Onsager’s Wien Effect on a Lattice

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The Second Wien Effect describes the non-linear, non-equilibrium response of a weak electrolyte in moderate to high electric fields. Onsager’s 1934 electrodiffusion theory$^1$ along with various extensions$^2,3$ has been invoked for systems and phenomena as diverse as solar cells$^5,6$, surfactant solutions$^7$, water splitting reactions$^8,9$, dielectric liquids$^{10}$, electrohydrodynamic flow$^{11}$, water and ice physics$^{12}$, electrical double layers$^{13}$, non-Ohmic conduction in semiconductors$^{14}$ and oxide glasses$^{15}$, biochemical nerve response$^{16}$ and magnetic monopoles in spin ice$^{17}$. In view of this technological importance and the experimental ubiquity of such phenomena, it is surprising that Onsager’s Wien effect has never been studied by numerical simulation. Here we present simulations of a lattice Coulomb gas, treating the widely applicable case of a double equilibrium for free charge generation. We obtain detailed characterisation of the Wien effect and confirm the accuracy of the analytical theories as regards the field evolution of the free charge density and correlations. We also demonstrate that simulations can uncover further corrections, such as how the field-dependent conductivity may be influenced by details of microscopic dynamics. We conclude that lattice simulation offers a powerful means by which to investigate system-specific corrections to the Onsager theory, and thus constitutes a valuable tool for detailed theoretical studies of the numerous practical applications of the Second Wien Effect.
Onsager’s 1934 theory of the Wien effect is in all respects a remarkable achievement: a theory of a non-linear non-equilibrium problem of great complexity, with widespread relevance to real problems. Considering how bound ion pairs (Bjerrum pairs) dissociate into free ions and vice versa: 

$$\text{(+−)} \rightleftharpoons \text{(+)} + \text{(+−)}$$

Onsager showed that the dissociation constant $K$ changes as an explicit function of electric field $E = |\vec{E}|$ and temperature $T$. For an electrolyte of charges $±q$ and permittivity $\epsilon = \epsilon_0 \epsilon_r$, he found the scaling form:

$$K(E)/K(0) = F(x) = I_1(\sqrt{8x})/\sqrt{2x} = 1 + x + x^2/3 + O(x^3)$$  \ (1)

where $x = q^3 E/8\pi\epsilon k_B T^2$ and $I_1$ is a modified Bessel function. The result is universal in that initial concentrations and mobilities disappear from the dimensionless argument $x$, which can be cast as the ratio of two lengths: the Bjerrum length $\ell_T = q^2/8\pi\epsilon k_B T$ and the field length $\ell_E = k_B T/qE$ (see Fig. 1). The leading linear term signals the non-equilibrium nature of the effect, as it would be forbidden by symmetry in equilibrium. It gives a remarkably large response at small fields, making the Wien effect a dominant phenomenon in many experimental situations.

The increase in $K(E)$ is manifest in the relative change in free ion concentration $n_f(E)/n_f(0)$. The strong and weak electrolyte are those limits in which there is an exhausted or an inexhaustible source of charge, respectively. For the strong electrolyte, the relative change $n_f(E)/n_f(0)$ is a function not only of $F(\ell_T/\ell_E)$, but also of the initial density. In the weak electrolyte limit, the free charge concentration evolves in a universal manner: $n_f(E)/n_f(0) = \sqrt{F(\ell_T/\ell_E)}$, while the bound pair concentration is buffered, i.e. replenished rapidly from the reservoir so that $n_b(E)/n_b(0) = 1$.

New charges appear in the form of closely bound pairs yielding a double equilibrium between charge source, pairs and free charges: (0) $\rightleftharpoons$ (+−) $\rightleftharpoons$ (+) (+−). The ‘vacuum’ (0) may be a classical electrolyte of molecules which can dissociate into charges, while more general charge vacua occur in many chemical and physical processes. Important examples are $2\text{H}_2\text{O} \rightleftharpoons [\text{H}_3\text{O}^+ \text{HO}^-] \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$, in the case of both water and ice; thermal and optical electron-hole generation in semiconductors$^{14}$; or magnetic monopole generation in spin ice$^{21,22}$. These effects together with the intrinsic interest in discretizing a continuum model, for example as a basis for a renormalization group treatment, motivated our study of the Wien effect on a lattice.

We present extensive numerical simulations of the Wien effect, which allow us to compute bulk quantities – density, conductivity – at the same time as microscopic correlations. The absence of Wien effect simulations in the literature appears in part due to the technical difficulties involved: a combination of low ion densities, strong correlations and long-range interactions pose formidable obstacles. However, as we show below, we are able to simulate a regime where the Wien effect is observable – in fact, strong – and which is relevant for many problems.

Monte Carlo simulations were performed on a 1 : 1 symmetric electrolyte on a diamond lattice, with periodic boundaries and with the field placed along the [100] cubic axis (see Methods). The diamond structure was chosen because its four-fold coordination is applicable to many experimental situations, such as proton transport in water and ice, electron transport in germanium and silicon...
and effective magnetic monopole transport in spin ice materials.

