

## Charge-transfer excitations in the cuprate superconductors

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First-principles calculations of the dielectric matrix of the key structural element of the copper-oxide superconductors show a weakly damped resonance at 3.5 eV which contains most of the oscillator strength in charge-transfer excitations. Such excitations have been proposed as a mediating boson for superconductive pairing. Although this mode is a well-developed and robust excitation, we find its energy to be too large to give high superconducting transition temperatures.

Since the discovery of the high- $T_c$  superconductors in 1986, much effort has been put into investigating the underlying mechanism. It is clear that BCS theory,<sup>1</sup> which proved excellent for the “conventional” materials, is inadequate here. Central to the phenomenon of superconductivity is the pairing of electrons (in momentum space), and the question of how this occurs in the cuprate materials has been the subject of much debate.<sup>2</sup> A number of models<sup>3–5</sup> suggest low-energy ( $\sim 0.5$  eV) charge fluctuations as the mediating boson, and our purpose is to calculate the dielectric matrix from first principles to investigate this hypothesis and the underlying ideas.

Common to the entire class of high- $T_c$  superconducting materials is the presence of planes of copper and oxygen atoms. Between these planes is found a variety of atomic contents; their effect is to maintain the formal valence close to  $\text{Cu}^{2+}\text{O}^{2-}$ .<sup>6</sup> A calculation of the dielectric matrix for any one such compound is not the most desirable approach to the problem, not only because of the immense computational expense required for such complex structures, but also because we are seeking properties general to all the cuprates. To this end, we have performed calculations on a hypothetical tetragonal lattice of  $\text{CuO}_2$ , with Cu at  $(0,0,0)$  and O at  $(\frac{1}{2},0,0)$  and  $(0,\frac{1}{2},0)$ , and parameters chosen so that the edge length of the  $\text{CuO}_2$  squares and the interplanar spacing were equal to those of typical superconducting compounds. As this model structure stands, the valences on the copper and oxygen atoms correspond to a heavily hole-doped compound. By doping our structure with extra electrons, we are able to confer appropriate valences on the atoms. An undoped superconductor would correspond in our system to a doping of two electrons per unit cell. Numerous band-structure calculations for various high- $T_c$  materials<sup>7</sup> have demonstrated the presence of a half-filled or nearly-half-filled  $\text{Cu}(3d)\text{-O}(2p)$  hybrid band with strongly two-dimensional character. The band structure of our model solid as calculated in the local-density approximation (LDA) is shown in Fig. 1. It is not only in good general agreement with those of the complete structures, but also reproduces quantitatively (and with the correct symmetry) the major bands near the Fermi energy—the most important ones as far as dielectric response is concerned.

We first report the technical scheme of our calculations, which use the time-dependent local-density approximation (TDLDA). The results for the  $q \sim 0$  response at low energies are dominated by a low energy, weakly damped, resonance involving charge-transfer fluctuations (CTF) between copper and oxygen, consistent with the scenario of Varma *et al.*<sup>3,8,9</sup> We then compare our results with previous calculations on model Hamiltonians and discuss the limitations of our approach.

The central quantity evaluated in our work is the dielectric matrix  $\epsilon$ , which gives the relation (in reciprocal space) between changes in the total internal potential  $\phi_{\text{tot}}$  in a crystal and the applied potential  $\phi_{\text{ext}}$  as

$$\delta\phi_{\text{tot}}(\mathbf{q} + \mathbf{G}, \omega) = \sum_{\mathbf{G}'} \epsilon_{\mathbf{G}\mathbf{G}'}^{-1}(\mathbf{q}, \omega) \delta\phi_{\text{ext}}(\mathbf{q} + \mathbf{G}', \omega). \quad (1)$$

(In matrix notation we would write this as  $\delta\phi_{\text{tot}} = \epsilon^{-1} \delta\phi_{\text{ext}}$ .)  $\epsilon$  is in general a function of the wave vector  $\mathbf{q}$  and frequency  $\omega$  of the potential.

