

Geometric quantization of curvature energy in equipotential surfaces of ionic crystals

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The curvature energies of triply periodic minimal surfaces (TPMS) and zero equipotential surfaces (ZEPS) of ionic crystals are both quantized with the Euler–Poincaré characteristic as the “quantum number,” and the curvature energy of the TPMS larger than that of the corresponding ZEPS. Quantization is imposed by the charge-defined metric. © 2002 American Institute of Physics.
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“There is nothing in the world except empty curved space. Matter, charge, electromagnetism and other fields are only manifestations of the curvature of space.”
John Archibald Wheeler (1957)

INTRODUCTION

Triply periodic minimal surfaces (TPMS) are surfaces for which the mean curvature, $H=(k_1+k_2)/2$ is zero at every point, where k_1 and k_2 are the principal curvatures. The Gaussian curvature is defined as $K=k_1k_2$. At most points $k_1=-k_2\neq 0$, so that K is negative. Exceptionally, there are “flat points” where $k_1=k_2=0$. TPMS are omnipresent in the natural and manmade worlds, providing a concise description of many seemingly unrelated structures,¹ which can be described in terms of curved nets folded onto periodic minimal surfaces.^{2,3} TPMS are essentially soap films, the surface areas of which are minimized by the (two-dimensional) surface tension forces. They are of interest not only to the structural chemist, but also to the biologist,⁴ structural engineer and the materials scientist.⁵ For example, the structure of the zeolite analcime is described by the G surface;² the P surface occurs in etioplasts and in sea urchin spines;⁴ and the D surface is found in glyceryl mono-oleate–water mixtures.⁶ TPMS may even have applications in cosmology as membranes (or “branes”).⁷

An equipotential surface is a surface of constant potential within a distribution of positive and negative charges. In crystal structures, the $V=0$ surface is known as the zero equipotential surface (ZEPS). It is thus the result of (three-dimensional) electrostatic interactions. The ZEPS are triply periodic and closely resemble the TPMS. For example, the

ZEPS of CsCl it is close to the P TPMS. The ZEPS are denoted by an asterisk to distinguish them from their TPMS counterparts. We have expressed the P^* ZEPS for the CsCl lattice, considered as a periodic distribution of ideal point charges, in terms of Jacobi’s elliptic theta functions as⁸

$$\int_0^\infty t dt (\vartheta_3 \vartheta_3 \vartheta_3 - \vartheta_4 \vartheta_4 \vartheta_4) = 0,$$

where the arguments of the theta functions are πx , πy , and πz and $\exp(-t^2)$. The charge density distribution is given in terms of finite sums of periodic δ functions as

$$\rho(\underline{r}) = \sum_{j=1}^N q_j \sum_{\underline{k}=-\infty}^{\infty} \delta(\underline{r} - \underline{r}_j - \underline{k}),$$

where the unit cell contains N charges q_j at points $(\underline{r}_j - \underline{k})$, and the components of \underline{k} take integer values. Using the fundamental formula of crystallography we rewrite this expression as a three-dimensional Fourier series

$$\rho(\underline{r}) = \sum_{j=1}^N q_j \sum_{\underline{h}=-\infty}^{\infty} e^{2\pi i \underline{h} \cdot (\underline{r} - \underline{r}_j)}.$$

The potential φ is obtained by convoluting the charge distribution ρ with the $1/r$ decay of the potential generated by an isolated point charge

$$\varphi(\underline{r}) = \int d\underline{\xi} \rho(\underline{\xi}) / |\underline{r} - \underline{\xi}|.$$

The Fourier convolution theorem gives the coefficients of φ in terms of ρ multiplied point-wise by the Fourier transform of the decay function $1/r$, so that

$$\varphi(\underline{r}) = \frac{1}{\pi} \sum_{j=1}^N q_j \sum_{\underline{h}=-\infty}^{\infty} \frac{e^{2\pi i \underline{h} \cdot (\underline{r} - \underline{r}_j)}}{|\underline{h}|^2} = \frac{8}{\pi} \sum_{j=1}^N q_j \sum_{h,k,l=0}^{\infty} \frac{\cos 2\pi h(x-x_j) \cos 2\pi k(y-y_j) \cos 2\pi l(z-z_j)}{h^2 + k^2 + l^2}, \quad (1)$$

where the prime on the last sum indicates that terms are to be multiplied by $1/2$ for each zero index. This series is only conditionally convergent,⁹ and depends upon the order of summation. However, the potential at any point in a crystal

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lattice must be single-valued, which suggests that different orders of summation (i) correspond to different zero-point energies associated with the field; (ii) lead to an infinite set of potentials associated with any given array.