Figure 1: a, Reduced variables. Rough estimates of $|\mu^*| \text{ and } T^*$ for systems where the second Wien effect has been observed. Water and water ice are strong protonic conductors exhibiting the Wien effect. Molten phosphoric acid – the strongest known protonic conductor – was added as it should show interplay of the Wien effect and screening. The Wien effect was first measured in acetic acid. For further details see Supplementary Table 1 and References. The green shaded area is accessible to our simulations. Red shading corresponds to dilute weak electrolyte limit. The dashed line gives the limit of applicability of Onsager’s original theory. The dotted line shows validity of theory when extended to include screening.

b, Length scales in Coulomb gas for $\mu^* = -1.45$ (relative to diamond lattice site separation). At the Bjerrum length $\ell_T$ (blue line) thermal fluctuations become comparable with the Coulomb binding energy. The Debye length $\ell_D$ (green line) is the screening length. The mean charge separation $\ell_n$ (cyan line) shows the dilution of the electrolyte. The field length $\ell_E$ give the distance over which the field $E$ exerts work equal to thermal energy. The shaded region shows the extent of our simulations. Extreme dilution of the Coulomb gas prevents simulations at low temperatures, while at high temperatures the electrolyte is dense and highly correlated. The maximum system size simulated was $8 \times 24^3 = 110592$ diamond lattice sites corresponding to $L/a = 55.4$.

The system properties are controlled by two thermodynamic variables: the free charge chemical potential $\mu$ and the temperature $T$. It is appropriate to reduce these by the Coulomb energy at contact $U_0 = q^2/4\pi \epsilon a$, to create two dimensionless variables $\mu^* = \mu/U_0$ and $T^* = k_B T/U_0$. Fig. 1a shows how similar parameters represent a variety of different systems. Fields are likewise given in reduced units, $E^* = U_E/U_0$ where $U_E$ is the work done by field $E$ when a charge hops between neighboring sites. We choose $T^*$ and $\mu^*$ to obtain the dilute weak electrolyte regime $1 \gg n_f \gg n_b$.

Fig. 1b displays the accessible window in which the Wien effect can be analyzed in terms of the Bjerrum and field lengths as well as two other characteristic length scales of the Coulomb gas: the Debye length and the mean charge separation (See Supplementary Discussion 1 for a detailed discussion).

The evolution of $\Delta n_f/n_f$ with field at fixed temperature $T^* = 0.140$ is shown in Fig. 2a. The
Figure 2: **Second Wien effect** \((|\mu^*| = 1.45)\). a, The charge density increases strongly in field at \(T^* = 0.140\). The black curve is Onsager’s theory. The linear regime is visible for \(E^*\) below 0.04. Onsager’s theory extrapolates to a negative intercept on the ordinate, \(\gamma(0) - 1\). The breakdown of screening occurs when \(\ell_E\) exceeds \(\ell_D\), and the intercept on the abscissa corresponds to the field where the two lengths are equal, at low temperature. Liu’s theory (grey curve) accounts for screening in the lowest fields. At high fields, finite size effects appear (see Supplementary Discussion 6). b, The total zero-field density (circles) is well modelled by Bjerrum theory (full black line). Simpler theories, including Debye–Hückel (dashed line) and non-interacting theory (dotted line), underestimate the density. The extracted bound pair density (triangles) is slightly underestimated by Bjerrum theory (blue line), but the temperature dependence is correct. Kinks on the lines appear because the lattice association constant is discontinuous where the Bjerrum length crosses subsequent lattice site separations. c, Zero-field free-charge activity coefficient \(\gamma(0)\) extracted from the density increase matches predictions of Bjerrum theory. Comparison with Debye–Hückel theory neglecting bound pairs is also shown. Inset: The quality of the fit \(\gamma(E^*)/\gamma(0)\) remains good for all temperatures shown, confirming that the Wien effect survives with appropriate corrections up to high temperatures and densities \(\sim 10^{-2}\). Extracted \(\gamma(E^*)/\gamma(0)\) for \(T^* = 0.140\) is compared with Liu’s function (grey line) and a fitted exponential decay of correlations (black line). Red line denotes the theoretical value of \(1/\gamma(0)\). d, The conductivity increase is similarly significant and also involves field dependence of the ionic mobility. It is reduced in the case also involving field dependence of Metropolis dynamics. The black curve represents Onsager’s theory adjusted for both Metropolis dynamics and the influence of the screening cloud on mobility.
first thing to notice is that there is a huge effect! A five-fold increase in the free charge density is induced for a field as small as $E^* = 0.125$, even though it provides the smallest energy scale in the problem. The second is that there is close agreement between numerics and theory. The data are compared with both Onsager’s original theory and the subsequent modification, which takes into account Debye screening effects, the latter being characterized by the activity coefficient $\gamma$. Coulomb interactions shift the effective chemical potential by $k_B T \ln \gamma$. The dissociation constant, $K$ is related to the densities through the concentration quotient, $K_c = (n_f/2)^2/(n_b/2) = K/\gamma^2$, so that if $n_b$ is independent of field

$$\frac{\Delta n_f(E)}{n_f(0)} = \sqrt{\frac{K_c(E)}{K_c(0)}} - 1 = \frac{\gamma(0)}{\gamma(E)} \sqrt{F(\ell_T/\ell_E)} - 1. \quad (2)$$

