An idealised approach of geometry and topology to the diffusion of cations in honeycomb layered oxide frameworks

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Honeycomb layered oxides are a novel class of nanostructured materials comprising alkali or coinage metal atoms intercalated into transition metal slabs. The intricate honeycomb architecture and layered framework endows this family of oxides with a tessellation of features such as exquisite electrochemistry, unique topology and fascinating electromagnetic phenomena. Despite having innumerable functionalities, these materials remain highly underutilised as their underlying atomistic mechanisms are vastly unexplored. Therefore, in a bid to provide a more in-depth perspective, we propose an idealised diffusion model of the charged alkali cations (such as lithium, sodium or potassium) in the two-dimensional (2D) honeycomb layers within the multi-layered crystal of honeycomb layered oxide frameworks. This model not only explains the correlation between the excitation of cationic vacancies (by applied electromagnetic fields) and the Gaussian curvature deformation of the 2D surface, but also takes into consideration, the quantum properties of the cations and their inter-layer mixing through quantum tunnelling. Through this work, we offer a novel theoretical framework for the study of multi-layered materials with 2D cationic diffusion currents, as well as providing pedagogical insights into the role of topological phase transitions in these materials in relation to Brownian motion and quantum geometry.

Nanotechnology has become the cornerstone of contemporary science for its role in the discovery of new materials with unprecedented chemical properties and unconventional physical phenomena. Typically these stellar properties are optimised and refined through manipulation of matter at an atomic or molecular level. As such, the fundamental understanding of the physical laws surrounding the interaction of atoms and atom clusters in the different phases of matter is invaluable in the evolution of this technology. Theoretical advancements into the connection between continuous symmetries of the action and conservation laws (Noether’s theorem) in quantum field theory and geometry has played an enormous role in revealing exemplary quantum effects in condensed matter systems. This has singled out materials comprising simple geometric arrangements of atoms as exemplars of Noether’s theorem whilst offering a great segue into crystallography. This rationale has generated interest particularly in two-dimensional (2D) honeycomb layered oxides whose heterostructural layout plays host to an assortment of desirable electrochemical, magnetic and topological properties\(^1\,4\).

Honeycomb layered oxides generally can be envisaged to adopt the following compositions of ordered structures: 

\[ \begin{align*}
A_2^{+} L^{2+} D^{4+} O_5 (A_6^{+} L^{2+} D^{4+} O_2), & \quad A_2^{+} L^{2+} D^{4+} O_6 (A_6^{+} L^{2+} D^{4+} O_2) \text{ or } A_1^{+} L^{2+} D^{4+} O_2, \\
A_2^{+} L^{2+} D^{4+} O_5 (A_6^{+} L^{2+} D^{4+} O_2), & \quad A_2^{+} L^{2+} D^{4+} O_6 (A_6^{+} L^{2+} D^{4+} O_2), \text{ or } A_1^{+} L^{2+} D^{4+} O_2, \\
A_2^{+} L^{2+} D^{4+} O_5 (A_6^{+} L^{2+} D^{4+} O_2), & \quad A_2^{+} L^{2+} D^{4+} O_6 (A_6^{+} L^{2+} D^{4+} O_2), \text{ or } A_1^{+} L^{2+} D^{4+} O_2. 
\end{align*} \]

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\((A^+_{11}, L^{1+}_{11/6}D^{3+}_{11/6}O_2)\), where \(L\) can be \(\text{Zn, Mn, Fe, Co, Cu, Ni, Cr, Mg}\); \(D\) can be \(\text{Bi, Te, Sb, Ta, Ir, Nb, Sn, Ru, Mo, Os}\); \(A\) and \(A^+\) can be alkali atoms (such as \(\text{Li, Cu, K, Rb, Cs, Ag and Na with } A \neq A^+\)), transition metal atoms, for instance \(\text{Cu or noble metal atoms (e.g., Ag, Au, Pd, etc.)}\).

From a crystal outlook, this family of layered oxides consists mainly of alkali cations (labeled in the above list of compositions as \(A^+\)) sandwiched between parallel slabs (stackings) of transition metal oxides (\(\text{LO}_6\) and \(\text{DO}_6\) octahedra). Some of the oxygen (\(O\)) atoms coordinate with \(A^+\) cations to form inter-layer bonds whose strength is dependent on the inter-layer distance between the slabs. In fact, there is a correlation between the stacking structure and the resulting electrochemical performance of the honeycomb layered oxides that can be traced to the differing sizes of the \(A^+\) cations. For instance, \(A^+\) cations with smaller ionic radii such as \(\text{Li}^+\) tend to form stronger inter-layer bonds as a result of the smaller inter-layer distance\(^1\),\(^2\),\(^18\),\(^22\),\(^24\)\(^-\)\(^25\),\(^30\),\(^33\),\(^37\)-\(^39\).

However, \(A^+\) has a vastly larger ionic radius with a correspondingly larger inter-layer distance and hence forms weaker inter-layer bonds. Generally, \(A^+\) cations with larger ionic radii such as \(\text{K}^+\) and \(\text{Na}^+\) form weaker inter-layer bonds in the aforementioned compositions resulting in layered oxides with prismatic or octahedral coordination of alkali metal and oxygen (technically referred to as \(\text{P-type or O-type layered structures, respectively}\))\(^3\),\(^4\),\(^5\),\(^13\)-\(^16\),\(^19\),\(^20\),\(^27\),\(^34\)\(^-\)\(^36\). The weaker inter-layer bonds in prismatic layered (\(\text{P-type}\)) structures create more open voids within the transition metal layers allowing for facile two-dimensional diffusion of alkali atoms within the slabs\(^41\). This gives rise to the high ionic mobility and exceptional electrochemical properties innately in honeycomb layered oxides.

In our study, we focus on the prismatic subclass of honeycomb layered oxides that generally adopt \(A^+_{11}L^{2+}_{11/6}D^{6+}_{21/6}O_6\) (or equivalently \(A^+_{11}L^{2+}_{11/6}D^{3+}_{11/6}O_2\)) compositions, where \(A = \text{K, Li or Na}\) is an alkali cation (potassium, lithium or sodium) owing to their exemplary electrochemical and physical properties\(^1\),\(^2\),\(^4\),\(^5\),\(^13\)-\(^16\),\(^19\),\(^20\),\(^28\),\(^30\),\(^33\),\(^37\)-\(^39\). We explore their cationic diffusion by envisioning an idealised model of multi-layered oxides in an attempt to gain an effective description of the diffusion mechanisms along the honeycomb layers using concepts of 2D curvature and topology. We proceed to link geometric properties such as the Gaussian curvature and the genus of the honeycomb surface to the inter-layer distance\(^2\),\(^18\),\(^22\),\(^24\)\(^-\)\(^25\),\(^30\),\(^33\),\(^37\)-\(^39\). This term contains only three electromagnetic fields: the electromagnetic vector potential and \(\mu\) component of the electric field along the direction pointing in the \(z\) plane, \(\chi\) component of the magnetic field along the \(z\) direction (shown in Fig. 1) which we assume are negligible due to the condition \(\Delta z \gg d\), where \(d\) is also the screening length for the electromagnetic interactions along the \(z\) direction.

Considering a single honeycomb layer; viewing the cations as a fluid of charge density \(\rho\) (where \(\rho = \rho_{\text{cations}}\)) and \(\delta\) is the Gaussian curvature\(^44\) of the honeycomb surface \(\text{area} \times \text{thickness} = \sigma_{xy}(\vec{n} \times \vec{E})\) where \(\sigma_{xy}(\vec{n} \times \vec{E})\) is the conductivity of the cations in the \(x - y\) plane, \(\sigma_{xy}(\vec{n} \times \vec{E})\) is the electromagnetic vector potential and \(\epsilon^{\text{abc}}\) is the totally anti-symmetric Levi–Civita symbol. This solution means that electromagnetic theory in 2D naturally leads us to the Chern–Simons term \(\chi\),\(^4\)\(^2\),\(^4\)\(^3\). This term contains only three electromagnetic fields: the \(x\) component of the magnetic field pointing in the \(z\) direction, \(B_x = \partial A_y/\partial x - \partial A_x/\partial y\) and the \(x\) and \(y\) components of the electric field, \(E_x = \partial A_y/\partial x - \partial A_x/\partial y\) and \(E_y = \partial A_y/\partial y - \partial A_x/\partial t\) pointing in the \(x\) and \(y\) direction respectively, as displayed in Fig. 2a,b.