The absence of local-field effects would result in the dielectric matrix being diagonal. Clearly in an inhomogeneous system such as is being considered, these effects are essential, especially insofar as charge-transfer fluctuations *within* a unit cell are concerned, and we take them fully into account by our calculation of the off-diagonal elements. Earlier cal-

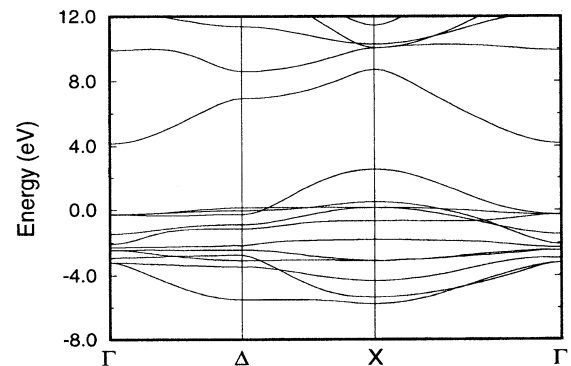


FIG. 1. Band structure of the model solid.

culations of the dielectric function of a cuprate material<sup>10</sup> (in that case based on a tight-binding fit to a LDA band structure) focused on the  $G = G' = 0$  element of the dielectric matrix and so do not contain local-field effects.

The presence of a resonance means that  $\phi_{\text{tot}}$  is nonzero when  $\phi_{\text{ext}}$  is zero. Relation (1) shows that for this to occur the determinant of  $\epsilon$  must vanish. These resonances are the electronic charge excitations of the system.

$\epsilon$  can be formulated in terms of the unscreened density response function  $\chi^0$ , which is defined by the electron-density change  $\delta n = \chi^0 \delta \phi_{\text{tot}}$ . The random-phase-approximation (RPA) expression  $\epsilon = 1 - V^c \chi^0$ , where  $V^c$  is the Coulomb interaction, can be extended to include exchange and correlation effects, within the time-dependent local-density approximation, by writing  $\epsilon = 1 - V^c \chi^0 - K_{\text{xc}} \chi^0$ . Note that the function  $\epsilon$  that we are considering describes the response not of a test charge, but of the electrons themselves. ( $\delta \phi_{\text{tot}}$  includes the exchange-correlation term.) This is clearly the appropriate quantity for electronic excitations. Here  $K_{\text{xc}}$  is calculated in the local-density approximation:  $K_{\text{xc}}^{\text{LDA}}(\mathbf{r}, \mathbf{r}') = K(n(\mathbf{r})) \delta(\mathbf{r} - \mathbf{r}')$ , where  $K(n)$  is the derivative of the exchange-correlation potential with respect to density for a homogeneous electron gas of density  $n$ .

$\chi^0$  can be written in terms of the single-particle wave functions  $\psi_i$  and energies  $E_i$  that solve the unperturbed problem  $(-\frac{1}{2}\nabla^2 + V_{\text{ion}} + V_H + V_{\text{xc}})\psi_i = E_i \psi_i$ .  $V_H$  is the Hartree potential,  $V_{\text{xc}}$  is calculated within the LDA, and  $V_{\text{ion}}$  is the electron-ion term, which we calculate using non local norm-conserving pseudopotentials optimized for plane-wave convergence.

The resulting expression for  $\chi^0$  (Ref. 11) is

$$\chi^0(\mathbf{r}, \mathbf{r}', \omega) = 2 \sum_{i,j} (n_i - n_j) \frac{\psi_i(\mathbf{r}) \psi_j^*(\mathbf{r}) \psi_i^*(\mathbf{r}') \psi_j(\mathbf{r}')}{E_i - E_j - \omega - i\delta}, \quad (2)$$

where the  $n$  are occupation numbers and  $\delta$  is a positive infinitesimal. The corresponding quantity in reciprocal space,  $\chi_{\text{GG}'}^0(\mathbf{q}, \omega)$ , takes the form of a sum of terms, each of which is of the form

$$\int_{1\text{st BZ}} \frac{A(\mathbf{k}, \mathbf{k}')}{E_{l\mathbf{k}} - E_{m\mathbf{k}'} - \omega - i\delta} d^3k, \quad (3)$$

where  $l$  and  $m$  are band indices. Thus  $\chi^0$  has branch cuts along parts of the real  $\omega$  axis. The integral over the first Brillouin zone in (3) is, in practice, computed as a discrete sum. The terms in this sum contain poles at real values of  $\omega$  and as a result the function cannot be calculated efficiently on the real axis.

