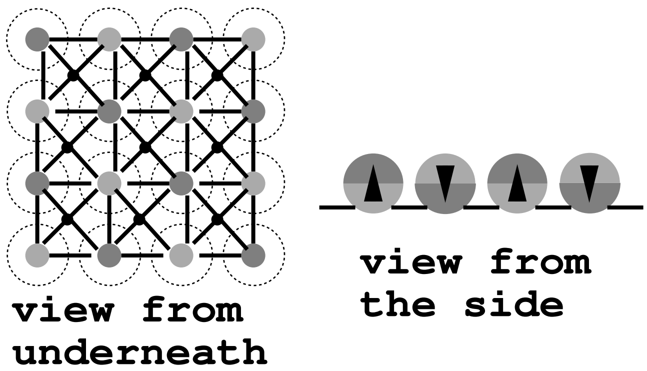

Figure 4: 2D marble array. Marbles rest in depressions (drilled holes of diameter smaller than the marbles themselves) in a "printed circuit board." Regard each marble as a "square" in a "checkerboard;" neighboring squares (either vertically, horizontally, or diagonally) are electrically linked via conductors printed on the board contacting points on the *undersides* of each marble.

Again we use an array of rotatable (but not translatable) marbles, each containing a bar magnet inside, and each made of two hemispheres. The North hemispheres are made of a comparatively insulating material; the South ones are made of a comparatively conductive material which (we assume) obeys Onsager_2 EQ (2) exactly and in a nontrivial way, i.e. $\sigma(\vec{H}) = \sigma^T(-\vec{H})$, but $\sigma(\vec{H}) \neq \sigma^T(\vec{H})$, at some $\vec{H} \neq \vec{0}$. The array is 2-dimensional. (One can also consider 3D arrays made by layering the 2D arrays with buffer materials sandwiched between them.) Unlike in the previous marble-array construction EQ (7), we now assume there is zero externally applied magnetic field, and the magnetic dipoles μ are strong enough so that

$$k_B T \ll \mu^2 \mu_0 L^{-3} \tag{11}$$

so that we have an *antiferromagnet.* In other words, all the "red squares" of the checkerboard have magnetic moments $\uparrow$, and all the black squares have magnetic moments $\downarrow$. The net magnetization is *zero.* Only the red squares make much contribution to the macroscopic electrical conductivity, therefore. But these all see an environment with an *internally generated* upward magnetic field – forcing EQ (1) to be false. The other ground state (red $\downarrow$, black $\uparrow$) will have these same electrical properties (it is just a matter of mentally recoloring the squares, which makes no physical difference). Hence a 50-50 (or any other percentage) mixture of these two "phases" will also have these same electrical properties. Any way you look at it, EQ (1) is false.

Defenders of Onsager could argue[18] that Onsager had intended for EQ (1) to apply only to materials without *any* magnetic field, either internally or externally generated. But since most materials, whether "magnetic" or not, have some internal magnetism and some internal conductivity variation, and since there is no known algorithm available to bound the discrepancy in EQ (1) for a material inequivalent to its reversal, we then would be forced to conclude (in this interpretation) that Onsager_1 was, although *valid*, usually *useless* (cf. footnote 6) as a generally applicable theoretical tool.

Previous remarks apply again: the fact that this is an "artificial material" in no way alters the logical strength of my conclusion; the material is exactly linear EQ (3) by design; and the corrected Onsager relations EQ (6) remain valid here despite the demolition of the uncorrected ones EQ (1). The "reversed" material needed in EQ (6) is not equivalent to the original material under any set of rigid motions and/or permutations of the marbles, nor is it possible to alter (in particular to "reverse") this material by temporarily placing it in an external magnetic field, no matter how strong (cf. §6.1) and indeed no macroscopic physical operation will convert our material into its reversal.

8 Almost a counterexample

It is also possible to devise a counterexample to Onsager_1 (EQ 1) which nowhere involves either magnetism or chirality. How can this be? Well, strictly speaking, this is not really a counterexample, but experimentally it could seem like one. See figure 5.

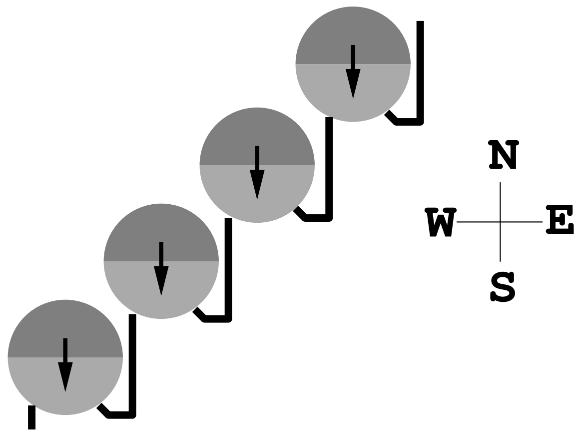

Figure 5: Another counterexample?

In this figure, we again have 2-sided rotatable marbles whose hemispheres are made of highly conductive and

[18] A contention supported by [30] p.425: "...these relations will break down in cases where magnetic or Coriolis forces are acting".

highly non-conductive materials, and again they are linked in a 1D array by electrical links. But now, inside each marble is *not* a bar magnet, but instead an electret containing a permanent *electric* dipole moment.

If we expose this material to a Southward-pointing E-field, we'll get a large current flowing Southwest. The marbles will prefer to orient themselves so their conductive sides face South, so each marble's two electrical links will be shorted by highly conductive stuff.

Instead, expose to a East-pointing E-field. The conductive sides of the marbles will face East so that the two contacts on the South side of each marble will not be shorted. Hence, we will have very small electrical current.

Conclusion: an E-field pointing South causes a large Southwest current; but an E-field pointing East causes only a tiny current. Therefore, EQ (1) is false; the "cross terms" the other way are not equal. Notice, in this example, no magnetism was needed anywhere.

What is going on?

Well, actually, this is not really a counterexample to Onsager$_1$, because Onsager$_1$ is not actually applicable here because the material is not electrically "linear." (E-field up $\Longrightarrow$ tiny current; E-field down $\Longrightarrow$ large current, hence non-ohmic diode-like behavior.)

But matters are not quite that simple, because the nonlinearity of the material of figure 5 may be tremendously disguised. Consider *two* parallel SW-NE 1D arrays (each as shown in figure 5), but the second array has the electrets in each marble pointing the other way. Now

1. Southward E-field causes large component of Westward current, and
2. Northward E-field " Eastward current, *but*
3. Westward E-field does not cause any large current, and
4. Eastward E-field does not cause any large current.

The diode-like non-ohmic behavior now has vanished, but the violation of EQ (1) remains.

Indeed, the only non-ohmicity in this material occurs at small voltages (small enough that the electrostatic energy of a marble's orientation is $\ll k_B T$) at which the current would be very small and might be swamped by thermal noise.

Additional disguise can be laid on (similarly to in footnote 10) to make the material seem exactly to obey full-*matricial* linearity (EQ 3) except, again, at small voltages. In that case any departure from exact linearity will only occur at small voltages where the currents are small and perhaps swamped in thermal noise (cf. §3.3). But at the same time the departure from Onsager$_1$ will be very measurable and very dramatic.

So (to modify our previous moral): Although the ideas of this section do not, strictly speaking, lead to a new counterexample to Onsager$_1$, they do create a good imitation of that.

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