In the first case, one assumes that the Debye screening cloud surrounding a charge is destroyed by the applied field, so that $\gamma(E) = 1$. This describes all data except for the lowest fields ($E^* = 0.02$). For smaller fields Liu proposed a logarithmic field dependence for $\gamma(E)$ (see methods). From Fig. 2a (inset) one can see that we find close agreement with Liu’s theory in the low field region. At higher fields the theory underestimates the observed Wien effect by around 5%. This difference can be traced to finite size effects in the simulation (see Supplementary Discussion 6). We note that in making these comparisons, there are no fitting parameters, as the activity coefficient is a quantity calculated independently (see Methods).

Also shown in Fig. 2a, is the relative increase in bound pair density as a function of field, $\Delta n_b/n_b$. Bound charges are defined as being separated by less than the Bjerrum length, but we find that the functional form is independent of the details of this definition. $n_b$ does indeed remain approximately constant up to $E^* = 0.04$, hence confirming the buffering hypothesis. Above this threshold there is an increase in bound pair concentration, but at a reduced rate compared with $\Delta n_f/n_f$. The field therefore generates a considerable increase in the total charge concentration.

The activity coefficient used in the comparison was calculated using Debye–Hückel–Bjerrum theory, which regards free charges and bound pairs as distinct chemical species. The quality of this approximate theory for the values of $T^*$ and $\mu^*$ chosen, is illustrated in Fig 2b, where we show the evolution of the total density and of $n_b$ as a function of $T^*$ for zero external field. The density is predicted accurately and $n_b$ to a reasonable approximation. In Fig 2c we compare the calculated and measured values $\gamma(0)$ for the free particles, which in the dilute regime can be expressed as the ratio of ideal gas density and actual density: $\gamma(0) = 2 \exp(\mu^*/T^*)/n_f < 1$. Numerics matches theory for the Wien effect to below $\gamma(0) = 0.6$, well beyond the formal limit of validity $\gamma(0) \to 1$. In Fig. 2b (inset) we show the evolution of $\gamma(E)$ for $T^* = 0.140$, this time extracted from simulation using equation (2). The crossover to an asymptotic regime with $\gamma(E) \sim 1$ occurs for $E^* \sim 0.02$, as can be expected from Fig. 2a. While Liu’s expression captures the initial increase of $\gamma(E)$, it turns out that an exponential decay of screening captures the crossover better.

The Wien effect was originally observed in measurements of conductivity, $\sigma(E)$, which exhibits
large non-Ohmic corrections to the zero field value, $\sigma(0)$. In many of the systems listed above, $\sigma = q^2 \omega n_f$, is of great practical importance. It can be used as a diagnostic for the Wien effect if the mobility, $\omega$, is field independent, or if its field dependence is known. In Figure 2d we show the relative increase in conductivity from numerical simulation at $T^* = 0.140$. Again we remark that the increase is large; the conductivity triples over the field range studied. However, the increase falls systematically below that predicted from equation (2).

The shortfall arises because the mobility is a decreasing function of field, as shown in figure 3 for Metropolis dynamics. For non-interacting particles, Metropolis dynamics yields: $\omega_0(E^*)/\omega_0(0) = 1 - \exp(-E^*/T^*)/(E^*/T^*)$. For strong fields, the simulated mobility clearly approaches this asymptotically, while for small fields it is Coulomb interactions which lead to a reduced value. A crossover function can be constructed by first estimating the relative zero-field reduction, $h(\ell_T, \ell_D)$, from Fuoss-Onsager theory for the conductivity\textsuperscript{20} and then estimating the suppression of this reduction by the field, $g(\ell_D/\ell_E)$ from Wilson’s theory for the first Wien effect (details in Supplementary Discussion 5):

$$\frac{\omega(E^*)}{\omega(0)} = \frac{1 - h(\ell_T, \ell_D) g(\ell_D/\ell_E)}{1 - h(\ell_T, \ell_D)} \frac{1 - \exp(-E^*/T^*)}{E^*/T^*}. \tag{3}$$

The data in Fig. 3 accurately follows this expression. Supplementing the Wien effect theory (2) with an analysis of the field dependent mobility restores a good agreement of theory and simulations in Fig. 2d.

Figure 3: Relative mobility change with field ($\mu^* = -1.45$, $T^* = 0.155$). The high field mobility is dominated by a reduction characteristic of Metropolis dynamics employed in our simulations, while at low fields the interactions influence the mobility. Mobility at lowest fields is noisy as the drift speed becomes very small.

Over and above the numerical verification of the existence of the Wien effect we see here that simulation can provide deep insight into the role of the microscopic dynamics for this non-Ohmic phenomenon, providing specific information on the field dependent mobility both in model and in
experimental systems. Simulations such as ours can thus be used for the development of models for microscopic dynamics.