We seek frequencies at which the determinant of  $\epsilon$  vanishes; however, these cannot be found by merely evaluating the above expressions. If we write  $\epsilon^{-1}$  in the Lehmann representation,<sup>12</sup> we see that it is an analytic function of complex frequency—with the exception of branch cuts along the real axis. The absence of poles in  $\epsilon^{-1}$  implies that it is never possible for the determinant of  $\epsilon$  to equal zero. This apparent contradiction is resolved by noting that this Lehmann representation applies to the first Riemann sheet of the function only; any frequencies at which the determinant does

equal zero must lie on another Riemann sheet, which can be reached by performing an analytic continuation<sup>13</sup> of  $\chi_{\text{GG}'}^0$  across the usual position of the branch cut. Since the frequency dependence of  $\chi^0$  is known explicitly [from (2)], it is an easy matter to form its derivatives (and thence the derivatives of  $\epsilon$ ) at a complex frequency  $\omega_e$  (with positive imaginary part) and thus construct a Taylor series to evaluate  $\epsilon$  at another frequency  $\omega$  (with nonpositive imaginary part) by analytic continuation.

The dielectric matrix was calculated for various (complex) values of  $\omega$ , and at each frequency, its (right) eigenvalue of lowest modulus,  $\lambda_1$ , was evaluated. This located the frequency  $\omega_0$  at which the eigenvalue, and hence determinant, vanished. The inverse lifetime of the resonance is given by  $\text{Im}(\omega_0)$ . As (1) shows, the right eigenvector corresponding to the zero right eigenvalue of  $\epsilon$  is the response of the internal potential at the resonance. We denote this eigenvector by  $\delta V_{\text{res}}$ . The charge fluctuation at the resonance  $\delta n_{\text{res}}$  is then given by  $\delta n_{\text{res}} = \chi^0 \delta V_{\text{res}}$ . It should be noted that  $\epsilon$  is not Hermitian and so does not in general have real eigenvalues. The eigenvectors and corresponding charge density are also complex, yielding information about the (spatially varying) phase of the charge-transfer wave: The physical charge-density fluctuation is given by  $\text{Re}[\delta n_{\text{res}}(\mathbf{r}, \omega_0) e^{i\omega_0 t}]$ .

The results we now present are from calculations on the tetragonal  $\text{CuO}_2$  structure, with lattice parameters  $a = 3.86 \text{ \AA}$  and  $c = 3.94 \text{ \AA}$ , and for various levels of doping. For the calculation of  $\chi^0$  we used the results of a well-converged LDA calculation with an  $8 \times 8 \times 2$  mesh of  $\mathbf{k}$  points in the first Brillouin zone and summed over 495 reciprocal lattice vectors and 30 bands, which tests showed to give good convergence. Throughout we set  $\mathbf{q} = (0, 0, 0.5)$  (in reciprocal lattice units). This avoids certain numerical problems associated with setting  $\mathbf{q}$  exactly equal to zero, but is a very close approximation, as the dispersion along the  $k_z$  direction is very small (typically less than 0.5 eV across the Brillouin zone). It was found that the presence of the  $K_{\text{xc}}$  term in  $\epsilon$  did not affect the results qualitatively.

