Comment on "Simple electrostatic model of the structural phase transition" [Am. J. Phys. 54, 403 (1986)]: Not that simple

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Recently it was discovered[1] that four equal charges on a sphere can undergo a structural transition when placed in a uniform electric field **E**: The equilibrium arrangement has C_3 symmetry when $E < E_0$, but C_4 symmetry when $E > E_0$, where $E_0 = 0.732q/R^2$ is the critical value of E, q is the charge, and R is the radius of the sphere. If the field is applied in the z direction, the C_3 phase has one charge on the intersection of the z axis with the sphere and three charges on the vertices of an equilateral triangle perpendicular to the z axis; in the C_4 phase, all four charges are in the same plane, perpendicular to the z axis, at the corners of a square. Both cases can be characterized by a single structural variable, α, the polar angle of the charges. The $C_3 \rightarrow C_4$ transition is visualized as a sudden jump of the polar charge of the C_3 arrangement into the plane of the other three charges, followed by a rearrangement in this plane and a change in α.

The purpose of the present note is to point out that a third phase exists, with C_2 symmetry. This phase has a lower energy than both the C_3 and C_4 arrangements in the range $E_1 < E < E_2$, with $E_1 = 0.541q/R^2$ and $E_2 \approx 1.2q/R^2$. With increasing field the symmetry changes as $C_3 \rightarrow C_2 \rightarrow C_4$. There is no structural discontinuity in the $C_2 \rightarrow C_4$ transition; rather, C_4 must be considered as a degeneracy of C_2, which develops only gradually.

The C_2 arrangement is closely related to the C_4 arrangement: Whereas the two diagonals of the C_4 square cross at the same height, α, they are at different heights, α_1 and α_2 (but still crossing at right angles and perpendicular to the field) in the C_2 configuration, thus requiring *two* structural variables, rather than one. Thus C_4 is a special case: $\alpha_1 = \alpha_2$. In Table I, the energy $W(C_2)$ is compared with the energies $W(C_3)$ and $W(C_4)$, reported in Ref. 1, for different values of the field E; Table II compares the structural variables for C_4 and C_2 geometries.

As is evident from Table I, there are two transition points. The first, at $E_1 = 0.541q/R^2$, is sharp and corresponds to a rotation of the distorted tetrahedron about an axis, perpendicular to the field, and parallel to one of the sides of the equilateral triangle. Although C_2 now becomes more favorable, C_3 remains metastable: The corresponding minimum in the potential energy surface persists as E is increased, albeit as a local rather than a global minimum.

The second transition, somewhere between 1.1 and 1.2 q/R^2, is gradual, without dramatic changes in the structure or its orientation in the field. The two structural variables α_1 and α_2 merely approach each other and become equal (cf. last column of Table II), which makes the symmetry C_4. Since the average, $\frac{1}{2}(\alpha_1 + \alpha_2)$, is very close to $\alpha(C_4)$, it was suspected that the C_4 arrangement might correspond to a saddle point in the potential energy surface, rather than to a (local) minimum. In order to verify this, W was calculated as a function of $\Delta\alpha$ for C_2 structures characterized by $\alpha_{1,2} = \alpha(C_4) \pm \Delta\alpha$.

The results are shown in Fig. 1, for a few values of E around the $C_2 \rightarrow C_4$ transition point [full lines; $W(C_4)$ taken as reference]. Indeed, for $E < 1.2q/R^2$, W has a local

Table I. Energies W (in units q^2/R) for different equilibrium geometries of four equal charges q on a sphere with radius R in an electric field **E** (in units q/R^2). The lowest value is marked with an asterisk.

	W		
E	C_3[a]	C_4[a]	C_2
0.0	3.674235*	3.828427	3.674235*[b]
0.1	4.061170*	4.207698	4.061684
0.2	4.420000*	4.547351	4.422814
0.3	4.749416*	4.851932	4.754910
0.4	5.050500*	5.126858	5.056320
0.5	5.325992*	5.377149	5.328427[c]
0.6	5.579209	5.606996	5.574851*
0.7	5.813335	5.819751	5.799647*
0.8	6.031138	6.018062	6.006406*
0.9	6.234926	6.204032	6.198049*
1.0	6.426593	6.379340	6.376889*
1.1	6.607695	6.545346	6.544773*
1.2	6.779512	6.703162*	⋯
1.3	6.943107	6.853706*	⋯
1.4	7.099369	6.997749*	⋯
0.541	5.432315	5.473650	5.432331

[a] Data partially from Ref. 1.
[b] $3\sqrt{3/2}$.
[c] $5/2 + 2\sqrt{2}$.