**Ansatz 1.** Given that, in the absence of the applied voltage the cations form a 2D honeycomb lattice, the diffusion current (mobile cations) across the honeycomb lattice is assumed to be extracted by the potential energy of the applied voltage/electric fields (as shown in Fig. 2b). A correlation between the total number of these mobile cations (\(\rho \in \text{integer}\)) (as in Fig. 2c) and the quasi-2D configurations shown in Fig. 2d–f can be inferred, since each configuration is expected to supply a unit charge \(q\) (where \(q = +e \approx 1.6 \times 10^{-19}\text{C}\) for \(A = \text{K, Na, Li, etc.}\)) which leaves a vacancy in the lattice whilst simultaneously constituting a diffusion current equivalent to the spatial component of the Chern–Simons term, \(\rho_{\text{diffusion}}(\vec{n} \times \vec{v}) = \partial_x \equiv \sigma_{xy}(\vec{n} \times \vec{E})\).

\[\sigma_{xy}(\vec{n} \times \vec{E}) = \chi = 2 - 2g\] is the Euler characteristic of the honeycomb surface \(M\) after extraction of \(g\) cations which satisfies the definite integral (Gauss–Bonnet theorem\(^45\)) \(\int_M d(\text{Area})K(x, y) = 2\pi \chi\) and \(\chi = 2 - 2g\) is the Euler characteristic of the honeycomb surface \(M\).
of the unbounded surface $M$ with $g \in \text{integer}$ the genus of $M$. This means that $\int_M d(Area) \rho_{xy} \approx g/d$ for $g \gg 1$ leading to $\int_M d(Vol) \rho_{xy} = \int_M d(Area) \int_A dz \rho_{xy}(x,y) \approx g$. Thus, the Gauss–Bonnet theorem sets further constraints on our model by linking the Gaussian curvature and the genus of the honeycomb surface (which is treated as a differentiable manifold) to transport quantities related to the electrodynamics of the cations such as their number density.

**Ansatz 2.** To incorporate quantum theory along side diffusion occurring along the 2D honeycomb layer, we introduce a second ansatz,

$$\int dt \langle \psi \frac{\partial}{\partial t} \psi \rangle = iS(t,\vec{x}) + \frac{1}{2} \int d\vec{x} \cdot \vec{n} \times D^{-1} \vec{v},$$  

(2a)

where $S(t,\vec{x})$ is the classical action, $\langle \psi \rangle$ is the quantum mechanical wavefunction (kernel) of the charged fluid of the cations respectively and $D$ is the diffusion coefficient of the cations. Note that for a finite velocity $d\vec{x}/dt = \vec{v}$, the kernel has the solution $\langle |\psi\rangle \rangle = \exp(iS)$ as expected from Feynman's path integral reformulation of quantum mechanics$^{46}$ (and thus satisfies the normalisation condition, $\langle \psi |\psi\rangle = 1$), since the second term becomes

$$\frac{1}{2} \int dt \langle d\vec{x}/dt \rangle \cdot \vec{n} \times D^{-1} \vec{v} = \frac{1}{2} \int dt \langle dx^k/dt \rangle D^{-1} \varepsilon_{ijk} n^i v^j = 0$$

which identically vanishes in an open path.

In contrast, the second term need not vanish for a closed path given by $\partial M$. Thus, plugging Eq. (1) into Eq. (2a) for a closed path yields,

$$\frac{1}{2} \int_{\partial M} d\vec{x} \cdot \vec{n} \times \frac{\sigma_{xy}}{qD\rho_{xy}} \vec{E} = \frac{1}{2} \int_M d(Area) \nabla_{xy} \cdot \frac{\sigma_{xy}}{qD\rho_{xy}} \vec{E}$$

$$= \frac{1}{2} q\beta \int_M d(Area) \nabla_{xy} \cdot \vec{E},$$

where we have applied Stokes' theorem, Einstein–Smoluchowski relation $D = \mu\beta^{-1}$ and the Langevin result for ionic conductivity $\sigma_{xy} = q^2 \mu \rho_{xy}$ to arrive at our result. It is now evident that non-vanishing electric fields which constitute a diffusion current require the modification of the Kernel via this second term as per ansatz 2. For electrodynamics described by Chern–Simons theory, the 2D charge density is proportional to the flux within the boundary $\partial M$ shown in Fig. 2b. (In Maxwell’s theory, the charge density is given by the Gauss’ law of electromagnetism $\nabla \cdot \vec{E} = 4\pi j^0/\epsilon$, where $j^0$ is the charge density and $\epsilon$ is the permittivity of the material.) Thus, we

**Figure 1.** The polyhedral view of the layered structure of $A_2Ni_2TeO_6$ from the $z$-axis [001] (left) and along the $z$-axis [110] (right): $A$ atoms are brown spheres, $O$ atoms are small red spheres, Ni and Te atoms are enclosed within the purple and blue octahedra of oxygen atoms respectively. The left figure depicts a fragment of the honeycomb structure along the $x$–$y$ plane ([001] zone axis) with a two-dimensional (2D) motion of $A$ ions that reside above or below the honeycomb slabs.
\[ \nabla_{x,y} \cdot \mathbf{E} = \frac{8\pi \rho_{x,y}}{q} = -2K(x,y)/qd, \] where the factor of $8\pi$ is required for consistency with Eq. (7) and the argument of $|\psi|^2$ transforms as $S \rightarrow S + i2\pi \beta m \Phi$ where we have defined the potential $\Phi$ as,

\[ \int \text{d}(\text{Area}) \, K(x,y) \equiv -2\pi \Phi(x,y). \] (2b)

Consequently, the solution for $|\psi|^2$ transforms to,

\[ |\psi|^2 = \exp i(S - i2\pi \beta m \Phi). \] (2c)

This requires that $\Phi(x,y) \equiv \frac{1}{4\pi} \int \text{d}\mathbf{x} \cdot \mathbf{n} \times \mathbf{v} \cdot \mathbf{v} = -2K(x,y)$ such that $1/v = m\mu = mD/k_B T$ is the mean free time between collisions of the cations where $\Phi(x,y)|M = -\chi$ and $m = 1/d$ acts as the effective mass of the cations. The definitions $\Phi(x,y) = (4\pi m)^{-1} \int \text{d}\mathbf{x} \cdot \mathbf{n} \times \mu^{-1} \mathbf{v}$ and $\nabla_{x,y} \cdot \mathbf{E} = 8\pi \rho_{x,y}/q$ are consistent with
the Langevin equations 0 = dμ/τ = -μ⁻¹ν + qE + ƞ and 0 = dη/τ = -μ⁻¹n × ν + qη × E + η with the 
random force η = 0 [See also Eqs. (4b) and (9c)]

Bosonic identity. Notice that Φ(x, y) is reminiscent of a fictitious imaginary Aharonov–Casher phase: 
Aharonov–Casher phase given by ΦAC = -∮M dS · μ × E is the geometric phase acquired by the wavefunc-
tion of a neutral particle along a path ∂M around charges, where μ is the magnetic moment of the neutral 
particle⁴⁰,⁵⁰. Moreover, ∫ d(φV)|ψ⟩= ⟨ψ|ψ⟩= exp (4πβmΦ) = ⟨n⟩ takes the form of a Boltzmann factor 
which gives the average number of free cations constituting the diffusion current. (Alternatively, since the wave-
function is no longer normalised when Φ ≠ 0, it is clear that ⟨n⟩ ≡ Z can also be interpreted as a Lehmann 
weight renormalising the wavefunction |ψ⟩ → |ψ⟩ = |ψ⟩ = exp (4πβmΦ) and |ψ⟩ = (n)⁻¹ exp(iS) implies ∫ d(φV)|ψ⟩= ⟨ψ|ψ⟩ = ∫ d(φV)(ρxy) = -⟨χ⟩/2 = ⟨ψ⟩ - 1 leading to the bosonic identity,

⟨ψ⟩ = (n) = 1.