Figure 4: Charge correlations ($\mu^* = -1.45$, $T^* = 0.140$). a, Pair correlation function ($g_{\pm} - 1$) for $E^* = 0.021$ along the $\hat{z}$ axis; averaged over the azimuthal angle and mirrored for clarity. The statistical weight is strongly peaked at nearest-neighbour sites, which are most affected by the lattice structure, while asymmetry develops in the field. The black circle marks the Bjerrum volume. b, The decrease in the ion association $1/K_c = \sum_{|\vec{r}|<\ell_T} g_{\pm}$. The Wien effect leads to reduction of correlations initially linear with field as the charges escape bound pairs. In the low field region the quadratic field dependence is recovered due to screening. Different symbols show that restricting the bound pairs from the Bjerrum volume to nearest neighbours or up to second-nearest neighbours yields similar behaviour because the nearest-neighbour contribution dominates the correlations. The Onsager function is common to all definitions of bound pairs, while $\gamma(0)$ differs slightly for different definitions of free charges, which can be best observed at high fields. The zero-field value of the association constant differs from the continuum value found by Bjerrum, but their relative change is universal.

Complementing macroscopic quantities, the microscopic processes at the heart of the Wien effect are also accessible to our simulations. Particularly important is $g_{\pm}(\vec{r}) = (\langle n^+(\vec{r})n^-(0) \rangle - \langle n^+(0) \rangle \langle n^-(0) \rangle)/\langle n^2(0) \rangle$, the correlation function between a negative charge at the origin and a positive charge at position $\vec{r}$, where $\langle \cdot \rangle$ denotes thermal average. The pair correlation function is shown in Fig. 4a, where in finite field an asymmetry develops along the field axis. The amplitude of the correlations at small $r$ decreases strongly with increasing field.

The correlation function divides into symmetric and anti-symmetric parts, $g_{S/A}(\vec{r})$, with respect to inversion $\vec{r} \rightarrow -\vec{r}$ or $\vec{E} \rightarrow -\vec{E}$. The sum of $g_{S}(\vec{r})$ over $|\vec{r}| < \ell_T$ gives access to the observables of the Wien effect: $\sum_{|\vec{r}|<\ell_T} g_{S}(\vec{r}) = 1/K_c$. This is confirmed in Fig 4b where we compare the evolution of $K(0)/K(E^*)$ evaluated directly from $g_{S}(\vec{r})$, with the theoretical expressions. An agreement is found both in the low field, screened region, and the higher field region, thereby linking microscopic correlations with bulk (experimental) observables.
Future simulations could be adapted to incorporate a diverse range of system details, such as competing dynamical processes, disorder, finite size and tunable boundary conditions. A first example concerns the competition of Brownian diffusion with variable range hopping and the various injection processes in Poole-Frenkel conduction in semiconductors. Here the possibility of a Wien effect for fractionalized carriers on ‘frustrated’ lattices can also be tested. A second example concerns the generation of photocurrents in solar cell devices, varying the role of an exciton as a short lived transient or as an effective ion pair. Other examples include ionic conduction in oxide glasses, where there is experimental evidence of the Wien effect, but where non-rigid networks, disorder and rough energy landscapes are complicating factors; protonic conduction in hydrogen-bonded networks like water ice or phosphoric acid, where correlated Grotthus-type conduction competes with other processes; or magnetic monopole conduction in spin ice or artificial spin ice, where similar constraints apply and where one also has to contend with the effects of large amplitude internal fields.

More generally, the advantages offered by finite lattice simulations could be exploited to assess the effect of boundaries or of a vanishing number of ion pairs, as might be relevant to liquids in the highly confining environment of biophysical systems, or else to explore the influence of the Wien effect on films confined between membranes, or the electrical double layer, where large gradients of electrical potential can be created. In this context dynamical studies of the Wien effect would also be relevant. Thus our method may in the future be specialized to treat outstanding problems of non-linear conduction across a wide variety of scientific fields, from electrochemistry and biochemistry to solid state physics and electrical engineering.
Methods

The zero-field concentration can be computed iteratively from the following set of equations:

\[ n = \frac{2 \exp(\mu^*/T^*)}{\alpha \gamma + 2 \exp(\mu^*/T^*)} \]  
\[ \gamma = \exp\left(-\frac{\ell_T}{\ell_T + \ell_D/\sqrt{\alpha}}\right) \]  
\[ \alpha = \frac{2}{1 + \sqrt{1 + 2K_A \gamma n}} \]  
\[ \ell_D = \sqrt{\frac{1}{8\pi \ell_T n}} \]  

where the first equation gives the density of a lattice gas with chemical potential \( \mu^* \), degree of dissociation by \( \alpha = n_f/(n_f + n_b) \), and free charge correlations described by \( \gamma \). The activity coefficient \( \gamma \) follows the Bjerrum mean field theory, while \( \alpha \) results from the chemical equilibrium between free and bound charges given by association constant \( K_A \). The last equation is the definition of the Debye length. The Bjerrum association constant \( K_A \) is obtained by lattice summation:

\[ K_A = \sum_{\{\vec{r}_r \leq \ell_T\}} \exp\left(-\frac{2\ell_T}{r}\right) \]  

Using the continuous approximation to \( K_A \) overestimates the concentration at low temperatures and underestimates it at high temperatures. Concentrations are related to the volume per site and correspond to molar fractions of individual species. Association and dissociation constants are related by \( K_A = 1/K \).