The top part of Fig. 2 is a contour plot showing how  $|\lambda_1|$  varies over a region of the complex  $\omega$  plane. The calculation here used a doping of 2.0 electrons per unit cell (achieved by moving the Fermi energy for the dielectric calculations, giving a formal valence of  $\text{Cu}^{2+}$ ), and the analytic continuation was performed with  $\text{Im}(\omega_e) = 13.6 \text{ eV}$  and 14 terms in the Taylor expansion.  $|\lambda_1|$  has a well-defined minimum of zero, located at  $\omega_0 = (3.4 - 0.36i) \text{ eV}$ . We thus deduce the presence of a resonance with energy 3.4 eV and lifetime  $\sim 10^{-14} \text{ s}$ . A cross section through this contour plot along the line  $\text{Im}(\omega) = -0.36 \text{ eV}$  is given in the lower part of Fig. 2, and for comparison it is accompanied by the corresponding results for lower levels of doping. Line segments between discontinuities come from calculations using different  $\text{Re}(\omega_e)$  for the Taylor expansion points. The small size of the discontinuities indicates the reliability of the analytic continuation. All the curves show a minimum close to zero in the range 3.4–3.7 eV, indicating that doping—over the large range considered—has a minimal effect on the existence and energy of the excitation.

In Fig. 3 is a snapshot in time of the resonant charge density change  $\delta n_{\text{res}}$  within the  $\text{CuO}_2$  plane. It shows the variation over a  $3 \times 3$  mesh of  $\text{CuO}_2$  cells. Each peak (white)

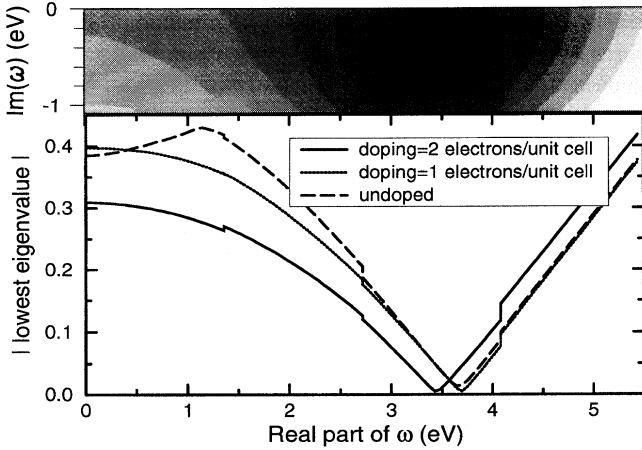


FIG. 2. Contour plot (top) shows the variation of  $|\lambda_1|$  over a region of the complex  $\omega$  plane (doping=2 electrons/unit cell). The shading classes range linearly from zero (darkest) to 0.4 (lightest). The graph (bottom) gives  $|\lambda_1|$  against  $\text{Re}(\omega)$  for various doping levels.  $\text{Im}(\omega) = -0.36$  eV for all the curves.

is located at a copper site and each trough (black) at an oxygen site. The resonance takes the form of a charge-transfer oscillation between the copper and oxygen atoms. The variation of charge density within the interstitial region is much smaller. This behavior is displayed for all doping levels.

The spectral strength of the mode can be characterized by

$$S = \frac{1}{\pi} \int \lambda_1^{-1}(\omega) d\omega \approx \left[ \left| \frac{\partial \lambda}{\partial \omega} \right|_{\omega_0} \right]^{-1},$$

which we find to be 7.6 eV. An alternative view of the dominance of the mode for the low-frequency charge fluctuations

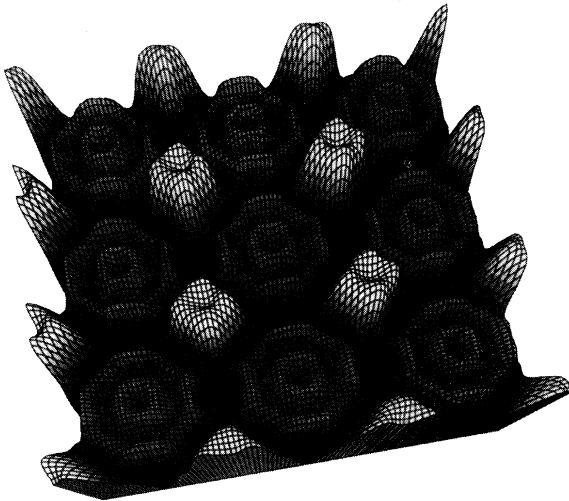


FIG. 3. Snapshot in time of the physical charge-density fluctuation in the  $\text{CuO}_2$  plane. A mesh of  $3 \times 3$  cells is shown. Peaks (white) are at copper sites, troughs (black) at oxygens.

