

No "direct force" in electromigration

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In electromigration, a uniform field is applied and a dipole moves from one crystallographic site to another. The dipole has the same strength at the two sites. Because electrostatic fields are conservative, the translation occurs without change of electrostatic energy. Accordingly, the "direct force" is identically zero. Objections to this conclusion are considered. It is emphasized that in any experiment in which an electron wind is present it is important to measure Z^* in the lattice frame of reference.

I. INTRODUCTION

Some problems in physics are inherently simple. The "direct force" of electromigration is one of these.

The simplicity inheres in the concept that electrostatic energy is a conservative quantity; to specify the electrostatic energy of a particle we only need to know the charge upon it and the electric potential at the point which it presently occupies. We do not need to know the path by which it came to occupy its present position. Equally, if we wish to know the change in electrostatic energy on moving a particle from one position to another, we do not need to know the path followed between the two positions, we only need to know the electric potential at the two end points and the charge which has moved from one end point to the other.

Likewise, if we have a system of many particles and we wish to know its change of electrostatic energy on going from one configuration to a second configuration, we only need to have information about the initial and final states, and not about the several paths followed by the particles.

The two end points with which we are presently concerned are two crystallographically equivalent sites in a crystalline solid. Our problem is that something (yet to be defined) moves from one equivalent site to the other. We assess the difference in the electrostatic energies of the system in the initial and final states. Let the difference be ΔE . If we specify that the two sites are separated by a distance \vec{d} , we may define an electrostatic force \vec{F} pushing the "something" from one site to the other. We require no more than the basic definition that energy is the dot product of force and distance:

$$\vec{F} \cdot \vec{d} = -\Delta E, \quad (1)$$

$$\vec{F} = -\nabla E. \quad (2)$$

In electromigration, the experimenter applies

and the theorist considers an electric field which is spatially uniform on a macroscopic scale. Clearly, this applied field is the same at our two equivalent sites, at our two end points.

If, then, the "something" which moves from one site to the other is an electric dipole, of equal positive and negative charges and of zero total charge, it is a dipole which has the same strength at the two equivalent sites.

Because electrostatic fields are conservative, because we are concerned only with end points and not with paths followed, it does not matter that the strength of the dipole fluctuates, with the periodicity of the crystal lattice, as the dipole moves along any path between the two sites. The fluctuations are not a parameter of our present problem. Accordingly, for simplicity and for ease of comprehension, we may think of the dipole as having constant strength. The problem then becomes very simple, and its solution immediately obvious: a dipole of constant strength moves in a uniform field. As it moves, its electrostatic energy does not change. Hence the electrostatic force upon it is zero.

Thus the elementary concept (or definition) that electrostatic fields and energies are *conservative* is of prime importance. Because these fields are conservative, the "direct force" of electromigration is not merely small, or negligible in some circumstances, it is always identically zero; it does not exist.

II. EQUIVALENT SITES

The essence of the problem is therefore the realization that in electromigration a dipole moves across a background of unchanging electrostatic energy between two sites which are fully equivalent.

The initial and final sites are locally equivalent and they also have long-range equivalence. Local equivalence is easily seen. In a solid, a lattice vacancy or an impurity atom is translated between

two crystallographic sites, through an integral number of lattice vectors. In a liquid there is no lattice, but, simply because experiments sum over a large number of sites the local character of which does not change with time, we may still consider the elementary act of electromigration to occur between sites which have full local equivalence.

In general, we do not have full long-range equivalence. When a lattice vacancy or an impurity atom is translated between two crystallographic sites, it moves closer to one specimen boundary and further from another. The condition of long-range equivalence, therefore, is that we restrict consideration to sites which are remote from the specimen's boundaries and we restrict the translation vector to a length very much smaller than any dimension of the specimen. Long-range equivalence is universally subsumed, in both experiment and theory. It is an adequate assumption. I merely make it explicit.