CURVATURE ENERGY

Quantum mechanics attributes the existence of zero-point energy to the curvature of the wave function describing the ground state. The curvature energy of a surface is given by the Helfrich Hamiltonian¹⁰

$$\mathcal{H} = \int dS [2\alpha(H - \gamma)^2 + \beta K], \quad (2)$$

where H and K are the mean and Gaussian curvatures, respectively, and integration is over the total surface area. The bending rigidity α ($\alpha > 0$) and saddle-splay β ($|\beta| > 0$) are the two elastic moduli, while γ is the spontaneous curvature, which vanishes for balanced surfaces (those which interchange the partial sub-spaces which they divide).

The Gauss–Bonnet theorem relates Gaussian curvature to the Euler–Poincaré characteristic, χ , via $-2\pi\chi = \int K dS$, so that the contribution to the curvature energy from the saddle-splay deformation is $-8\pi\beta$ for both surfaces. In turn, the genus, g , of a surface is related to the Euler–Poincaré characteristic by $g \equiv 1 - \chi/2$. Since the genus must be equal to zero or to a positive integer, χ can take the integer values of 2, 0, -2 , -4 ...

Equation (2) can be used to calculate the relative curvature energies of the (balanced) P and P^* surfaces, assuming that α and β have the same magnitude and sign for both. Both surfaces have the same Euler–Poincaré characteristic of -4 . As the mean curvature of a minimal surface vanishes everywhere, for the P surface the contribution to the curvature energy from the bending component is zero, and the curvature energy of P^* is larger by an amount $2\alpha \int H^2 dS$. The P surface can, therefore, be considered as the ground state in terms of curvature energy with a zero-point energy of $-8\pi\beta$.

A very close nodal approximation for the P^* surface is¹¹ $f_p = \{1,0,0\} + 0.090\,039\,5 \{1,1,1\}$, where $\{h,k,l\}$ are reflection planes of the space group $Pm\bar{3}m$ (No. 221).¹² We have calculated the integral $2\int H^2 dS$ numerically by summing the components of H^2 at the center of gravity of each tessalating polygon over the surface. The distribution of H^2 is shown in Fig. 1(a) by assigning a color cyclically to each value and scaled such that the minimum to maximum spans blue to red. The mean of the distribution of H^2 over the surface is 1.092 38, and the variance is 3.7251, with a minimum value of zero and a maximum value of 6.163 88. The curvature energy of the P surface is thus lower than that of the P^* surface by 2.18476 α .

Gozdz and Holyst¹³ generated a surface of genus 45 with the symmetry of the P surface, a surface of genus 73 with the symmetry of the D surface, and surfaces of genera 53, 69, 109, and 157 with the symmetry of the G surface. In terms of symmetry, these high genus surfaces are the equivalents of the P , D , and G TPMS, which are the ground curvature energy states of ZEPS of corresponding symmetry. This sug-

gests that multiple solutions of distinct genus, which we consider a quantized topological index, occur for a range of different crystal arrays. The Helfrich Hamiltonian for TPMS reduces to a simple expression, which via the Gauss–Bonnet theorem may be written as $\mathcal{H} = -2\pi\beta\chi$, where $|\beta| > 0$.

The excited states of the crystal constitute an infinity of different ZEPS forming the complete set. For the CsCl lattice, this is the manifold of surfaces of increasing curvature, quantized by the Euler–Poincaré characteristic, with the same symmetry as the P (“Schwarz”) TPMS, which represents the archetypal structure for this crystal symmetry. Parametrization of the P surface has allowed us to calculate its coordinates analytically.¹⁴ Alternatively, the coordinates of this surface can be given in the form $f(x,y,z)$ as a two-term nodal expansion of its generating space group $Pm\bar{3}m$ as $f_p = \{1,0,0\} - 0.150\,763\{1,1,1\}$.¹¹