For the second quantisation formalism, the kernel can be defined as a bosonic Bogoliubov transformation⁴⁸,

ψ = (g)¹/²  a + (n)¹/² exp(iS)a†,
(3b)

ψ † = (g)¹/²  a† + (n)¹/² exp(-iS) a,
(3c)

where  a and a† are harmonic oscillator annihilation and creation operators respectively satisfying the 
commutation relation [a, a†] = (ψ, ψ†) = 1 which is equivalent to Eq. (3a). Thus, the operators in Eq. (3b) act on 
the harmonic oscillator ground state as a|0⟩ = 0 and (0)a† = 0 which guarantees that we recover the Kernel by 
ψ † = |ψ⟩ and  |ψ⟩ = (0)|ψ †. Finally, Boltzmann's entropy formula, S = k_B ln g, where the genus g ≥ 1 is taken 
as the number of microstates in the system, guarantees the entropy vanishes when n = 0 where the g = 1 torus 
given in Fig. 2d represents the ground state of the system.

Typical diffusion dynamics in 3D versus our model. We first note that typical diffusion is effectively 
described by Brownian motion. Consequently, the charge density function ρ of diffusive charges at equilibrium 
temperature satisfies the 3D Fokker–Planck equation⁵¹,

0 ≡ dρ/dt = -∇ · (ρv + ∇ · D∇ρ),
(4a)
equivalent to the Langevin equation

0 = m dV/dt = -1/μ ν + qV,
(4b)

where the Boltzmann factor ρ ∝ exp(-βqV) is typically used to derive σxy = q²μρxy = qμρ and the Ein-
stein–Smoluchowski relation D/k_B T = μ.

In contrast, the dynamics of the cations confined in 2D is captured by the Boltzmann factor ⟨n⟩ = exp(4πβmΦ) 
instead, where 4πmΦ = ∫ dS · n × μ⁻¹ν = qV defined in ansatz 1 and 2, is directly linked to the topology of 
the 2D surface. Thus, setting ⟨n⟩ ∝ ρ, we find that the appropriate 2D Fokker–Planck equation at equilibrium 
for ρ is given by,

0 = dρ/du = -∇ · (n × ρv) + ∇ · D∇ρ.
(5)
The Fokker–Planck equation is solved by Fick's first law of diffusion, j = D∇ρ, together with the Chern–Simons 
current density j = σ_{xy} ε^{lab} da_A a_b to yield Eq. (1).

The kernel in 2D + 1 dimensions. It is necessary to establish the equation of motion for the kernel |ψ⟩ = exp(iS - i2πβmΦ). In standard quantum mechanics, |ψ⟩ simply satisfies the Schrodinger equation, 
idi|ψ⟩/dτ = ε |ψ⟩ where -∂S/∂t = ε is the energy of the system. The presence of a finite screening length of 
electromagnetic interactions along the z direction presupposes that the inter-layer crystalline structures such as 
NiO₃ and TeO₂ octahedra shown in Fig. 1 will act as tunnel barriers for the cations in the layers of the mani-
fold M. This implies that, when Δz ≫ d, the action (quantum phase) S satisfies the dynamics of a large tunnel 
junction⁵²,

∂μ S = d²/qnμ F_{μν},
(6a)

∇μ F_{μν} = 8πρ_{xy} U_{ν},
(6b)

where F_{μν} = ∂_μ A_ν - ∂_ν A_μ is the electromagnetic field tensor, nμ = (0, n) is the unit normal four-vector along 
the z direction. Then, it is straightforward to show that |ψ⟩ = \sqrt{(n)} exp iS now obeys, \partial_μ |ψ⟩ = qdn^μ F_{μν} |ψ⟩ 
whose solution is given by,
\[ \langle \psi \rangle = \exp(-i q d' \int dx^n f_{\mu \nu}), \]  

(6c)

which corresponds to the transformation \( S \rightarrow \ln \langle \psi \rangle \) and \( F_{\mu \nu} \rightarrow f_{\mu \nu} = \partial_\mu A_\nu - \partial_\nu A_\mu + \frac{ie}{\hbar} \epsilon_{\mu \nu \sigma \rho} \partial_\sigma A_\rho \) in Eq. (6a) where \( f_{\mu \nu} \) is equivalent (in vector notation) to the Riemann–Silberstein tensor\(^9\) vector \( F = E + iB \) and its dual, \( G = B + iE \). (Strictly speaking, \( f_{\mu \nu} \) is in the form of the (self-dual) Cabibbo–Ferrari tensor\(^9\) given by \( \partial_\mu A_\nu - \partial_\nu A_\mu + \frac{ie}{\hbar} \epsilon_{\mu \nu \sigma \rho} \partial_\sigma A_\rho \), where \( A_\mu = \frac{i}{\hbar} A_\mu \) is the dual of the electromagnetic potential, \( A_\mu \). This self duality is taken as a consequence of the proportionality of flux and charge in 2D.\(^3\)

**Connection of the kernel to Gaussian curvature.** In Riemannian geometry, the Gaussian curvature of a bounded 2D manifold \( M \) is given by, \( K = \frac{\partial}{\partial \theta} \) where \( \theta \) is the Ricci scalar of the manifold. Moreover, in ansatz 2, we assumed that \( \nabla_{xy} \cdot E = 8 \pi \frac{\partial}{\partial z} \) by assuming the proportionality (equivalence) of charge and flux in 2D\(^4\). By introducing a Hermitian tensor \( K_{\mu \nu} = R_{\mu \nu} - iqF_{\mu \nu} \) defined on a 3D + 1 Reimannian manifold, it is possible to impose the condition,

\[ \nabla^V K_{\mu \nu} = - \frac{8 \pi}{m} \psi^* \partial_\mu \psi, \]  

(7)

where \( R_{\mu \nu} \) is the Ricci tensor, \( \nabla_\mu \) is the metric compatible covariant derivative and \( \partial_\mu g_{\mu \nu} = 0 \). Note that \( K_{\mu \nu} \) defined as above satisfies \( [D_\mu, D_\nu]U^\mu = K_{\mu \nu} U^\mu \) with \( D_\mu = \partial_\mu - iqA_\mu \) the covariant derivative and \( m U_\mu = \partial_\mu S \) the velocity four-vector. Thus, it certainly follows that a new field \( g_{\mu \nu} \), viewed as an emerged gravitational field e.g. from entropic considerations\(^3\), is introduced by Eq. (7). Thus, it is important to check that \( g_{\mu \nu} \) satisfies Einstein Field Equations\(^6\). Using Eqs. (9a), (8a) and (8b) together Bianchi identity, Eq. (7) can be shown to transform to \( R_{\mu \nu} = \frac{1}{2} \partial_{\mu \nu} \) + \( \delta_{\mu \nu} \) with \( \partial_{\mu \nu} = \partial_\mu \partial_\nu - \partial_\nu \partial_\mu \). In General Relativity, \( \kappa = 8 \pi G \) where \( G \) is the gravitational constant and \( \epsilon_0 \) is the permittivity of free space. Comparing the two theories implies that our approach is equivalent to Einstein's gravitational theory with a charged particle of Planck mass \( m = \sqrt{G^{-1}} d^3 = \frac{d^3}{2} \) and Planck charge \( q = \sqrt{8 \pi \epsilon_0} \). That this idealised model introduced so far has a gravity description is not entirely unexpected since the partition function is given by \( Z = \frac{1}{m} \exp(4 \pi \beta m \Phi) \) and thus the free energy of the system \( F = -\beta^{-1} \ln Z = -\frac{4 \pi \beta m \Phi}{m} \) is proportional to an attractive potential energy \( m \Phi \), proportional to mass, \( m \), of the cations.