Liu’s formula: In the case where screening dominates the Wien effect (\( l_E \gg l_D \)), Liu and Onsager solved perturbatively the two body dynamics in the Debye potential with the first order result:

\[ \frac{K_c(E)}{K_c(0)} = 1 + \frac{\ell_T/\ell_E + (2\ell_T/\ell_D)f(\ell_D/\ell_E)}{1 + 2\ell_T/\ell_D} + O\left(\left(\frac{\ell_T}{\ell_E}\right)^2\right) \]  
\[ f(x) = \frac{\ln(1 + x)}{x} \]  

Note that this formula only captures the linear term \( \ell_T/\ell_E \) of the Wien effect and uses the following approximation of the activity coefficient \( \gamma = \exp(-\ell_T/(\ell_T + \ell_D/\sqrt{\alpha})) \approx 1 - \ell_T/\ell_D \). To this degree of approximation the activity coefficient in field is approximate \( \gamma(E) = \gamma(0)^f(\ell_D/\ell_E) \).

Monte Carlo: Simulated systems were blocks of diamond lattice with \( 8 \times L^3 \) sites, with \( L \) up to 24 and with periodic boundary conditions. Each site can be empty or occupied by a positive or a negative unit charge. Updates proceed by selecting a bond between two sites chosen at random and creating or annihilating a pair of charges (at fixed chemical potential \( \mu^* \)), or by moving a charge along the bond. Acceptance probabilities are given by the Metropolis algorithm. The Coulomb interaction between charges is treated by Ewald summation. Sample systems are first equilibrated.
in zero-field, the [001] field is set to a given value. After the transient effects vanishes, the in-field values are extracted. Free charges are separated from bound pairs using $K_c = n_f^2/(2(n - n_f))$, where $K_c$ is extracted from the pair correlation function.

In our simulations the constant field generates a direct current flowing through the periodic boundaries[[23]], with energy dissipation of $qLE$ per charge passing through the periodic cell. The fundamental problems of applying an electric field on a torus are bypassed here as the stochastic dynamics of the Metropolis algorithm are intrinsically non-ballistic, which ensures a finite value of $\sigma$. The current is computed as a bulk quantity, therefore any process moving a positive charge in the field direction gives a positive current and vice versa.

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Author Contributions
VK conducted the simulations. All four authors contributed equally to the formulation and development of the project, as well as to the text of the paper.

Competing Financial Interests
The authors declare no competing financial interests.

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Supplementary Information

1. Supplementary Discussion: Characteristic length scales

There are multiple length scales relevant to the physics of an electrolyte in addition to the Bjerrum length $\ell_T = q^2/(8\pi\epsilon k_B T)$ and the field length $\ell_E = k_B T/qE$: the Debye length $\ell_D = \sqrt{k_B T V_0/q^2 n}$, above which the Coulomb interaction is screened through the formation of a correlated charge cloud ($V_0$ is the volume per lattice site); the mean charge separation, $\ell_n = (V_0/n)^{1/3}$; a minimum length $a$ for the separation of two charges, as well as the macroscopic scale $L$ of our numerical simulation box. The main result of Onsager’s theory, equation (1), is valid in the limit that $\ell_D$ and $L$ exceed $\ell_T$ and $\ell_E$, which in turn must exceed the microscopic length $a$. The small field limit exposing the linear field dependence requires the rigorous separation of scales: $L \gg \ell_D \gg \ell_n \gg \ell_E \gg \ell_T \gg a$, which can only be approached for temperatures well below the temperature scale set by the chemical potential, $\mu$. In Fig. 1b of the main text we show the evolution of these lengths with temperature for our lattice electrolyte. The window of application available to our simulations, in which the Wien effect can be measured, is bounded from above by the crossover, $\ell_D < \ell_T$ and from below by the finite size limit, $L < \ell_n$, below which we have, on average fewer than one pair of particles in our simulation box.