Table II. Structural parameters (deg) for C_4 and C_2 equilibrium geometries of four equal charges on a sphere in an electric field **E** (in units q/R^2).

	C_4[a]	C_2			
E	α	α_1	α_2	$\frac{1}{2}(\alpha_1+\alpha_2)$	$\frac{1}{2}(\alpha_1-\alpha_2)$
0.0	90.00[b]	125.26	54.74[c]	90.00[b]	35.26
0.1	84.10	120.11	51.03	85.57	34.54
0.2	78.64	113.54	48.35	80.94	32.59
0.3	73.87	105.68	46.60	76.14	29.54
0.4	69.79	97.52	45.56	71.54	25.98
0.5	66.33	90.00[b]	45.00[b]	67.50	22.50
0.6	63.39	83.29	44.85	64.07	19.22
0.7	60.85	77.52	44.91	61.21	16.30
0.8	58.64	72.56	45.09	58.82	13.73
0.9	56.70	68.07	45.46	56.76	11.30
1.0	54.98	63.77	46.20	54.98	8.78
1.1	53.45	59.58	47.32	53.45	6.13
1.2	52.06	⋯	⋯	⋯	0
1.3	50.80	⋯	⋯	⋯	0
1.4	49.65	⋯	⋯	⋯	0

[a] Data partially from Ref. 1.
[b] Exact value.
[c] arctan ($\sqrt{2}$).

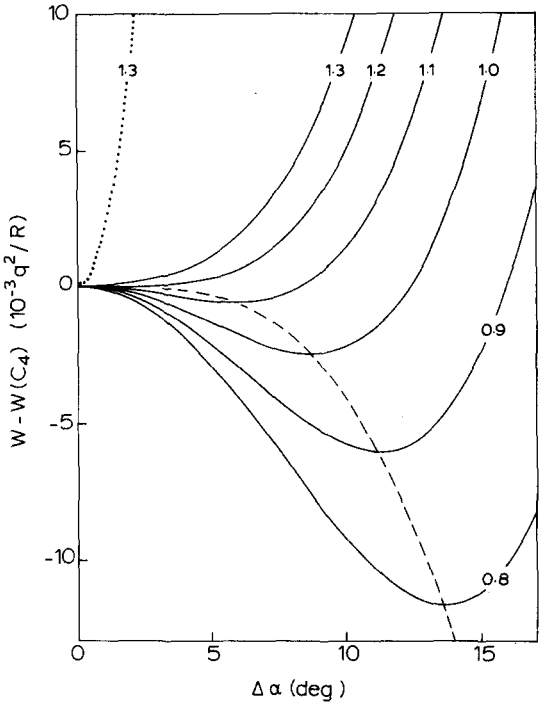

Fig. 1. Energy difference $W - W(C_4)$ as a function of $\Delta\alpha$ [$= \frac{1}{2}(\alpha_1 - \alpha_2)$, see text] for different values of the field $E(q/R^2)$ (full lines). Dotted curve: same, but with $\alpha_1 = \alpha_2$ (see text).

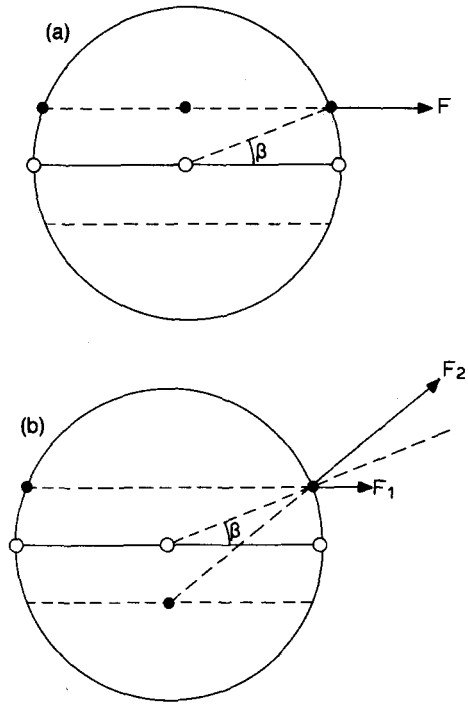

Fig. 2. Different departures (black dots) from the $E = 0$, C_4 configuration (open circles). The view is along one of the diagonals of the $E = 0$ square (the fourth charge is hidden). (a) symmetry conserving; (b) symmetry lowering ($C_4 \rightarrow C_2$).