Substituting \( S = m \int dx^n U_\mu = -m \int dt \langle \psi \rangle = \sqrt{\beta G} \exp(i S) \) where \( U_\mu \) is the four-velocity vector of the cations and using the Bianchi identity \( \nabla^V R_{\mu \nu} = \partial_\mu R_{\nu \lambda} \) and the real part and imaginary parts of Eq. (7) become,

\[ \partial_\mu R = - \frac{8 \pi}{m} \delta_\mu \rho_{xy}, \]  

(8a)

\[ \nabla_\mu F_{\mu \nu} = 8 \pi \rho_{xy} U^\mu / q, \]  

(8b)

respectively. The solution for Eq. (8a) is given by \( R_{\mu \nu} = R = \frac{4 \Lambda}{\epsilon_0} = \frac{4 \Lambda}{\epsilon_0} \) where \( R \) is the 3D + 1 Ricci scalar and \( 4 \Lambda / \epsilon_0 \) is taken as the initial curvature of the manifold with no cations extracted from the \( x \) \( y \) plane by the electric field. As such, ansatz 1 requires that the curvature variation \( \delta R \rightarrow \theta \) be projected to the 2D Ricci scalar \( \theta \) under certain conditions satisfied by the honeycomb layered oxide. Since \( K(x, y) \) is independent of \( t \) and \( z \), the limit \( \theta \rightarrow 2K(x, y) \) requires the Ricci scalar \( R \) to also be independent of \( t \) and \( z \). Particularly, this limit entails introducing a time-like Killing vector \( \xi^\mu = (1, 0) \) and a space-like Killing vector \( \nu^\mu = (0, \hat{n}) \), which impose the conditions \( \partial^\mu \partial_\mu R = \partial^\mu \partial_\mu = 0 \) and \( m \partial_\mu \partial_\mu = \partial_\mu \partial_\mu = 0 \) (A Killing vector \( K^\mu \) satisfies\(^9\) \( K_{\mu \nu} = R_{\mu \nu} = K_{\nu \mu} \)). Using the anti-symmetry relation \( \nabla_\mu K_{\nu \lambda} = -\nabla_\lambda K_{\nu \mu} \) and the Bianchi identity \( \nabla_{\nu \mu} = \frac{1}{2} \nabla_k R_{\mu \nu} \), the divergence \( \nabla_\mu K_{\nu \lambda} = \nabla_\mu (K_{\nu \lambda} - K_{\lambda \nu}) = \frac{1}{2} K^\mu (\xi^\nu \nabla_\nu \xi^\lambda - \xi^\lambda \nabla_\nu \xi^\nu) \). This in turn imposes energy and momentum conservation (in the \( z \) coordinate) in accordance with Noether's theorem. Thus, computing the time component of Eq. (6), we arrive at Eq. (2a),

\[ \int dt \langle \psi | \frac{\partial}{\partial t} \rangle \psi = \left\{ \int dt d^3 x \sqrt{-det(g_{\mu \nu})} \psi^* \partial_\mu \psi \xi^\nu \right\} = -\frac{1}{8 \pi d} \int d^3 x \sqrt{-det(g_{\mu \nu})} \nabla_\mu R_{\mu \nu} \xi^\nu \]

\[ = \frac{1}{8 \pi d} \int d^3 x \sqrt{-det(g_{\mu \nu})} \nabla_\mu R_{\mu \nu} \xi^\nu + \frac{q}{8 \pi d} \int d^3 x \sqrt{-det(g_{\mu \nu})} \nabla_\mu F_{\mu \nu} \xi^\nu \]

\[ = - \frac{1}{8 \pi d} \int d^3 x \sqrt{-det(g_{\mu \nu})} \partial_\mu \partial_\nu R_{\mu \nu} + \frac{q}{8 \pi d} \int d^3 x \sqrt{-det(g_{\mu \nu})} \partial_\nu \partial_\mu F_{\mu \nu} \xi^\nu \]

\[ = \frac{- \beta m}{\sqrt{det(g_{\mu \nu})}} \int d^3 x \sqrt{-det(g_{\mu \nu})} R_{\mu \nu} + \frac{q}{8 \pi d} \int d^3 x \sqrt{-det(g_{\mu \nu})} \partial_\nu \partial_\mu F_{\mu \nu} \xi^\nu \]

\[ = \frac{- \beta m}{\sqrt{det(g_{\mu \nu})}} \int d^3 x \sqrt{-det(g_{\mu \nu})} K + \frac{q a d}{2} \int d^n \xi^\nu F_{\mu \nu} = 2 \pi \beta m \Phi + i \xi, \]

where we have set \( \sqrt{-det(g_{\mu \nu})} = 4 \pi \beta m \sqrt{det(g_{\mu \nu})} \), \( \int dx^n m = d \), \( \int d^3 x \sqrt{-det(g_{\mu \nu})} = 4 \pi d^2 \), \( \int d^3 x \sqrt{-det(g_{\mu \nu})} = \int d(Area) \) and assumed that \( n^\mu F_{\mu \nu} \) is fairly constant over the surface given by \( d^2 \int d^3 x \sqrt{-det(g_{\mu \nu})} \). This result is equivalent to Eq. (2a) in ansatz 2 where we have used Eq. (6) in the last line. In order to preserve the Einstein–Smoluchowski relation \( \mu = \beta D \) and the 2D Fokker–Planck relation Eq. (5),
the projection requires the factor of $4\pi \beta m$ between the 3D and 2D metrics. Nonetheless, this factor can be absorbed by the redefinition of $\Phi$ in Eq. (2b).

Results of the model
Electrodynamics of the cations. Notice that Eq. (7) is invariant under the gauge transformation $\partial_\mu \to \partial_\mu - \partial_\mu b$, and $S = m \int dt + q \int b \cdot U^{\mu} dt$ where $b$ is a gauge potential. The choice $b_\mu = \frac{1}{2} \varepsilon_{\mu \rho \sigma} \partial_\rho A_\sigma$ with $\epsilon_{\mu \rho \sigma}$ the Levi-Civita symbol where $\epsilon_{\mu \rho \sigma} b_\sigma = B_\mu$ and $\epsilon_{\mu \rho \sigma} b_\rho = \sigma_{\mu \nu}$ Eq. are the magnetic and electric fields respectively, leads to the equation of motion for the cations, given in Eq. 9a. This equation of motion for the cations has been derived as follows: $\partial_\mu S = m U^\mu + q b^\mu$ and $\nabla_\mu b_\mu = m \nabla_\mu U^\mu + q \nabla_\nu b_\nu$.

Using the fact that $\nabla_\nu b_\mu = \epsilon_{\nu \lambda \mu} S$ is symmetric, we find $m \nabla_\nu U^\mu - m \nabla^\mu U_\nu = q \nabla_\nu b_\nu - q \nabla_\nu b_\mu$. Contracting the expression with $\nabla^\nu$ and using $U^\mu U_\mu = -1 \to \nabla_\nu (U^\mu U_\mu) = 2 U^\nu \nabla_\nu U_\mu = 0$, we find $m U^\nu \nabla_\mu = q U^{\mu} (\nabla_\mu b_\nu - \nabla_\nu b_\mu)$ equivalent to,

$$m U^\nu \nabla_\mu = \frac{q}{2} U_\nu \varepsilon^{\mu \rho \sigma} \partial_\rho A_\sigma.$$  

(9a)

Recall, we introduced a $\delta$-like vector $\xi^\mu$ and $z$-like Killing vector $n^\mu$ to guarantee the independence of the Ricci scalar $R$ on these coordinates. We wish to consider the weak field limit, which entails making the approximation, $\text{diag}(g_{\mu \nu}) = (1, -1, -1, -1) + \text{small corrections}$ where the 'small corrections' are related to the Newtonian potential. In particular, since $U^\mu U^\nu = \varepsilon^{\mu \rho \sigma} A_\rho A_\sigma / 2$ is the Christoffel symbol, in the weak field limit given by $\text{diag}(g_{\mu \nu}) = (g_{00}, -1, -1, -1)$, the symbol is non-vanishing only for $\Gamma^0_00 = \varepsilon^{00} n_0 = \varepsilon^{00} \pi / 2$. Thus using with $U^\mu \sim \exp(\Phi(1, y))$ and $U_\mu \sim \exp(\Phi(-1, -y))$ such that $U^\mu U_\mu = -1 \to U^\mu dt / dt = \exp(\Phi) = 1 / \sqrt{1 - y^2}$. Eq. (9a) reduces to,

$$m \frac{dU^0}{dt} = \frac{-q}{2} \nabla^0 \cdot \vec{B},$$  

(9b)

$$\frac{d \vec{\Phi}}{dt} = m U^0 \vec{V}_{\infty} / 2 + \frac{q}{2} \vec{B} + \frac{q}{2} (\vec{n} \times \vec{E}),$$  