2. Supplementary Discussion: Reduced units

In the main text, reduced units for corresponding states of electrolytes were introduced: $\mu^* = \mu/U_0$ and $T^* = k_B T/U_0$, $E^* = U_E/U_0$. In table S1 we list appropriate parameters for Dy$_2$Ti$_2$O$_7$ spin ice at 0.5 K, for water ice at 253 K, for pure liquid water at 298 K and several other materials. We added phosphoric acid, since it is the strongest known protonic conductor and should exhibit a screened version of Wien effect (with defect concentrations $\sim 0.07$). Note that the relative permittivity for water ice is not the bulk value but instead the high frequency value, as advocated by Onsager and Dupois, from which other parameters are taken. The low frequency value was assumed for liquid water and phosphoric acid. For the spin ice/lattice electrolyte parameters, the corresponding charge concentration of order $n \sim 10^{-5}$ is possible to handle numerically, while being sufficiently small to represent the low density limit in general. Likewise, Debye–Hückel and Bjerrum corrections for this parameter set are small but non-negligible. Hence it is a suitable system on which to test the expectations outlined above.
Table 1: Parameters for the double equilibria

| System                          | $a$ [Å] | $q/e$       | $\epsilon_r$ | $T$ [K] | $|\mu|$ [K] | $T^*$ | $\mu^*$ |
|---------------------------------|---------|-------------|--------------|---------|------------|-------|--------|
| Spin ice Dy$_2$Ti$_2$O$_7$      | 4.33    | 1/112       | 1            | 0.5     | 4.46       | 0.163 | 1.453  |
| Water ice                       | 2.75    | 0.58        | 3.1          | 253     | 6670       | 0.038 | 1.01   |
| Pure water                      | 3.01    | 1           | 80.1         | 298     | 6000       | 0.44  | 8.93   |
| Acetic acid (aq) (1 mmol/dm$^3$) | 0.98    | 1           | 80.1         | 298     | 4350       | 0.14  | 2.06   |
| AOT in cyclohexane (0.1 mmol/dm$^3$) | 25      | 1           | 2.02         | 298     | 4900       | 0.09  | 1.48   |
| Anhydrous orthophosphoric acid   | 2.6     | 1           | 61           | 383     | 3300       | 0.36  | 3.13   |
| Na-Ca-SiO$_2$ glass             | 5       | 1           | 8            | 302     | 2000       | 0.07  | 0.5    |
| Methemoglobin (83 µmol/dm$^3$)   | 1.6     | 1           | 80.1         | 298     | 3200       | 0.23  | 2.74   |

In this study, we simulated a system corresponding to Dy$_2$Ti$_2$O$_7$ spin ice parameters between 0.41 K and 0.8 K. We also simulated a lattice electrolyte with parameters $\{a = 5Å, q/e = 1, \epsilon_r = 20\}$, chemical potentials ranging from 2500 K to 2900 K ($T^* = 0.162–0.221$), and at temperatures between 270 K and 370 K ($|\mu^*| = 1.496–1.735$). All systems confirm the conclusions presented in the main text.

3. Supplementary Discussion: Non-equilibrium quantities

Conceptually, it is important to draw a distinction between thermodynamic quantities in equilibrium and their extension to the field-driven case. Practically, the only observable out of equilibrium is the concentration quotient $K_c(E) = n_f(E)^2/(2n_b(E))$. If we relate it to the dissociation constant and the activity coefficient in the same way as in equilibrium, $K_c(E) = K(E)/\gamma^2(E)$, we face the problem of separating the increase in free charge density – because the field increases the dissociation – from the decrease in free charge density – due to the reduced screening.

The conductivity measurements in strong electrolytes show that the ionic atmosphere cannot establish itself in strong external fields (first Wien effect). It is safe to assume $\gamma(E) \rightarrow 1$ in high fields. Practically, strong fields in this context corresponds to the length scale ordering $\ell_E < \ell_D$. In this limit Onsager’s prediction matches the simulations and experiments well. Onsager’s expression for $K(E)$ is justified and $\gamma(E)$ goes from $\gamma(0)$, as predicted by Bjerrum’s theory, to high field limit of unity.

An early discussion of non-equilibrium quantities in the context of Wien effect can be found in Patterson and Freitag, where an “un-screening coefficient” was proposed as a designation for the non-equilibrium activity coefficient.

4. Supplementary Discussion: Buffering

Two types of double equilibrium can be distinguished by the source of charges: dissociating molecules or creation from the vacuum. The creation from vacuum can also be modelled as a
“reaction” of two empty sites in case of ice and spin ice. In this section, we present a simple
calculation to explicitly show how the double equilibrium shifts due to the second Wien effect.
The result for dissociating molecules is stated in Onsager’s paper without calculation. Charge
generation exhibits similar properties. Both cases show buffering of the bound charge concentration
in the dilute weak electrolyte limit \( n_e \gg n_f \gg n_b \).

In the following, \( n_m, n_e, n_f, \) and \( n_b \) are the densities of molecules, empty sites, free ions, and
bound ions, respectively. Densities after the equilibrium shifts are denoted with a prime, e.g. \( n'_f \).