The curvature energy of the basis set of allowed states is, therefore, quantized with the Euler–Poincaré characteristic as the quantum number. There is thus a connection between quantum field theory and surfaces which describe the basis sets of wave functions of the field. We assume that selection rules governing allowed and forbidden transitions exist. In CsCl, where field states are described by the P^* surface and its higher genus counterparts, quantum transitions may take place from a state of Euler–Poincaré characteristic χ_1 to a state of characteristic χ_2 , with transition energy $-2\pi(\chi_2 - \chi_1)\beta$. There may also be a transition from a state χ_1 of one crystal lattice (e.g., CsCl, β_a), to the state χ_2 of a different crystal lattice (e.g., ZnS, β_b), with transition energy $-2\pi(\beta_b\chi_2 - \beta_a\chi_1)$. An example of the latter case is the martensitic transition in steel,¹⁵ from a structure of the CsCl type, described by the P surface ($\chi = -4$), to the ZnS type, described by the D surface ($\chi = -16$), via the intermediate G surface ($\chi = -8$). The transition is defined by a single parameter, the Bonnet angle.^{14,16,17}

To summarize, the TPMS are the zero equipotentials of the field Hamiltonian. The energy is given by $E_{\alpha\chi} = -2\pi\chi\beta_\alpha$ for a surface $f_{\alpha\chi}$, where α denotes the symmetry type, and χ is the Euler–Poincaré characteristic of a member of the manifold of allowed states. The scalar potentials are described by TPMS, whose energy is the minimum possible under the Helfrich Hamiltonian. This curvature energy is quantized in units of $2\pi\chi$, which is the consequence of the curvature of the scalar potential, from which the field is derived by differentiation, with the minimization of self-energy making the surface minimal. The charge distribution determines the metric of the potential and hence the field.

VECTOR POTENTIAL

The mean curvature of a surface is equal to the divergence of the unit vector, \hat{n} , normal to the surface,¹⁸ given by $\hat{n} = \nabla f(\underline{r})$, where the function $f(\underline{r})$ describes the surface. Hence $H = \nabla \cdot \hat{n} = 0$ at every point. A vector with zero divergence and nonzero curl can be represented as the curl of the vector potential, \underline{A} , defined as¹⁹

$$\underline{A} = -\underline{r} \times \int_0^1 \lambda^2 \hat{n} d\lambda, \quad (3)$$