(9c)

where $\vec{\Phi} = m U^0 \vec{n}$ is the momentum vector, $g_{00} = 1 + \text{small corrections}$ is the time-time component of the metric tensor related to $\xi^\mu = (1, 0)$ by $g_{0\nu} = \xi^\mu \xi^\nu$. Substituting Eq. (9b) into Eq. (9c) and identifying $\vec{y} = \vec{n} / \sqrt{1 - (1 / U^0)^2}$ as the velocity vector of the cations (pointing solely in the $z$ direction), reduces Eq. (9a) to, $\dot{\Phi} = 2 \pi / m \vec{V}_{\infty} \vec{B}/\vec{E} \cdot \vec{n} / \sqrt{1 - (1 / U^0)^2} = \dot{\Phi} \sim \sqrt{2m} / \vec{B} \cdot \vec{E}$, and $\nabla \Phi = -\varepsilon^{xy} \sqrt{1 - (1 / U^0)^2} \sim \frac{\sqrt{2m}}{2} \vec{n} \times \vec{E}$, where we have substituted $g_{00} = 1 + \Phi$ thus identifying $\Phi$ as a Newtonian potential satisfying the weak field limit $0 \leq \Phi \ll 1$ and $U^0 \sim \exp(\Phi) \sim 1 + \Phi$. Finally, rescaling $\Phi \to (2 \pi \Phi)^{1/2}$ allows one to write,

$$\tilde{\Phi} = 4 \pi \beta m \alpha^2 \Phi \sim q \beta \epsilon^{abc} \partial_\nu A_c,$$

(9d)

which is consistent with Eq. (6c). Such a rescaling corresponds to appropriately renormalising the $\vec{E}$ and $\vec{B}$ fields, where the function of $\Phi$ rescaling the electromagnetic fields is understood as a Lehmann weight.

Equilibrium properties of the cations near $g \simeq 1$. In the weak field static limit when the magnetic field vanishes as shown in Fig. 2b, $0 = \partial \Phi / \partial t = q \beta \epsilon / 4\pi m$, Eq. (8a) reduces to,

$$\frac{1}{4} \nabla^2 \tilde{g}_{00} = \frac{4\pi}{m} \rho c_0 U^0 \tilde{g}_{00} \Rightarrow \nabla^2 \tilde{g}_{00} = -K \exp(2\tilde{\Phi}).$$  

(10)

Equation (10) takes the form of the well-known Liouville’s equation where $K = -4\pi \beta c_0 / m$ is evidently the Gaussian curvature. To achieve constant conductivity $\sigma_{xy} \propto \rho_{xy}$ at equilibrium, the charge density should vary spatially very slowly and an approximation can be made to solve Eq. (10) with a constant Gaussian curvature $\rho \propto K = K_0 + \delta K \simeq K_0$. Since the shift from 3D to 2D ($\vec{V} \to \vec{V}_{\infty}$) is a consequence of imposing the Killing vector $n^\mu$ on the metric tensor $g_{\mu \nu}$ in 3D + 1 dimensions, we first solve Eq. (10) in 3D to yield,

$$g_{00} = 1 - \ln K_0 r^2 = 1 + 2 \Phi$$

with $\vec{x} = (x, y, z)$, $\vec{x}_0 = (x_0, y_0, z_0)$ and $\vec{x}_0 = \vec{x}_0 / \sqrt{1 - (1 / U^0)^2},$ which requires that $(K_0 r^2)^{-1} \to 1 / \sqrt{1 - (1 / U^0)^2}$. This approximation suggests that perturbing $K_0$ around the ground state, $\chi / 2 \to 1 - \chi / 2 - g$ to 0 of the system leads to $(K_0 r^2)^{-1} \to 1 - \chi / 2 = g$, an expression that characterises the discrete areas of the manifold, $\text{Area}(g) \sim K_0^{-1} g r^2$, where in our case we can freely choose $\text{Area}(g) = 1 \sim r^2$ to be the unit area of the quasi-stable configuration with $g = 1$ vacancy as depicted in Fig. 2d. Thus, through this expression the entropy of the system $\delta S = k_0 \ln g = -k_0 \ln(K_0 r^2)$ is derived.

Moreover, in Chern–Simons theory, the conductivity $\sigma_{xy}$ is inversely proportional to the level $g \in \mathrm{integer}$ of the Chern–Simons action $\mathcal{S}_C = \frac{1}{4} \int \varepsilon^{abc} \partial_a A_b \partial_c A_d + \frac{1}{2} \delta \epsilon^{a b c} \partial_a A_d \partial_c A_d + \partial^a A_a$, which leads to an effective action $\mathcal{S}_e = \int \frac{1}{4} \varepsilon^{a b c} \partial_a A_b \partial_c A_d$, which we will use as an effective action with respect to $A_4$, we get the Chern–Simons current density $j^i = -\frac{\partial}{\partial x^i} \epsilon^{abc} \partial_a \partial_b A_c$, Varying the effective action with respect to $A_4$, we find $-\frac{\partial}{\partial x^i} \epsilon^{abc} \partial_a \partial_b A_c$. Comparing it with Eq. (1), we find $-\frac{\partial}{\partial x^i} \epsilon^{abc} \partial_a \partial_b A_c$. Using $\sigma_{xy} = q^2 \rho_{xy} \mu$ and $K_0 = -4\pi d\rho_{xy}$, we find

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\[-q^2/2 \partial_{\varepsilon} g = \sigma_{xy} = q^2 \rho_{xy} \mu = -q^2 K_0 \mu / 4\pi d = -q^2 \mu / 4\pi d r_M^2, \] which implies that the mobility of the cations is given by \(\mu = 2r_M^2.\)

**Bose–Einstein condensate of cations.** We define the order parameter of the cations in the 2D honeycomb layer as \(\Psi = \sqrt{\rho_{xy}} \exp(i\theta)\) where \(\theta = \int \sigma \cdot \nabla x \times D^{-1} \sigma.\) Plugging this definition together with \(\Phi = \Phi_0 + \delta\Phi \propto \exp(\sigma \pi m)\) in Eq. (10) where \(\delta\Phi \sim small\) is an infinitesimal fluctuation of \(\Phi\) from its initial ground state value given by,

\[\Phi_0 = -\frac{1}{2} \ln(K_0 \mu / 2) \sim \frac{1}{2} \ln g \quad (11a)\]

we find,

\[-\frac{4\pi \exp(2\Phi_0)}{m} \left| |\Psi| \right|^2 = \frac{1}{4\pi \beta m} \frac{v^2_{xy}}{\left| \Psi \right|^2} \left( \frac{\nabla^2_{xy}|\Psi|}{|\Psi|^2} \right) \left( \frac{\nabla^2_{xy} \Psi}{|\Psi|^2} \right) = \frac{1}{2\pi \beta m} \left( \frac{\nabla^2_{xy}|\Psi|}{|\Psi|^2} \right) - 8\pi \beta m (\nabla^2_{xy} \Phi)^2.\]

Recalling that since \(\Phi = \frac{1}{\pi} \int d\sigma \times \nabla \times \sigma,\) we get,

\[\frac{\beta \nu m}{2} \left( \nabla \times \nabla \nabla \right) = \frac{1}{2\beta \nu m} \left( \frac{\nabla^2_{xy}|\Psi|}{|\Psi|^2} \right) - 4\pi^2 \frac{\exp(2\Phi_0)}{m} |\Psi|^2 = 0,\]

which represents the sum of kinetic and potential energies. Together with local charge conservation \(0 = \partial\beta / \partial t = -\nabla \cdot \nabla \cdot j\) guaranteed by Chern-Simons theory where \(j = q\rho_{xy} (\nabla \times \nabla) = q(D(\nabla^\Phi_{xy} \Psi - \nabla^\Phi_{xy} \Psi^*)/2i,\) we can re-write it as the 2D Gross–Pitaevskii equation:\(^{9,66}\)

\[0 = i \frac{\partial}{\partial t} \Psi = \left( -\frac{1}{2m} \nabla^2_{xy} - \frac{4\pi^2 \beta \exp(2\Phi_0)}{m} |\Psi|^2 \right) \Psi, \quad (11b)\]

where we have used \(\mu = 1/mv = \beta D.\) Equation (11b) is consistent with our treatment of the cations as bosons. Note that \(\pi^2 \beta \exp(2\Phi_0) \equiv a_s\) is the cation–cation (boson–boson) scattering length where the self-interaction term is attractive. Thus, this determines the fixed potential of the perturbed ground-state as,

\[\Phi_0 = \frac{1}{2} \ln(a_s k_B T / \pi), \quad (11c)\]