The double equilibrium \((0) \rightleftharpoons (\mp) \rightleftharpoons (+) + (\mp)\) where charges are created from molecules is
described by:

\[
\frac{n_b}{2} = K_m n_m \quad (10) \\
\frac{(n_f/2)^2}{2} = K_c n_b/2 \quad (11) \\
2n_m + n_b + n_f = 1, \quad (12)
\]

where we have normalized the total concentration to unity (mole fraction). Substituting the first
two equations into the last gives:

\[
2(n_f/2)^2(1 + 1/K_m)/K_c + n_f - 1 = 0, \quad (13)
\]

which is equivalent to the equation for free charge density in case of a single equilibrium \((\mp) \rightleftharpoons (+) + (\mp)\) with dissociation concentration quotient \( K_d = K_c/(1 + 1/K_m) \). The Wien effect gives
for the dissociation constant in field \( K_d(E) = K_d\gamma(0)^2 F(\ell_T/\ell_E) \):

\[
\gamma(0)^2 F(\ell_T/\ell_E)n_f^2/2 + n'_f - 1 = 0. \quad (14)
\]

Expressing \( n'_f \) in terms of the equilibrium concentration gives:

\[
\frac{n'_f}{n_f} = \gamma(0)^2 F(\ell_T/\ell_E)n_f \sqrt{1 + \frac{4(1 - n_f)}{\gamma(0)^2 F(\ell_T/\ell_E)n_f^2} - 1} \quad (15)
\]

If \( n_f \ll 1 \), we can expand into series:

\[
\frac{n'_f}{n_f} = \gamma\sqrt{F(\ell_T/\ell_E)} - \gamma(0)^2 F(\ell_T/\ell_E) + O(n_f^2) = \gamma\sqrt{F(\ell_T/\ell_E)} + O(n_f). \quad (16)
\]

The total concentration of bound pairs and molecules \((1 - n_f) \approx 1\) stays essentially unchanged as
well as the equilibrium between them. The bound pair concentration is constant to first order:

\[
\frac{n'_b}{n_b} = 1 + O(n_f). \quad (17)
\]
The bound pairs in this case can be considered as precursors of the fully associated molecules. The Wien effect is a non-equilibrium process where the actual rates whose ratio gives the dissociation quotient matter. In addition, the actual rates of transformation between molecules and bound pairs have to be faster than the rates involving exchange between free and bound charges.

The double-equilibrium with charge generation 

\[ (00) \rightleftharpoons (\sigma^+ - \sigma^-) \rightleftharpoons (\sigma^+ \sigma^-) \]

studied in the main text can be described by the following set of equations:

\[
\frac{n_b}{2} = K_c n_e^2 \tag{18}
\]

\[
\left(\frac{n_f}{2}\right)^2 = K_c n_b / 2 \tag{19}
\]

\[
n_e + n_b + n_f = 1. \tag{20}
\]

Application of the external field shifts the concentration quotient \( K_c \) to \( K_c(E) = K_c \gamma(0)^2 F(\ell_T / \ell_E) \), while the creation constant \( K_c \) stays constant. Solving for the in-field concentrations \( n'_f \), and \( n'_b \) in terms of the zero-field ones, we find:

\[
\frac{n'_f}{n_f} = \frac{\gamma(0)^2 F(\ell_T / \ell_E)n_f}{2 n_b} \times \left[ \left( 1 + \frac{1 - n_b - n_f}{\gamma \sqrt{F(\ell_T / \ell_E)n_f}} \right)^2 + \frac{4n_b}{\gamma(0)^2 F(\ell_T / \ell_E)n_f^2} - \left( 1 + \frac{1 - n_b - n_f}{\gamma \sqrt{F(\ell_T / \ell_E)n_f}} \right) \right] \tag{21}
\]

\[
\frac{n'_b}{n_b} = \frac{\gamma(0)^2 F(\ell_T / \ell_E)n_f^2}{4 n_b^2} \times \left[ \left( 1 + \frac{1 - n_b - n_f}{\gamma \sqrt{F(\ell_T / \ell_E)n_f}} \right)^2 + \frac{4n_b}{\gamma(0)^2 F(\ell_T / \ell_E)n_f^2} - \left( 1 + \frac{1 - n_b - n_f}{\gamma \sqrt{F(\ell_T / \ell_E)n_f}} \right) \right]^2 \tag{22}
\]

Expanding the previous result \( (n_e \gg n_f \gg n_b) \) yields:

\[
\frac{n'_f}{n_f} = \sqrt{F(\ell_T / \ell_E)} + \left( \gamma \sqrt{F(\ell_T / \ell_E)} - \gamma(0)^2 F(\ell_T / \ell_E) \right)n_f + O(n_b, n_f^2) \tag{25}
\]

\[
\frac{n'_f}{n_f} = \sqrt{F(\ell_T / \ell_E)} + O(n_b, n_f) \tag{26}
\]

\[
\frac{n'_b}{n_b} = 1 + 2 \left( 1 - \gamma \sqrt{F(\ell_T / \ell_E)} \right)n_f + O(n_b, n_f^2) = 1 + O(n_b, n_f) \tag{27}
\]

The fraction of bound pairs stays constant up to a linear order in \( n_b \), which is of the order \( 10^{-5} \) at \( \{\mu^* = -1.45, T^* = 0.140\} \).