III. STEADY BACKGROUND

In electromigration, at an interval of several days or weeks, successive measurements are made of the distribution of a radioactive tracer or the position of a surface scratch or an embedded filament. During the interval, a steady temperature and a steady electric current are maintained in the specimen.

The background must therefore be steady in two respects: it must be steady over the time interval in which each measurement takes place and it must be steady over the longer interval between the two measurements.

Each measurement of distribution or position integrates over a large number of atoms ($\geq 10^{12}$) and over a large number of lattice oscillations ($\geq 10^{12}$), and fluctuations at any one atomic site are lost in the two integrations. This is even more true of the longer interval during which electromigration is actually taking place. The dependent experimental variable, the flux \vec{J} of the species of interest, is without question an average value.

As a phenomenon of linear response, electromigration falls within the scope of linear thermodynamics, and in the usual notation

$$\vec{J} = L\vec{X}, \quad (3)$$

where L is the coefficient of the response and \vec{X} is the thermodynamic force driving the electromigration. There are alternative ways of treating Eq. (3). We might take microscopic values of L and \vec{X} , form the microscopic products, and take an average of all such products. Alternatively,

we might take from some ancillary experiment a macroscopic value of L . We would then write into Eq. (3) a macroscopic value of \vec{X} , an average value. In the analysis of any electromigration experiment we always choose the second alternative, we use a macroscopic, experimental value for the diffusion coefficient D of one unit of the species of interest. We take

$$L = Dc/k, \quad (4)$$

where c is the volume concentration of the species of interest and k is Boltzmann's constant. Therefore, when we come to write

$$\vec{X} = (\vec{F} + \vec{F}_w + \dots)/T, \quad (5)$$

where T is the local temperature (a macroscopic parameter) we require macroscopic values of \vec{X} and of \vec{F} , \vec{F}_w , etc. In Eq. (5), \vec{F} is the electrostatic force of Eq. (2), \vec{F}_w is the force of the electron wind,¹ and the dots indicate the inclusion of all the forces which produce electromigration.

The sequence of Eqs. (3)–(5) and the use of a macroscopic value of D indicate that we require a macroscopic value of \vec{F} ; the background is *steady* in the sense that we are to ignore fluctuations, both the fluctuations in time, such as occur at one lattice site within a crystal, and fluctuations in space, such as occur with the periodicity of the lattice. As long as we conceive of electromigration as having some concern for experimental observables we are free to ignore fluctuations.

IV. DIPOLE

In electromigration, we have a metal specimen and a source of electric current, a battery or a power pack. It is useful to regard the current source as part of the world outside the specimen. We accept electrons from the negative terminal of the source and we surrender them to the positive terminal, but when these electrons are outside the specimen we have no interest in them—we do not suppose that they produce electrostatic forces within the specimen. This is a universal assumption.

Thus, in assessing electrostatic energies and electrostatic forces, we are concerned only with the world within the specimen and not with the world outside. The faces of the metal specimen are the boundary of our region of interest; they define "the system" of Sec. I and Eq. (1).

It is useful to think of the boundary of the specimen as a *box*. The box contains a number of ions and a number of electrons. We may redistribute the ions within the box but we may not take them out. The box is therefore of constant volume, unchanging with time. Electrons flow into the box, through one face, at a steady rate, and they flow

out, through the opposite face, at the same steady rate. Electrons enter and leave, but the *number* of electrons within the box is stationary, unchanging with time.

I make the explicit assumption that the electron flow is nondivergent. The shape of the box is then stationary, unchanging with time.

Thus we have a box, of constant volume and constant shape, which contains a constant number of ions and a constant *number* of electrons. In the elementary act of electromigration we rearrange the ions and the electrons within the box. We assess the change in electrostatic energy brought about by the rearrangement, we apply Eq. (1) and thereby discover the electrostatic force \vec{F} . The displacement \vec{d} is an integral number of unit vectors in the real lattice of the metal.