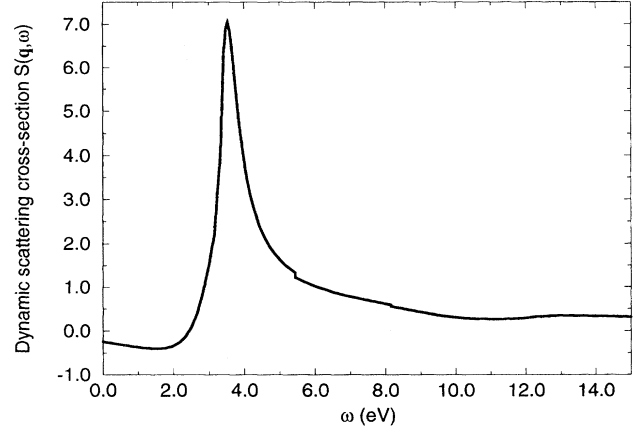


FIG. 4. Dynamic scattering cross section  $S(\mathbf{q}, \omega)$ .

is shown in Fig. 4, where we plot the dynamic scattering cross section  $S(\mathbf{q}, \omega) = \text{Im}[\epsilon_{\text{GG}}^{-1}(\mathbf{q}, \omega)]$ , which shows a large peak, more than an order of magnitude above the background.

This mode has the same symmetry ( $A_{1g}$ ) and orbital character as the CTF mode found earlier in two-dimensional extended Hubbard models which incorporate both a repulsive on-site Coulomb repulsion  $U$  on Cu sites and a repulsive nearest-neighbor Cu-O interaction  $V$ .<sup>8,14</sup> The oscillator strength for this mode arises from transitions between bonding and antibonding  $\text{Cu}(3d)\text{-O}(2p)$  hybrids, which are separated in the band structure by energies of 4–8 eV. The excitonic binding promoted by  $V$  moves this oscillator strength to lower energies, and it was found that the mode could soften entirely if the effective interaction became large enough; this would correspond to a valence instability of the system. Weak-coupling calculations showed that a low-frequency CTF mode would promote  $s$ -wave pairing.<sup>9</sup> From a different point of view, Wilson<sup>5</sup> has argued that the copper oxides lie close to a mixed-valence instability. Our LDA calculations confirm that there is a large binding of this oscillator strength into a sharp resonance. However, in our calculation the parameters appear not to be such as to place the copper oxides close to the valence instability and thus unlikely to promote robust  $s$ -wave pairing. Comparing to the weak-coupling calculations<sup>9</sup> and noting that the CTF must lie in a regime where the binding energy is not strongly doping dependent and is  $\sim 0.5$  eV (the difference between the CTF energy found here and the onset of the continuum), it is possible to estimate a value of  $V/t \approx 0.8$ . This lies within the range of values estimated by constrained LDA calculations,<sup>15</sup> but is at least 50% too small to yield an appreciable superconducting instability. We do not find evidence for the  $d$ - $d$  excitons suggested in another model,<sup>4</sup> but as these involve  $d$  orbitals pointing out of the Cu-O plane they are expected to be more sensitive to the interplanar environment which may not be adequately represented by our hypothetical crystal.