maximum with respect to changes in $\Delta\alpha$, when $\Delta\alpha = 0$, and a local minimum [actually two minima: Fig. 1 may be mirrored across the ordinate, since $W(\Delta\alpha) = W(-\Delta\alpha)$] for values of $\Delta\alpha$ essentially equal to the values of $\frac{1}{2}(\alpha_1 - \alpha_2)$ in Table II. With increasing field strength, the minima shift to lower values of $\Delta\alpha$; at the same time, the well depth decreases (broken line; the figure suggests zero slope in the origin). Eventually,the well vanishes and $W(0)$ becomes a local minimum with respect to $\Delta\alpha$; although there must be a critical value E_2 of E, it cannot be calculated with the same precision as E_1, at least with numerical methods. The minimum is very shallow, when compared to that of the perpendicular cross section of the potential energy surface: $\alpha_1 = \alpha_2 = \alpha(C_4) + \Delta\alpha$ (dotted curve; $E = 1.3q/R^2$). This will have consequences for the dynamical behavior of the system.

The mechanical origin of the C_4 saddle point is illustrated in Fig. 2, for the simple $E = 0$ case. Small departures β from the $\alpha = 90°$ configuration (open circles), indicated by black dots, are considered. Two different modes are compared: (a) one symmetry conserving and (b) the other symmetry lowering. In the first case, the forces **F**, acting on the charges, are along the square diagonals, with downward tangential components that tend to restore the original configuration, i.e., this configuration is stable with respect to a symmetry-conserving perturbation. In the second case, the forces have different directions. To second order in β, $\mathbf{F}_1 = \frac{1}{4}(1 + \beta^2)$ and $\mathbf{F}_2 = \frac{1}{2}\sqrt{2}$ (in units of q^2/R^2); the normal to the spherical surface very nearly bisects the angle between $\mathbf{F}_1$ and $\mathbf{F}_2$. Thus the tangential component of the resultant force must be upward, tending to increase the perturbation. Consequently, the $\alpha = 90°$ configuration is unstable with respect to this type of perturbation.

From a physical point of view, the $C_3 \rightarrow C_2$ transition is the less interesting. In the absence of thermal motion, it would never occur, since the C_3 minimum persists beyond $E = E_1$ and remains separated from the C_2 minimum by a barrier, with an associated activation energy. Even if thermal motion were to be introduced in some way, the chances of finding the system in one or the other minimum would be almost equal for any $E \lesssim 0.7q/R^2$ in view of the small energy difference (about $0.01q^2/R$, as compared to the barrier height, about $0.40q^2/R$), which precludes a sharp transition point in practice. Moreover, large thermal amplitudes are required, in view of the large (angular) separation between the two modifications, thus obscuring any ordered structure by chaotic motion. The significance of the value $E_1 = 0.541q/R^2$ for E can, however, be demonstrated if the field is applied in a direction that bisects the angle between the radius vector to a vertex and a radius vector through the midpoint of an adjoining edge of the undistorted tetrahedral arrangement. If the field exceeds E_1 when it is switched on, the whole assembly performs a clockwise rotation; if $E < E_1$ the rotation will be in the opposite direction.

The second transition ($C_2 \rightarrow C_4$) is interesting in that it has some elements of an order–disorder transition, a well-known phenomenon in solid-state physics. Let us consider the situation at $E = 1.3q/R^2$ (cf. Fig. 1). If the model does not allow for thermal motion, the system will adopt the configuration corresponding to the true minimum at $\Delta\alpha = 0$, i.e., with C_4 symmetry. The anisotropy of the potential well becomes apparent when thermal motion is introduced: The in-phase motion of all charges is a small-amplitude, high-frequency ("acoustic") mode of vibration, whereas the out-of-phase ("butterfly") motion is a large-amplitude, low-frequency ("optic"[2]) mode. The time average of the symmetry remains C_4 (actually C_∞ as a result of the unhindered rotation about the z axis). The second derivative $d^2W/d(\Delta\alpha)^2$, which is proportional to the squared frequency of the vibration, is clearly positive. However, when the intensity of the field is reduced, it be-

comes negative, as is evident from the 0.8 curve. Consequently, for some value of E (close to $1.2q/R^2$) the butterfly motion has zero frequency ("soft mode"). With a further reduction of the field, the structure is frozen-in in either of the two minima that flank the saddle point. However, if the temperature is raised, the saddle point barrier may be crossed occasionally, and the system will spend half of the time in either minimum. An observer would see the average structure (C_4), with large vibration amplitudes, although the structure is actually disordered. The probability for such a jump-over to occur decreases with decreasing field, i.e., the degree of order increases and the symmetry becomes C_2.