Consider first the simplest of several rearrangements, the movement of an interstitial impurity ion from a site with a position vector \vec{A} to a site with a position vector \vec{B} ,

$$\vec{d} = \vec{B} - \vec{A}. \quad (6)$$

Suppose that the impurity has a valence z . This means that the ion carries a charge of z proton charges. Within a distance of the ion which is small by comparison with the specimen dimensions,²⁻⁷ a detection device which, like the instruments of real experiments⁵⁻⁷ requires a macroscopic time for its operation, will detect a screening cloud of z conduction electrons. These z electrons are additional to the conduction electrons which would be present in the absence of the impurity ion.

Thus, locally within the box, there is a *perturbation* which consists of z proton charges at the ion and z electron charges in a small volume around the ion. The total charge on the perturbation is zero for the simple reason that when we add an impurity to a metal we add an uncharged *atom*. However, the proton and electron charges within the perturbation are polarized, by the applied field, they do form a dipole.

When the ion moves from \vec{A} to \vec{B} , through a displacement \vec{d} , z screening electrons move through precisely the same displacement \vec{d} ; the moving entity is the dipole.

When the impurity is interstitial we may readily visualize (or specify) that it moves through an inert, nondiffusing solvent; we may readily visualize the motion of a dipole against a steady background.

When the impurity is substitutional, we require only slightly greater sophistication. We first imagine a pure metal, of identical ions in a sea of conduction electrons. We replace one ion, at \vec{A} , by an impurity ion and we now let z be the valence of the impurity minus the valence of the

host.

Again we have a perturbation of z proton charges surrounded by z conduction electron charges.

Again we have a dipole. Initially, the dipole is at \vec{A} and there is no perturbation at \vec{B} . Finally, there is a dipole at \vec{B} and no perturbation at \vec{A} .

The lattice vacancy may be classed as a substitutional impurity. We may map the applied field, the field which is to produce electromigration, throughout the box. It is uniform and nondivergent; the voltage gradient is everywhere the same.

Across this map of electric potential we may move ions and conduction electrons. If we interchange two identical ions of the solvent metal we (clearly) do not affect the electrostatic energy of the system. If we interchange two (indistinguishable) conduction electrons we (clearly) do not affect the electrostatic energy of the system. On a macroscopic scale, the background against which we are to move the perturbing dipole is of a steady, unchanging electrostatic energy.

The problem thus reduces to a translation of the perturbing dipole through the distance \vec{d} , and because the dipole has the same strength at the two sites \vec{A} and \vec{B} , the translation does not change the electrostatic energy of the system; in Eq. (1) both ΔE and \vec{F} are zero.

V. INDISTINGUISHABLE ELECTRONS

If we interchange two conduction electrons within the box we do not affect the electrostatic energy of the system. We cannot even detect the change; electrons are indistinguishable and we have no means of labeling either electron.

If we interchange a *conduction* electron in one region of the box with a *bound* electron from an ion in a second region of the box we again do not affect the electrostatic energy of the system. We have no label by which we may recognize that an electron now free was once bound. These electrons too are indistinguishable; the bound state and the conduction state are distinguishable, but the electrons which occupy them are not.

Suppose we could label a conduction electron which is at some instant one of the z electrons screening the impurity ion at \vec{A} . By the time the impurity ion reaches \vec{B} the labeled electron is at some remote part of the box, its place in the screen having been taken by another electron. Suppose now that we interchange these two electrons. Only if the two electrons carried different electric charges should we affect the electrostatic energy of the system. Alternatively, suppose that when the impurity ion reaches \vec{B} we interchange the distant, labeled electron and one

of the bound electrons of the ion. Again, only if the two electrons carried different charges should we affect the electrostatic energy of the system.

I have spelled out at length this very simple conclusion in order to emphasize that *the extent of the binding between electrons and ions is not a parameter of the problem*; it has no bearing on the existence of the "direct force."

VI. FRAMES OF REFERENCE

The absence of an electrostatic force is not dependent on any choice of a frame of reference.