Comparing this to Eq. (11a), we find \(1/g \sim K_0 \mu / 2 = \pi / a_s k_B T.\) Thus, the number of mobile cations increases with temperature as expected. Moreover, using the Einstein-Smoluchowski relation \(\mu = D_0 / k_B T\) we arrive at the expression for the scattering length \(a_s = 2\pi / D_0 k_B.\) Note that the transition to the diffusion phase with free cations ought to occur when \(g = n + 1 \geq 1.\) Plugging in \(g \sim T / T_c,\) where we have defined \(\pi/(a_s k_B) \equiv T_c\) as the critical temperature above which a finite number of cations become diffusive, we find that \(0 \leq n = (T / T_c - 1) \Theta(T / T_c - 1)\) with \(\Theta\) the Heaviside function (which satisfies the condition, \(\Theta(n) = 1\) when \(n \geq 0\) whereas \(\Theta(n) = 0\) when \(n < 0\) which \(n = g - 1 \geq T / T_c - 1\) to guarantee that a transition to the conductive diffusion phase occurs at \(T \geq T_c\) corresponding to the states with \(g \geq 1\) as expected. Proceeding, we employ Eq. (11c) to obtain the free energy of the cations using the average number \(n = \exp(4\pi m \Phi_0).\) Thus, the free energy is given by \(F = \beta^{-1} \ln(n) = \beta^{-1} \ln \exp(4\pi m \Phi_0) = -4\pi m \Phi_0 \sim -2m \ln(T / T_c).\) Around \(T \simeq T_c\) or equivalently \((g \simeq 1),\) the free energy becomes \(F = -2m \ln(1 + T / T_c - 1) \sim -2m \ln(T / T_c - 1) \sim -2m \ln T\) as expected. This result can be confirmed by measuring the Arrhenius equation \(n = \exp(-B/F)\) for varied lithophile elements \(A = K, Na, Li,\) etc. in the sub-class \(A^+ L_2^+ T^2 ^{O6}\) using muon spectroscopic measurements where the critical temperature \(T_c \sim 1/a_s\) is determined from the hopping rate of the cations\(^i\).

Moreover, the Gross–Pitaevskii equation given in Eq. (11b) provides a straightforward method to include interactions of adjacent honeycomb layers by exchange of cations through quantum tunnelling. In particular, since the Lagrangian for Eq. (11b) is given by,

\[\mathcal{L} = \int d^3x \left[ i \bar{\Psi} \gamma^0 \bar{\Psi} / \partial t - i \bar{\Psi} \gamma^0 \bar{\Psi}^* / \partial t - \frac{1}{2m} \nabla^2_{xy} \bar{\Psi}^2 + \frac{2\pi a_s}{m} |\Psi|^4, \right.\]

the generalised Lagrangian for the entire multi-layered crystal including interactions is given by,

\[\mathcal{L} = \int d^3x \left[ i \bar{\Psi}^0 \bar{\Psi} / \partial t - i \bar{\Psi} \gamma^0 \bar{\Psi}^* / \partial t - \frac{1}{2m} \nabla^2_{xy} \bar{\Psi}^2 + \frac{2\pi a_s}{m} |\Psi|^4 - U(|\Psi_j - \Psi_{j+1}|), \right. \]

where \(U(|\Psi_j - \Psi_{j+1}|)\) is the interaction energy term of the adjacent honeycomb layers and \(\sum_j\) is the sum over all the layers containing the cations. For instance, \(U(|\Psi_j - \Psi_{j+1}|) = |\Psi_j - \Psi_{j+1}|^2 / 2M(\Delta z)^2\) (where \(M\) is the anisotropic mass of the cations along the \(z\) direction and \(\Delta z \propto \mu_{\text{ion}}\) scales with the ionic radius \(r_{\text{ion}}\) of the cation \(A = K, Na, Li\) as shown in Figure 4) is the simplest interaction term that guarantees \(\nabla^2_{xy} \Psi \rightarrow \Psi\) in the limit \(\Delta z \rightarrow 0\) and \(M \rightarrow \infty.\) Such a term has long been considered within the context of anisotropic Ginzburg–Landau theory for stacked materials in the so-called Lawrence–Doniach model for stacked layers.
high-$T_c$ superconductors. It simply yields a Josephson tunnelling current in the $z$ direction given by $J_z = J_0 \sin(\theta - \theta_{j+1}) = q \rho_{j,j+1}$ where $J_0 = q \rho_{j,j} / m \varphi(\Delta z)$ under the substitution of $\Psi_j = \sqrt{\rho_j} \exp(i \theta_j)$ in Eq. (12). Taking $\Delta z = m_{\text{vert}} / M$ and comparing the Josephson current to the form of the velocity $\vec{v}$ used throughout Eq. (9), we find $\Phi_j = \ln U_0 = - \ln \cos(\theta_j - \theta_{j+1})$. This suggests that the genus of each surface labeled by $j$ scales as $g_j \sim 1 / \cos^2(\theta_j - \theta_{j+1})$, where we have used Eq. (11a). Consequently, the number of cations becomes $n_j = g_j - 1 = \tan^2(\theta_j - \theta_{j+1})$. Further discussion on the effect of other forms of the interaction term $U(|\Psi_j - \Psi_{j+1}|)$ on the dynamics of cations is the subject of future research.

**Topological order and phase transitions with charge vortices.** Since the velocity of the mobile cations depends on the potential $\Phi = \frac{1}{2\pi} \int d\vec{x} \cdot (\vec{a} \times \vec{v}^{-1}) = - \frac{1}{4} \ln(K_0 \theta^2)$, its divergence $\nabla \Phi = \frac{1}{2\pi} \mu \times \mu^{-1} \vec{v}$ yields the velocity vector of the diffusing cations to be $\vec{v}_{\text{diff}} = (\vec{a} \times \vec{r}) / r^2$, which is the solution for an irrotational charge vortex satisfying $\nabla \times \vec{v} = 0$. The charge vortices have a mass of $m_{\text{vert}} = 1 / 4 \pi m \rho_{j,j}$ and represent diffusion channels of the cations under small curvature perturbations $K - \delta K \approx K_0$ around the constant conductivity $\sigma_{xy} \propto \rho_{j,j}$. The kinetic energy of a single vortex can be computed as,

$$H_{\text{vort}} = (D_0 / 2) \int_0^{1/m} dz \int d^2 x \sqrt{\det(g_{ij}^{2D})} |\nabla \Psi|^2$$

$$= (D_0 \rho_{j,j} / 2m) \int d^2 x \sqrt{\det(g_{ij}^{2D})} (\nabla \theta)^2$$

$$= (\rho_{j,j} / 8 \pi \beta m^2 D_0) \int d^2 x \sqrt{-\det(g_{ij}^{2D})} r^2$$

$$= 2 \pi^2 \mu \rho_{j,j}^{1/\sqrt{K_0}} dr / r = - \pi^2 \mu \rho_{j,j} \ln(K_0 r_{j,j}^2) = - \pi m \Phi_0 / g,$$

where we have used $\Psi = \sqrt{\rho_j} \exp(i \theta)$ with $\theta = \int d\vec{x} \cdot (\vec{a} \times D_0^{-1} \vec{v})$, $\nabla \Phi = \rho_{j,j} / 4 \pi m \rho_{j,j}$, $D_0 = 1 / 2 \rho_{j,j}$ and Eq. (11a). Thus, since the emergent field $\Phi_0 = - \ln \Phi_0^{2D}$ will vanish when the vortices in the system have no kinetic energy, $H_{\text{vort}} = 0$, we conclude that the geometric description can be traced to these vortices.

Recall that the entropy of the system is given by $S = k_B \ln g$, where $g = 1 / K_0 r_{j,j}^2$ is the number of microstates in the system. Note that the Boltzmann factor for a vortex-antivortex pair at equilibrium temperature $T$ for a given microstate is $\exp(-\beta g H_{\text{vort}}) = \exp(4 \pi \beta m \Phi_0) = (n(g))$, which coincides with the average number of free cations. This means that the free energy of these vortices is $F \approx - \pi m / T (T_c - 1)$. Thus, we discover that $T_c$ corresponds to the Berezinskii–Kosterlitz–Thouless (BKT) transition temperature above which unpaired vortices appear in the system when $F < 0$. Finally, taking the sum over the microstates, we find $\sum_{g=0}^{\infty} (n(g)) = \sum_{g=0}^{\infty} (n(g)) - 1 = 1 / (\exp(\beta g H_{\text{vort}}) - 1)$ which is simply the Bose–Einstein distribution of the vortices.