To sum up, the requirements for the kinetics presented in the main text to hold are that empty sites dominate (weak electrolyte) and that the charge creation kinetics is faster than the bound pair dissociation. This is indeed the case in MC simulations, where charge creation is a single step process, while bound pair dissociation takes multiple steps.
5. Supplementary Discussion: Mobility – Metropolis algorithm, Onsager–Fuoss theory

The Metropolis algorithm yields a relative decrease of mobility with field, resulting from the unity probability of stepping in the field direction and probability \( \exp(-E^*/T^*) \) of moving against the field for each proposed step:

\[
\omega_0(E^*) = \frac{1 - \exp(-E^*/T^*)}{E^*/T^*},
\]

where \( \omega_0 \) is the mobility of an equivalent non-interacting particle. Note, that since the proposed steps are local, it should be possible to rescale the time by the acceptance probability to obtain a close approximation to the physical time.\(^{11}\) The mobility would still be field-dependent, as predicted e.g. for monopole hopping in spin ice.\(^ {10} \)

The full zero-field mobility \( \omega(0) \) of the Coulomb gas is further reduced because of the ionic atmosphere slowing down the charge. The zero-field correction is well approximated by Fuoss-Onsager conductivity theory\(^ {13} \) (which fails when the parameter \( \ell_T/\ell_D \) approaches unity, which happens around \( T^* = 0 \)). Fuoss-Onsager theory for a binary electrolyte takes the following form:

\[
\omega(0) = 1 - h(\ell_T, \ell_D) = \frac{2 - \sqrt{2}}{3} \ell_T
\]

\[
-\frac{1}{3} \left( \frac{\ell_T}{\ell_D} \right)^2 \ln \left( \frac{\ell_T}{\ell_D} \right) - \left( \frac{2\ell_T}{\ell_D} \right)^2 N \left( \frac{2\ell_T}{a} \right) + \left( \frac{\ell_T}{\ell_D} \right)^2 \gamma(0)^2 K_C
\]

\[
T_1 \left( \frac{2\ell_T}{a} \right) = \exp \left( -\frac{2\ell_T}{a} \right) \left( 1 + \frac{2\ell_T}{a} + \frac{1}{2} \left( \frac{2\ell_T}{a} \right)^2 \right)
\]

\[
N \left( \frac{2\ell_T}{a} \right) = 1.4985 + \frac{0.2071 T_1(2\ell_T/a) - 0.03066}{1 - T_1(2\ell_T/a)}
\]

\[
K_C \left( \frac{2\ell_T}{a} \right) = \frac{1}{3} \left( \text{Ei} \left( \frac{2\ell_T}{a} \right) - \frac{a}{2\ell_T} \left( 1 + \frac{a}{2\ell_T} \exp \left( \frac{2\ell_T}{a} \right) \right) \right).
\]

To describe the field dependence of this correction, we use Wilson’s calculation of the first Wien effect (for review see Eckstrom and Schmelzer\(^ {12} \)), which is known to give the field evolution of the term linear in \( \ell_T/\ell_D \) from the previous equation. We assume that the other terms decay in the same or similar fashion; an assumption that appears \textit{a posteriori} to be a good approximation. We obtain

\[
\frac{\omega(E^*)}{\omega_0(E^*)} = 1 - h(\ell_T, \ell_D) g(\ell_D/\ell_E),
\]

where

\[
g(x) = \frac{3}{(4 - 2\sqrt{2})x^3} \left[ x\sqrt{1 + x^2} - \arctan \left( \frac{x}{\sqrt{1 + x^2}} \right) - \sqrt{2}x + \arctan \left( \sqrt{2}x \right) \right].
\]

and \( g(x) \) is scaled to decrease from unity in zero field to zero in infinite field.
The relative change of the total mobility is thus given by:

\[
\frac{\omega(E^*)}{\omega(0)} = \frac{1 - h(\ell_T, \ell_D) g(\ell_D/\ell_E) 1 - \exp(-E^*/T^*)}{1 - h(\ell_T, \ell_D)} \frac{1 - h(\ell_T, \ell_D)}{E^*/T^*}.
\]

Note that in all calculations we only use terms from the relaxation field and exclude terms related to electrophoresis which does not occur because there is no hydrodynamics in our simulations, which have only stochastic dynamics.

6. Supplementary Discussion: Finite-size effects

Zero-field concentration of charges shows large finite-size effects if \( l_D > L/2 \). The concentration decreases with system size because the volume accessible is too small for a pair of particles to become unbound. For \( \mu^* = -1.45 \) and \( L = 24 \), the simulation temperature must stay above \( T^* = 0.130 \). Figures in the main text are at \( T^* \gtrsim 0.140 \), which is sufficiently far above the limit because concentration grows exponentially with temperature.

A different kind of finite size effects appears at high fields. The screening cloud becomes elongated and charges diffuse fast in the field direction. Due to periodic boundary conditions, the charges eventually start to interact with a copy of their screening cloud that has wrapped around the system – a partial revival of screening, which decreases \( \gamma(E) \), leading to the observed charge concentration exceeding that in thermodynamic limit. We confirmed the process by inspecting the pair correlation functions. For \( \mu^* = -1.45 \), \( L = 24 \), and \( T^* = 0.140 \) these effects set in above \( E^* = 0.08 \).

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