Having used the faces of the specimen as a frame of reference, let us now adopt a second frame, moving with a velocity \vec{v} , as seen from the first frame. Let \vec{v} be much less than the velocity of light. In the second frame, all specified velocities are increased by $-\vec{v}$. In the second frame, all coordinates are increased by *one* time-dependent quantity, $-\vec{v}t$, where t is the lapse of time from the coincidence of the origins of the two frames. Using the subscript 2 to specify coordinates in the second frame,

$$\vec{A}_2 = \vec{A} - \vec{v}t, \quad (7)$$

$$\vec{B}_2 = \vec{B} - \vec{v}t, \quad (8)$$

and

$$\vec{d}_2 = \vec{d}. \quad (9)$$

The translation vector is unaffected by the change to a second frame of reference. Other vectors which represent a difference between two specified points are likewise unchanged. The potential difference between any two points in the box is unchanged. The electrostatic energy of a particle in the applied field is unchanged. (Both the particle and the field are moving through the second frame with velocities increased by $-\vec{v}$). The electrostatic energy of interaction of two particles is unchanged. The electrostatic energy expended in moving a dipole from \vec{A} to \vec{B} is unchanged.

The belief^{8,9} that such a Galilean transformation ("the equivalence theorem"⁹) demonstrates the assertion that "the shielding of unbound charges is generally ineffective as far as the force on the shielded object is concerned"⁸ is quite without foundation. The equivalence theorem tells us nothing whatsoever about the presence or absence of a "direct force."

Equation (5) makes reference to \vec{F}_w , the electron wind force. This is the force arising from momentum transfer from the electron stream to a scattering center. If we properly account for all the momentum in the system, a computation of \vec{F}_w will not be affected by a Galilean transforma-

tion such as that just considered. A proper account *must include the momentum carried by the crystal lattice*. Only if we choose the special frame of reference of the crystal lattice do we obtain the useful simplification of being able to set the momentum of the lattice equal to zero. If we choose a frame which is steadily moving through the lattice and then ignore the momentum associated with the lattice, we get a wrong answer. This error is made by Herzig and Wiemann⁷ and has led them to conclude that they have evidence of a direct force (see Sec. XVI).

VII. SEPARABILITY OF \vec{F} AND \vec{F}_w

Consider an atom in a gas. If we apply a uniform electric field, such as we have been considering, we polarize the positive charge of the nucleus and the negative charge of the extranuclear electrons. We create a dipole. Because the potential gradient is spatially uniform, there is no electrostatic force upon the atom, no electrostatic force pushing it to one side of the container.

Suppose we now bombard the atom with electrons from a gun situated in one wall of the container. The electrons are scattered at the atom and momentum transfer from the electron beam provides a force pushing the atom away from the gun.

The atom is an uncharged entity, but it scatters electrons. This simple example makes it plain that we may have momentum transfer from a stream of electrons to *an uncharged object*. However, it is equally plain that in a spatially uniform field we do not have an electrostatic force on *an uncharged object*. In a uniform field, the electrostatic force on an object is proportional to the charge, q , on the object,

$$\vec{F} = -q\nabla V, \quad (10)$$

where ∇V is the potential gradient.

The electrostatic force on an object and the momentum-transfer force thus depend on different parameters of the object. The first depends on the total charge (but not on the charge distribution within the object), the second depends primarily on the charge distribution and only via the distribution does it depend on the total charge.

Since the two forces depend on different parameters, they are separable. The distinction between them is simple: *electrostatic*, as its name implies, is a function of position, of *coordinates*. Momentum transfer is a function of *velocities*. I see no reason to abandon the distinction between *coordinate* and *velocity*.

In electromigration the distinction is equally

plain. \vec{F} is a function of the equilibrium positions of a constant number of particles within a box. \vec{F}_w is a function of the velocity of particles through the entrance and exit faces of the box. Since \vec{F} is not a function of velocity and \vec{F}_w is not a function of equilibrium positions, distinction between the two is not merely permissible, it is mandatory.