**Discussion**

We are left to puzzle how a geometric theory emerges in the crystal and its explicit relation to the honeycomb framework. We note that the multi-layered crystal is considered electrochemically neutral when the 2D honeycomb structure bears no vacancies in the lattice. However, its intrinsic Gaussian curvature given by $\Lambda$ is not guaranteed to vanish. Since adiabatic variations from this intrinsic curvature is modeled to occur by extraction of cations from the honeycomb surface leading to vacancies which we identify as the genus $g$, the surface Gauss curvature $\kappa$ this links any curvature variations to changes in the number density of the extracted cations. In essence, we consider this as the origin of the geometric description. Moreover, the physics of these curvature deformations which affect the transport properties of the cations are captured by an emergent field $\Phi$ that has a gravitational description given by Liouville’s equation.

The extracted cations contribute to a diffusion current density via a Chern–Simons term that naturally arises in 2D electrodynamics. This extraction process occurs at a critical temperature $T_c \sim 1 / a_{j,j}$ related to the cation–cation scattering length $a_{j,j}$. In fact, we have showed that the cations, under the influence of the field $\Phi$ satisfying Liouville’s equation, admits a Bose–Einstein condensate description given by Eq. (11b) where curvature/charge density perturbations around the ground state of the system $(g = 1)$ leads to diffusion channels satisfying the irrotational vortex condition, $\nabla \times \vec{v} = 0$ and can be modeled by an order parameter $|\Phi|^2 \propto n \sim (T / T_c - 1) \theta (T / T_c - 1)$ representing a BKT phase transition for $T \geq T_c \sim 1 / a_{j,j}$. Above $T_c$, the kinetic energy of the charge vortices leads to the emergence of the field, $\Phi$, responsible for the diffusion dynamics of the cations in 2D. This places these vortices as central to understanding the link between cationic diffusion and our emergent geometric description.

**Conclusion**

An idealised model of the electrodynamics of the alkali metals cations in honeycomb layered oxide frameworks has been proposed. The model links the ionic transport of the cations to the geometry and topology of these materials by applying well-established approaches of Brownian motion, Liouville field theory and Chern–Simons theory. The overarching result is that ionic vacancies of the 2D honeycomb lattice are related to the Euler characteristic of the surface where the Gauss–Bonnet theorem is the charge density formula of the surface, as summarised in Fig. 2. Such a rich description of the transport phenomena within honeycomb layered oxide frameworks stems from the interdisciplinary approach of our model, which adopts established concepts from applied...
mathematics, chemistry and physics, as schematically shown in Fig. 3. Thus, the results presented herein elucidate previously unreported interconnections between geometry, thermodynamics and quantum theory, essential in unravelling the connection between topological order and phase transitions in these materials. Further connections, particularly the explicit relation of emergent phenomena such as charge vortices and the gravitational potential within our model remains vastly unexplored. Nonetheless, we believe the results presented herein bear particular significance across a diversity of disciplines where layered materials play a pivotal role in frontier applied fields of high-temperature superconductivity, quantum computing and energy storage.
Appendix: Inter-slab distance tuning. The correlation between the ionic radii of A and the inter-layer distance (Δz), as shown in Fig. 4, presents new avenues for tuning the inter-layer and intra-layer electromagnetic couplings in order to optimise the dimensionality of the magnetic lattice. This can be achieved through the introduction of A cations with larger ionic radii that leads to the increase of the inter-layer distance. Moving from Li, Na to K, it is clear that there is a propensity of the inter-layer distance to increase, which consequently should affect the transport properties (for example, diffusion nature of alkali A atoms) along the two-dimensional (2D) surface. Honeycomb layered compositions of $A_2^+\frac{1}{2}L_2^+\frac{1}{2}TeO_6^-$ ($A_2^+\frac{1}{2}L_2^+\frac{1}{2}TeO_6^-$) had initially been relegated to $A = \text{Li, Na}$; however, recent reports have shown that such compositions can be extended to lithophile large-atoms such as K. This is an additional advantage as these series of honeycomb compositions may be expanded to new compositions where $A = \text{Rb}^+$, $\text{Cs}^+$, $\text{Ag}^+$, $\text{Au}^+$, $\text{Cu}^+$, $\text{H}^+$, and so forth. Figure 1 depicts the honeycomb arrangement of K$^+$ in K$_2/3$Ni$_2$TeO$_6$ (K$_2$Ni$_2$TeO$_6$) which is greatly influenced by the arrangement of NiO$_6$ and TeO$_6$ octahedra that reside in the slabs.

Quasi-stable configurations as the analogues of Tori in 2D. We shall name each configuration as (3) three-(leaf) clover where each honeycomb area is taken as a single leaf in the clover. Consequently, each vacancy g lies within a 3-leaf clover at the leaf stalk. We label each cation in the honeycomb lattice as a vertex V, the line connecting to their adjacent neighbor as an edge E and each honeycomb unit area as A. Our approach then requires the number of honeycomb unit areas to be left unchanged by the extraction process even when the number of honeycomb faces F does not remain unchanged. Thus, for a honeycomb lattice with no vacancies, $A = F$ and $\chi = A - E + V = 2$ where $F$ is the number of faces. On the other hand, introducing g vacancies (equivalent to extracting g cations from the honeycomb surface) each at the stalk of the 3-leaf configuration, we find $A \rightarrow A$ with ($A \neq F$), $E \rightarrow E + 3g$ and $V \rightarrow V + g$. Thus, the Euler characteristic defined above transforms to $\chi \rightarrow \chi = A - (E + 3g) + (V + g) = (A - E + V) - 2g = 2 - 2g$ as expected.

References
1. Masese, T. et al. Rechargeable potassium-ion batteries with honeycomb-layered tellurates as high voltage cathodes and fast potassium-ion conductors. Nat. Commun. 9, 3823 (2018).
2. Sathiya, M. et al. Li$_4$NiTeO$_6$ as a positive electrode for Li-ion batteries. Chem. Commun. 49, 11376–11378 (2013).
3. Yang, Z. et al. A high-voltage honeycomb-layered Na$_4$NiTeO$_6$ as cathode material for Na-ion batteries. J. Power Sources 319, 319–323 (2017).
4. Yuan, D. et al. A honeycomb-layered Na$_3$Ni$_2$SbO$_6$: A high-rate and cycle-stable cathode for sodium-ion batteries. Adv. Mater. 26, 6301–6306 (2014).
5. Gupta, A., Buddie Mullins, C. & Goodenough, J. B. Na$_3$Ni$_2$TeO$_6$: Evaluation as a cathode for sodium battery. J. Power Sources 243, 817–821 (2013).
6. Masese, T. et al. A high voltage honeycomb layered cathode framework for rechargeable potassium-ion battery: P2-type K$_2/3$Ni$_2/3$Co$_1$TeO$_6$ 1/2. Chem. Commun. 55, 985–988 (2019).
7. Masese, T. et al. Sulfonylamide-based ionic liquids for high-voltage potassium-ion batteries with honeycomb layered cathode oxides. ChemElectroChem 6, 3901–3910 (2019).
8. Evstigneeva, M. A., Nalbandyan, V. B., Petrenko, A. A., Medvedev, B. S. & Kataev, A. A. A new family of fast sodium ion conductors Na$_2$M$_2$TeO$_6$ (M = NiCo, Zn,Mg). Chem. Mater. 23, 1174–1181 (2011).
9. Zheng, L. & Obrovac, M. N. Honeycomb compound Na$_3$Ni$_2$SbO$_6$ as positive electrode material in Na cells. J. Electrochem. Soc. 163, A2362–A2367 (2016).
10. Ma, J. et al. Ordered and disordered polymorphs of Na$_2$Sb$_2$Te$_4$: Honeycomb-ordered cathodes for Na-ion batteries. Chem. Mater. 27, 2387–2399 (2015).
11. Nalbandyan, V. B., Petrenko, A. A. & Evstigneeva, M. A. Heterovalent substitutions in Na$_3$Ni$_2$TeO$_6$ family: Honeycomb-ordered cathodes for Na-ion batteries crystal structure, fast sodium ion conduction and phase transition of Na$_2$LiFeTeO$_6$. Solid State Ionics 233, 7–11 (2013).
12. Li, Y. et al. A P2-type layered superionic conductor Ga-doped Na$_2$Zn$_2$TeO$_6$ for all-solid-state sodium-ion batteries. Chem. A Eur. J. 24, 1057–1061 (2018).
13. Li, Y. et al. New P2-type honeycomb-layered sodium-ion conductor: Na$_2$Mg$_2$TeO$_6$. ACS Appl. Mater. Interfaces 10, 15760–15766 (2018).
14. Wu, J.-F., Wang, Q. & Guo, X. Sodium-ion conduction in Na$_2$Zn$_2$TeO$_6$ solid electrolyte. J. Power Sources 402, 513–518 (2018).
15. Deng, Z. et al. Ca-doped Na$_2$Zn$_2$TeO$_6$ layered sodium conductor for all-solid-state sodium-ion batteries solid electrolyte. Electrochim. Acta 298, 121–126 (2019).
16. Dubey, M. et al. Structural and ion transport properties of sodium ion conducting Na$_2$M$_2$TeO$_6$ (M = MgNi and MgZn) solid electrolytes. Ceram. Int. 39, 121–126 (2013).
17. Kumar, V., Bhardwaj, N., Tomar, N., Thakral, V. & Uma, S. Novel lithium-containing honeycomb structures. Inorg. Chem. 51, 10471–10473 (2012).
18. Zvereva, E. A. et al. A new layered triangular antiferromagnet Li$_4$FeSbO$_4$: Spin order, field-induced transitions and anomalous critical behavior. Dalton Trans. 42, 1550–1566 (2013).
19. Derakhshan, S., Cuthbert, H. L., Greedan, J. E., Rahaman, B. & Saha-Dasgupta, T. Electronic structures and low-dimensional magnetic properties of the ordered rocksalt oxides Na$_{2}$Cu$_{2}$O$_{3}$ and Na$_{2}$Cu$_{2}$TeO$_{3}$. Phys. Rev. B Condens. Matter Mater. Phys. 76, 1–7 (2007).
20. Vicu, L. et al. Structure and basic magnetic properties of the honeycomb lattice compounds Na$_2$Co$_2$TeO$_6$ and Na$_2$Co$_2$SbO$_6$. J. Solid State Chem. 180, 1060–1067 (2007).
21. Morimoto, K., Itoh, Y., Miuchi, K., Kato, M. & Yoshimura, K. Magnetic excitation and Na-deficient effects on spin-gapped compound. J. Magn. Magn. Mater. 310, 1254–1256 (2007).
22. Derakhshan, S., Greedan, J. E., Katsumata, T. & Cranswick, L. M. D. Long-range antiferromagnetic ordering in the novel magnetically frustrated rock salt oxide system: Li3Mg2RuO6. Chem. Mater. 20, 5714–5720 (2008).