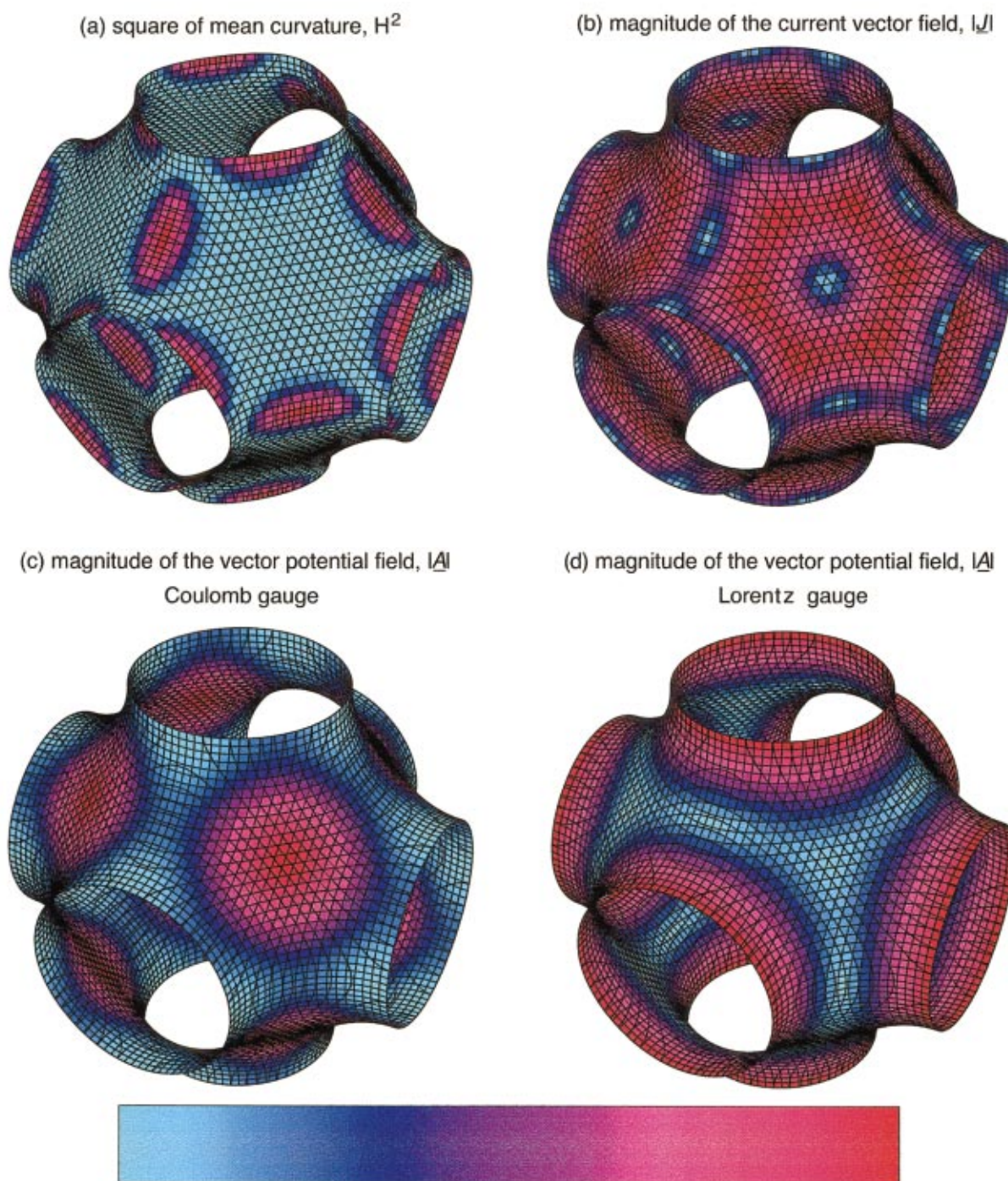


FIG. 1. (Color) (a) Plot of the distribution of the square of the mean curvature, H^2 , over the P^* zero equipotential surface. The color scale spans H^2_{\min} to H^2_{\max} from blue to red (see inset). (b) Plot of the magnitude of the current vector field $|J|$ permeating a CsCl unit cell at the surface of the P TPMS as the ground state zero equipotential surface within the crystal lattice (blue to red). (c) The magnitude of the vector potential field $|A|$, over the surface of the P TPMS (blue to red). Coulomb gauge ($\nabla \cdot A = 0$). The distribution of the magnitude of the vector potential in this gauge over the surface has a mean of 0.078 790 1, and a variance of 0.008 397 37, with a minimum value of zero and a maximum value of 0.160 725. (d) As in (c), but in Lorentz gauge ($A' = A + \nabla f_P^{\text{TPMS}}$). The distribution of the magnitude of the vector potential in this gauge over the surface has a mean of 3.280 66, and a variance of 10.7864, with a minimum value of 3.046 69 and a maximum value of 3.627 60.

where $r = (x, y, z)$. For an electromagnetic field within the CsCl lattice, the vector potential is an elementary current density on the P surface. By Maxwell's equations, the field within the lattice is electrostatic ($\nabla \times E = 0$ and $\nabla \cdot E \propto \rho$) and magnetostatic ($\nabla \cdot H = 0$ and $\nabla \times H \propto J$). We shall see that these equations are defined by geometry alone. The magnetic field H , is the curl of the vector potential, $H = \nabla \times A$. Max-

well's third equation gives the current density vector J in terms of the curl of the unit vector normal to the surface, as $J \propto \nabla \times \hat{n}$.

Figure 1(b) shows the magnitude of the current vector J on the P minimal surface calculated using the exact coordinates.¹⁴ The zero contour of the surface was plotted as tessellating polygons. The magnitude of the current vector

was calculated at the center of gravity of each polygon, and its distribution represented as a color, scaled such that the range from maximum to minimum spans blue to red. The value of $|J|$ spans the range 0–0.790 077 with a mean of 0.547 255 and variance 0.335 781 over 5002 tessellations of the surface. The choice of vector potential is arbitrary, since only curl A is required to reproduce a given field. We may, therefore, add the gradient of any scalar to Eq. (3) and write $A = A_0 + \text{grad } \psi$, since $\text{curl grad } \psi = 0$. We use the Coulomb gauge, which by convention for static fields is chosen such that $\text{div } A = 0$, and we have a transverse vector potential [Fig. 1(c)]. The magnitude and direction of the vector potential may vary considerably depending on the choice of gauge. Adding $\text{grad } f$ changes the picture markedly [Fig. 1(d)].

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