Those who still attach significance to experiment may like to note that \vec{F}_w , when treated as a separable quantity,¹ agrees with the firmest experimental data, those on the noble metals, to an accuracy of 10%. There is no indication from experiment that \vec{F} and \vec{F}_w are to be confused.

VIII. HELLMANN-FEYNMAN THEOREM

The Hellmann-Feynman theorem^{10,11} applies to forces within molecules. A molecule is a closed system. In such systems, to quote Feynman,¹¹ "the forces are almost as easy to calculate as the energies are . . . they can be considered as purely classical attractions involving Coulomb's law."

Feynman¹¹ distinguishes the steady state from the non-steady state and restricts the theorem to the former. It would therefore seem that we may only apply the theorem to electromigration if *all* the quantities which enter into our calculation are independent of time. Calculation of the electrostatic force satisfies this condition: we have a box of constant size and shape containing a constant number of particles and subject to a constant field and we calculate a time-independent quantity, the electrostatic energy when the impurity is at \vec{A} . We then calculate a second time-independent quantity, the electrostatic energy when the impurity is at \vec{B} . Admittedly the system is not closed, but we may ignore the world outside the box; it does not enter the calculation.

The theorem does not have the same immediate applicability to the electron wind force \vec{F}_w . A typical calculation¹² explicitly invokes the adiabatic approximation so that it may calculate a *time-dependent* quantity, "the time rate of change of the average momentum." I only wish to note, and not to discuss at length, that a scattering problem involving an obstacle, a lattice in which it is embedded, and a stream of electrons flowing through the lattice, does require considerable precaution to ensure that *all* the quantities entering the calculation are in fact independent of time. I think there is a case for using simpler methods¹ to calculate \vec{F}_w .

IX. STATIC POLARIZATION

For pictorial clarity, let me return to the atom in the gas considered in Sec. VII.

First, apply the uniform field but do not bombard with electrons. The field creates at the atom a dipole of such strength that each charge within the dipole is in equilibrium, under the combined action of the other charges in the dipole and the applied field. There are as yet no moving particles in the system, and I will accordingly label this dipole the *static polarization*.

Now switch on the electron gun and bombard the atom (but don't switch off the applied field). Because the atomic nucleus is more massive than the (bound) extranuclear electrons, the bombarding particles change the strength of the dipole. They also accelerate the atom away from the electron gun. We may take a time average of the acceleration and also of the *change* in strength of the dipole. I will call this average *change* in strength the *dynamic polarization*.

These two quantities, static and dynamic polarization, arise in electromigration. The extranuclear electrons are now not all bound; some are bound and form part of the ion and some are conduction electrons, but by the Friedel sum rule, all of them are still there. If we ask for a *time average* of the number of bound and conduction electrons screening the atomic nucleus, we obtain precisely the number of electrons in the neutral atom.

I therefore see no reason to omit the static polarization from the electromigration problem. It will be evident that I regard the static polarization as the agent by which the electrostatic force \vec{F} is made identically zero. As far as I can tell, many authors^{9,9,12-20} leave out the static polarization. The omission has its roots in the idea that it is simply the *ion* which moves. In the course of private, unpublished correspondence, I have met several gestalt switches from *atom* to *ion* and from *ion plus screen* to *bare ion*. These switches are hard to deal with because they go (apparently) unrecognized by the person making them but are crystal clear to the person trying to pin them down. I am sure that confusion as to the identity of the thing which moves is at the heart of the direct force controversy.

X. DIRECT FORCE

Two different but equally valid definitions of a "direct force" may be made, and there is some evidence that both are in use.

The direct force may be defined, as in Eqs. (1) and (2), as a total electrostatic force measured by the change of electrostatic energy caused by a displacement in a system of many ions and many electrons, the metal specimen.

Alternatively, the direct force may be defined,

equally validly, as the electrostatic force on one bare ion.