23. Zvereva, E. A. et al. Monoclinic honeycomb-layered compound Li4.5M0.5TeO6: Preparation, crystal structure and magnetic properties. Dalton Trans. 41, 572–580 (2012).

24. Upadhyay, S. K., Iyer, K. K., Rayaprol, S., Paulose, P. L. & Sampaikumar, E. V. A rock-salt-type Li-based oxide, Li4Ni2SbO6, exhibiting a chaotic ferrimagnetism with cluster spin-glass dynamics and thermally frozen charge carriers. Sci. Rep. 6, 31883 (2016).

25. Koo, C. et al. Static and dynamic magnetic response of fragmented Haldane-like spin chains in layered Li3Cu2SbO6. J. Phys. Soc. Jpn. 85, 084702 (2016).

26. Zvereva, E. A. et al. Orbitally induced hierarchy of exchange interactions in the zigzag antiferromagnetic state of honeycomb silver delafossite Ag2Co3SbO6. Dalton Trans. 45, 7373–7384 (2016).

27. Zvereva, E. A., Stratan, M. I., Shukav, I. L., Nalbandyan, V. B. & Vasil’ev, A. N. Effect of a structural disorder on the magnetic properties of the sodium–cobalt tellurate Na2Co3.11Te2O6. J. Exp. Theor. Phys. 124, 612–616 (2017).

28. Kumar, V., Gupta, A. & Uma, S. Formation of honeycomb ordered monoclinic Li3M2TeO6 (M = Cu, Ni) and disordered orthorhombic Li2NiTe2O6. J. Alloys Compd. 42, 14992 (2013).

29. Berthelot, R. et al. New layered compounds with honeycomb ordering: Li3Ni2BiO6, Li4NiM BiO6 (M = Mg, Cu, Zn), and the delafossite Ag2Ni2BiO6. Inorg. Chem. 51, 5377–5385 (2012).

30. Lahe, S. et al. New rock salt-related oxides Li2M2RuO6 (M = Co, Ni): Synthesis, structure, magnetism and electrochemistry. J. Solid State Chem. 203, 160–165 (2013).

31. Taylor, Z. N. et al. Stabilization of O–O bonds by d0 cations in Li14Ni5–24WO6(x ≤ 0.25) rock salt oxides as the origin of large voltage hysteresis. J. Am. Chem. Soc. 141, 7333–7346 (2019).

32. Roudnebush, J. H. et al. Structure and magnetic properties of Cu3Ni2SbO6 and Cu3xCo1–xSbO6 delafossites with honeycomb lattices. Inorg. Chem. 52, 6083–6095 (2013).

33. Uma, S. & Gupta, A. Synthesis and characterization of new rock salt superstructure type layered oxides Li4(M3)2TeO6 (M(III) = Cr, Mn, Al, Ga). Mater. Res. Bull. 76, 118–123 (2016).

34. He, Z., Guo, W., Cui, M. & Tang, Y. Synthesis and magnetic properties of new tellurate compounds Na4MTeO6 (M = Co and Ni) with a ferromagnetic spin-chain structure. Dalton Trans. 46, 5076–5081 (2017).

35. Hu, Z., Cui, M. & Qiu, C. Synthesis, structure and magnetic behaviors of a new spin-1/2 chain compound Na4Cu2TeO6. J. Alloys Compd. 748, 794–797 (2018).

36. Schmidt, W., Berthelot, R., Sleight, A. W. & Subramanian, M. A. Solid solution studies of layered honeycomb-ordered phases O3–Na3M2SbO6 (M = Cu, Mg, Ni, Zn). J. Solid State Chem. 201, 178–185 (2013).

37. Heymann, G. et al. Li3Co1.06TeO6: Synthesis, single-crystal structure and physical properties of a new tellurium compound with CuO2/CuII mixed valence and orthogonally oriented Li-ion channels. Dalton Trans. 46, 12663–12674 (2017).

38. Bette, S. et al. Crystal structure and stacking faults in the layered honeycomb, delafossite-type materials Ag3Li2RuO6 and Ag3Li2RuO6. Dalton Trans. 48, 9250–9259 (2019).

39. Grundlisch, N. S., Seymour, I. D., Henkelman, G. & Goodenough, J. B. Electrochemical properties of three Li3NiTeO6 structural polymorphs. Chem. Mater. 31, 9379–9388 (2019).

40. Bhattacharya, N., Gupta, A. & Uma, S. Evidence of cationic mixing and ordering in the honeycomb layer of Li4MSbO6 (M iii) = Cr, Mn, Al, Ga (S.G. C2/c) oxides. Dalton Trans. 43, 12050–12057 (2014).

41. Sun, Y., Guo, S. & Zhou, H. Adverse effects of interlayer gliding in layered transition-metal oxides on electrochemical sodium-ion storage. Energy Environ Sci. 12, 825–840 (2019).

42. Chen, S.-S. & Simons, J. Characteristic forms and geometric invariants. Ann. Math. 99(1), 48–69 (1974).

43. Dunne, G. V. Aspects of Chern-Simons Theory. arXiv: hep-th/9902115 (1999).

44. Chavel, I. The Riemann–Silberstein vector in classical and quantum theories of electromagnetism. J. High Energy Phys. 1909.00778 (2019).

45. Allendoerfer, C. B. & Weil, A. The Gauss–Bonnet theorem for Riemannian polyhedra. Ann. Math. 150(2), 319–338 (1999).

46. Feynman, R. P. & Brown, L. M. The Fokker–Planck Equation: Methods of Solution Applications. (Springer-Verlag, Berlin, New York, 1996).

47. Kosterlitz, J. M. and Thouless, D. J. Ordering, metastability and phase transitions in two-dimensional systems. J. Phys. C: Solid State Phys. 6(12), 1181 (1973).

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**Competing interests**
The authors declare no competing interests.

**Additional information**

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