The curves of Fig. 1 can be fitted approximately by a Landau-type expression for the free energy of a system, exhibiting a second-order phase transition, involving symmetry breaking,

$$W - W(C_4) \approx \tfrac{1}{2} A(E - E_2)^{\gamma}(\Delta\alpha)^2 + \tfrac{1}{4} B(E - E_0)(\Delta\alpha)^4, \quad (1)$$

with $\gamma = 1$, $A \approx 6.1\times10^{-4} qR$ deg^{-2}, $B \approx 2.0\times10^{-6} qR$ deg^{-4}, $E_2 = 1.21$, and $E_0 \approx 0.1q/R^2$. The critical exponent β in the expression

$$\Delta\alpha \approx (E_2 - E)^{\beta}, \quad E < E_2 \quad (2)$$

for the field dependence of the order parameter, is $\frac{1}{2}$.

The model appears to be extremely well suited to bring molecular-dynamics-type calculations within the capacity of small desktop computers. Since it involves only four particles with two degrees of freedom, interacting through simple central forces, the great number of time steps usually required in MD simulations is not necessarily prohibitive. Also, there is no need to worry about evaporation or periodic boundary conditions, and the results are easily interpreted, without the necessity of using statistical methods. Nevertheless, the dynamical simulation of a structural phase transition in the critical region is of considerable interest and may contribute to our understanding of the phenomenon.

[1] A. A. Berezin, Am. J. Phys. **54**, 403 (1986).

[2] The quotes are to indicate that the resemblance to acoustic and optic modes in a crystal is only partial: There is no wave propagation, and the vibrating masses have *like* charges; there is no translation symmetry.

Culvert whistlers revisited

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I. INTRODUCTION

Culverts ("echo tubes") are now installed as corridor demonstrations in some physics departments and science museums.[1] (There is a beauty at the San Francisco Exploratorium.[2]) You can hear "culvert whistlers" there, or at any roadside culvert.[3] Simpley clap your hands at one end of the culvert and listen. You will hear a sharp echo of the hand clap at the expected delay time $t_0 = 2L/c$, where L is the length of the tube and $c = 340$ m/s is the velocity of sound in air. But, surprisingly, the sharp echo is followed immediately by a "whistler," a sound that starts at a very high pitch and then descends swiftly to a long lingering final note at frequency $f_{\min} = 1/T_{\max}$, where $T_{\max} = 2W/c$ is the time it takes sound to travel directly back and forth across the tube of effective width W. (The effective width W is the tube diameter D divided by 1.17. Here, W is less than D because of contributions from rays that do not go through the axis of the tube and hence travel a transverse distance less than D between reflections from the walls. The factor 1.17 arises from the appropriate Bessel function.[3,4]) For the Exploratorium echo tube of length $L = 100$ ft and diam 18 in., one finds $t_0 = 0.179$ s, $T_{\max} = 0.002\,30$ s, i.e., $f_{\min} = 435$ Hz, with the final pitch audible for nearly a second. (Yes, the final sound agrees with a 440-Hz tuning fork!)

Unfortunately for many of the people hearing the whistlers, the explanation is usually given at the level of a junior physics major, something like: "Fourier analyze the handclap delta function into its broad spectrum of frequencies $f = \omega/2\pi$; show that the boundary conditions in the tube give the dispersion relation $\omega^2 = c^2k_z^2 + \omega_0^2$; from this find the group velocity $v_g = d\omega/dk_z$; then use the group velocity to get the delay time $t = 2L/v_g$. Finally, eliminate k_z and solve for $f = f_0/[1 - (t_0/t)^2]^{1/2}$, where $t_0 = 2L/c$, and $f_0 = c/2W$." To quote from Ref. 1 ". . .the explanation is much more complex than the construction." A simpler derivation is needed, at the level of high-school physics, giving the detected whistler frequency as a function of time. Such an explanation is readily given in terms of the detection times of the multiple reflections of the handclap. Using only Pythagoras' law we can get a simple formula for the time $t = t_N$ that the Nth pulse is detected. We find that the detected pulses are so closely spaced in time that they are not heard as individual pulses but as a pitch of frequency $f = 1/T_N$, where $T_N = t_{N+1} - t_N$. We do not need to use calculus to calculate f as a function of t, provided we calculate t_N and t_{N+1} to six digits with a pocket calculator so as to retain three-digit accuracy for T_N after the subtraction $t_{N+1} - t_N$ of two numbers t_N and t_{N+1} whose first three digits are the same. But we can use calculus if we wish, to get a simple formula for f as a function of t.

II. DERIVATION

The culvert is a cylindrical tube, open at both ends, of length L and effective width W. To keep the geometry of the derivation as simple as possible we generate the pulse at one side of the entrance of the tube and put the detector—a