The significant difference between the two definitions is that the first is the *observable* sought by experimentalists,^{6,7,21} and the second is not. As in Eq. (5), experiment seeks to divide the electromigration forces into two components only, a direct force and a wind force. Experimental analysis, therefore, by including within the term "direct force" *all* the electrostatic forces, adopts Eqs. (1) and (2).

By contrast, the second definition yields an observable only if the electrostatic forces on bare ions are the *only* electrostatic forces in the metal specimen. Since electrons are subject to electrostatic forces, this second definition yields an observable only if we can be assured that the electrostatic forces on the electrons in the system in some way disappear.

Either definition may be chosen, *but it is of the utmost importance to avoid mental switches from one definition to the other.*

In taking the direct force to be the \vec{F} of Eq. (1), I follow a recent review⁸ which speaks of "the direct action of the electric field on the moving atom."

XI. NUMBERS

To see the absurdity of the direct force as usually contemplated, it is only necessary to consider typical experimental figures for gold⁷ and to adhere consistently to one or the other of the alternative definitions of direct force.

All the cited theoretical work^{5,8,9,12-20} is applicable to pure metals and hence to the electromigration of gold atoms in gold.

Accepting the explicit statements^{8,12} that there is no appreciable screening out of the external field by the conduction electrons, the charge q [Eq. (10)] which we are to associate with an electromigrating gold atom is one proton charge.

There is nothing in the cited literature to suggest that the q of one gold atom differs from that of another, nor that ∇V at one atomic site differs from that at another site. We are entitled to suppose that all gold atoms in one block of gold have the same q and the same ∇V .

There is nothing to suggest that an atom must be *in motion* before the force \vec{F} of Eq. (10) can come into play. Calculation¹² explicitly assumes that "the ions are considered to be static."

There is nothing to suggest that a lattice vacancy must be close at hand before \vec{F} can come into play. The adiabatic approximation,¹² which decouples the ion from the lattice, excludes this possibility.

It is plain that a direct force which acts on one gold atom or ion in a block of pure gold acts equally on all the gold atoms or ions. And if there is "no appreciable screening" of one ion then there is no appreciable screening of any ion.

It is thus easy to sum the direct force on all the 2×10^{22} gold atoms or ions in a typical experimental specimen.⁷

The specimen⁷ is a cylinder, of 7 g mass, and having an end face of 30 mm² area. The voltage gradient is 10 V m⁻¹. The direct force on such a cylinder is 3.5×10^4 N, and this produces on the end face a pressure of 10³ MPa. This pressure is some eight times the room-temperature strength of gold—the mere survival of the specimen calls in question the concept of a direct force.

This enormous pressure cannot be discounted on the ground that "the direct force on each ion is ultimately transferred to the lattice via dynamic ion-lattice interaction." If we say that the forces are transferred to the lattice we are merely saying that they act upon the block as a whole. Thus we are not removing the pressure but merely saying that it should be experimentally measurable.

As a thought experiment, we might suspend the gold cylinder on long flexible current leads—a bifilar suspension. Conceptually, at least, we can make such current leads from superconductors. In a voltage gradient of 10 V m⁻¹, the direct force now accelerates the block, in the direction anode to cathode, at the quite respectable rate of $5 \times 10^5 g$ (some four orders of magnitude greater than experienced during re-entry into the earth's atmosphere). It seems reasonable to ask, what has happened to Newton's third law, what is going the other way? Nothing is going the other way, and the conclusion is surely self-evident, the concept of a direct force is unsound.

One may usefully contrast the direct force with the electron wind. The electron wind acts on irregularities embedded in a lattice, not decoupled from a lattice, and we obtain a simple answer only if we use the lattice as a frame of reference.¹ In the lattice frame of reference, the sum of the crystal momenta is identical to the sum of the real momenta.²² We may thereby include the lattice, we avoid the adiabatic approximation, and we preserve Newton's third law.

XII. BROKEN TORUS

To demonstrate the existence of a nonzero direct force, Huntington¹⁶ has considered a piece of metal in the form of a broken torus. The break is conceptually important. The emf which drives the electromigration appears across the break. Huntington carries out a thought experiment in which

an ion is displaced through a small distance, around the torus. The conduction electrons which shield the ion are first dispersed "equally in both directions around the homogeneous torus" and then reassembled at the new position to which the ion has moved. It is asserted, wrongly, that in the dispersal (and equally, in the reassembly) of the electrons "no current flows." The basis of the assertion is that the torus is *homogeneous*. There are thus two conflicting specifications, the torus is *broken*, in order that an emf may be applied, and it is *continuous*, in order that electrons may disperse equally in both directions.

If the dispersing electrons cross the break, they change their potential; there is a change in electrostatic energy in the system. We may either write down the detailed equations of the dispersal and reassembly or, more simply, we may say that electric potential is a *potential*, and therefore, *conservative*, so that we only need to write down the initial and final states of the electrons (before dispersal and after reassembly) in order to discover their change in electrostatic energy. By either method, we conclude that the ion has moved around the torus through a distance \vec{d} and a potential difference ΔV and that the screening electrons have moved through the same distance \vec{d} and the same potential difference ΔV . The charges on the ion and screening electrons are of equal magnitude but opposite sign, and the direct force is again zero.

XIII. THERMODYNAMICS

In Eqs. (3)–(5) I have used thermodynamic notation, but the only result I require in this context is the very simple idea that in planar Cartesian coordinates a straight line has everywhere one and the same gradient. Thus if, in a physical system, a dependent observable y has a *linear response* to an independent observable x we write

$$y = Lx, \quad (11)$$

and it is a matter of no great subtlety that the coefficient of the linear response, L , is a constant independent of x and having the same value at $x=0$ as it has at $x \neq 0$. This simple point has serious application to irreversible systems.^{1,22,23} In regard to the direct force, Eqs. (3)–(5) and (10) give

$$\vec{F} = - (Dc q/kT) \nabla V. \quad (12)$$

Like other writers, I postulate a *linear response*. Therefore,

$$Dc q/kT = \text{constant}, \quad (13)$$

a constant independent of ∇V . Now D , c , k , and T

are all independent of ∇V . Therefore, q is independent of ∇V and the value of q when $\nabla V \neq 0$ is identical to the value when $\nabla V = 0$.

When other perturbations are absent, the point $\nabla V = 0$ is the point of *thermodynamic equilibrium*. Therefore, the value of q which we require is the value pertaining to thermodynamic equilibrium. In texts which deal with equilibrium,²⁻⁴ the Friedel sum rule specifies that q is zero; the electrons *completely* screen each ion.

Therefore, the value of q which we require in *linear thermodynamic disequilibrium*, in electromigration, is also zero. Thus, in Eq. (10), \vec{F} is zero; there is no direct force.

The "linear response formalism" of Kubo²⁴ is another expression of Eq. (11) and of necessity it gives the same result.

XIV. ELECTROLYTES

By way of example, consider an aqueous solution of sodium chloride. During electrolysis, chlorine ions drift to the anode and are liberated as chlorine gas, but sodium ions do not drift to the cathode. Instead hydrogen is liberated at the cathode.

We may imagine, within the body of the electrolyte, a rectangular box. The box defines a volume. We may look within this box, at any instant, and compute the electrostatic energy of the particles in the box, the anions and cations. We may look at a subsequent instant, when a specified anion has drifted perhaps halfway across the box, and again compute the electrostatic energy of the particles in the box. We obtain the same trivial result as in electromigration; the electrostatic energy of the particles in the box has not changed, and if the specified anion has drifted a distance \vec{d} , Eq. (1), applied to the box, gives $\Delta E = 0$ and $\vec{F} = 0$.

As in electromigration, the total charge within the box is zero; the cation charges balance the anion charges.

We may increase the size of this imaginary box until two of its faces are close to the two electrodes. The conclusion continues to hold; for any \vec{d} , ΔE and \vec{F} are zero.

Within the definition of Eq. (1), the drift of anions and cations within the box is not due to an electrostatic force on each species, but to the input, or extraction, of ions, at the faces of the box, by *interface reactions at the electrodes*.

As with the electron wind of electromigration, the significant quantity is the flux of particles across the faces of the box. This flux is plainly dependent on the interface reaction, in that it may be changed by changing the material of the electrodes.

Within the definition of Eq. (1), and within the acceptance of *interface reaction* as the controlling quantity, we do not have to seek a reason why the chlorine ions drift and the sodium ions do not.

It is possible to set aside Eq. (1) and, as for the "bare ion" of Sec. X, to *postulate, ab initio*, an electrostatic force on each species of ion. As in Sec. X, this is a matter of definition, of concept, and one must follow where the definition leads. In the present example, it becomes necessary to explain why the chlorine ions drift under the influence of their electrostatic force but the sodium ions do not drift under the influence of *their* electrostatic force. Doubtless it can be done, but it is simpler to accept the more operational definition of Eq. (1).

XV. PLASMAS

If we apply an electric field across a gaseous plasma, we obtain a steep voltage gradient at the entrance and exit faces of the plasma, over a short distance, and a shallow voltage gradient in the body of the plasma.

Suppose we have a solid plasma instead of a gaseous plasma. We again have a steep voltage gradient over a short distance at the entrance and exit faces and a much shallower gradient in the interior. The conclusion that the direct force is identically zero can scarcely be strengthened, but the magnitude of the screening length²⁻⁴ gives a further cause to doubt the detection of a direct force by experiment.

XVI. EXPERIMENT

In the lattice frame of reference, for tin as an impurity in gold, Herzig and Wiemann⁷ find $-23.4 < Z^* < -14.1$ (their Table 3). An electron wind is admittedly present, and the lattice is therefore the appropriate frame of reference (see Sec. VI). The figures for tin, -23.4 to -14.1 , are comparable to those for gold in gold,^{1,5} -19 ± 5 . They are of the sign and magnitude to be expected from the electron wind alone.¹ They offer no immediate evidence of a direct force.

Herzig and Wiemann's Eq. (5) is an invalid Galilean transformation; it takes them away from

the lattice frame of reference without accounting for the momentum of the lattice itself. Their subsequent conclusions accordingly fail.

Erckmann and Wipf⁶ find $0.5 < Z^* < 2.5$ for hydrogen and deuterium electromigrating in solid vanadium, niobium, or tantalum. The positive sign and the magnitude (spanning the value +1) they consider to be evidence of an electrostatic force acting upon the single electric charge of a proton or deuteron.

A second explanation is possible; the gas atom may be *bound to a lattice vacancy* with a binding enthalpy of ~ 0.1 eV. If so, the observed Z^* is principally that of the vacancy. As thermal agitation frees the gas atoms from the vacancies, Z^* decreases with increasing temperature. At high gas concentrations, a greater fraction of gas is unbound and Z^* decreases with increasing concentration. (Both these variations are observed). It is possible to estimate Z^* for the electron wind,¹ and for lattice vacancies in V, Nb, and Ta one expects $Z^* \sim +1$. It is therefore possible that lattice vacancies dominate the results of Erckmann and Wipf.

The behavior to these same two gases in iron and nickel^{25,26} suggests that vacancies play a significant role. In particular, the reversal of the sign of thermomigration²⁶ at low temperatures indicates that gas atoms are then bound to lattice vacancies and move in the sense which the vacancies dictate.

Thus there is presently no strong experimental evidence of a direct force in electromigration.

XVII. ELECTRON WIND

In the absence of a direct force we may discard \vec{F} from Eq. (5).

If we have a simple expression for \vec{F}_w , which is free from adjustable parameters, we may assess the experimental data on a range of metals in the hope that electromigration is a tractable phenomenon with a comparatively simple cause. This appears to be the case.¹

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