Of course the LDA does not provide an adequate treatment of the strong local electronic correlations close to half-filling and fails to obtain the correct insulating antiferromagnetic ground state.<sup>6</sup> However, in the metallic and superconducting compounds, photoemission studies<sup>16</sup> have

found good agreement with LDA-derived Fermi surfaces; at these moderate hole densities, the optical signature of the 2-eV charge-transfer gap has largely disappeared.<sup>17</sup> Also, we note that while at half-filling the charge-transfer fluctuations must involve promotion of charge to the upper Hubbard band (thus paying the Coulomb penalty  $U$ ), in the doped compounds charge-transfer fluctuations can take place entirely in the manifold of the lower Hubbard band, and the cost of onsite Coulomb interactions is correspondingly reduced. Even in strong-coupling large- $U$  calculations on the extended Hubbard model,<sup>14</sup> the CTF mode can be low in energy.

In conclusion, we have presented first-principles calculations of the nonlocal dielectric matrix with no adjustable parameters. Our results confirm the hypothesis of a strong charge-transfer collective excitation. A single mode of  $A_g$  symmetry at about 3.5 eV dominates the low-energy charge fluctuation spectrum. However, the mode shifts little with doping and appears too high in energy to support robust superconductive pairing.

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<sup>1</sup>J. Bardeen, L. Cooper, and R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).

<sup>2</sup>For a recent discussion, see V. L. Ginzburg, *Contemp. Phys.* **33**, 15 (1992).

<sup>3</sup>C. M. Varma, S. Schmitt-Rink, and E. Abrahams, *Solid State Commun.* **62**, 681 (1987).

<sup>4</sup>W. Weber, *Z. Phys. B* **70**, 323 (1987); M. Jarrell *et al.*, *Phys. Rev. B* **38**, 4584 (1988).

<sup>5</sup>J. A. Wilson, *J. Phys. C* **21**, 2067 (1988).

<sup>6</sup>W. E. Pickett, *Rev. Mod. Phys.* **61**, 433 (1989).

<sup>7</sup>L. F. Mattheiss, *Phys. Rev. Lett.* **58**, 1028 (1987); L. F. Mattheiss and D. R. Hamann, *Solid State Commun.* **63**, 395 (1987); M. S. Hybertsen and L. F. Mattheiss, *Phys. Rev. Lett.* **60**, 1661 (1988); H. Krakauer and W. E. Pickett, *ibid.* **60**, 1665 (1988); L. F. Mattheiss and D. R. Hamann, *Phys. Rev. B* **38**, 5012 (1988); D. R. Hamann and L. F. Mattheiss, *ibid.* **38**, 5138 (1988); W. E. Pickett, *Rev. Mod. Phys.* **61**, 433 (1989); D. J. Crockford and W. Yeung, *Physica C* **199**, 95 (1992).

<sup>8</sup>P. B. Littlewood, C. M. Varma, S. Schmitt-Rink, and E. Abra-

hams, *Phys. Rev. B* **39**, 12 371 (1989).

<sup>9</sup>P. B. Littlewood, *Phys. Rev. B* **42**, 10 075 (1990).

<sup>10</sup>H. Chen, J. Callaway, N. E. Brener, and Z. Zou, *Phys. Rev. B* **43**, 383 (1991).

<sup>11</sup>S. L. Adler, *Phys. Rev.* **126**, 413 (1962); N. Wiser, *ibid.* **129**, 62 (1963).

<sup>12</sup>H. Lehmann, *Nuovo Cimento* **11**, 342 (1954).

<sup>13</sup>R. Daling, W. van Haeringen, and B. Farid, *Phys. Rev. B* **44**, 2952 (1991).

<sup>14</sup>E. R. Gagliano *et al.*, *Solid State Commun.* **64**, 901 (1987); C. A. Balseiro *et al.*, *Phys. Rev. B* **38**, 9315 (1988); M. D. Nunez-Regueiro and A. A. Aligia, *Phys. Rev. Lett.* **61**, 1889 (1988); R. Putz *et al.*, *Phys. Rev. B* **41**, 853 (1990); J. E. Hirsch *et al.*, *Phys. Rev. Lett.* **60**, 1668 (1990).

<sup>15</sup>M. S. Hybertsen *et al.*, *Phys. Rev. B* **39**, 9028 (1989).

<sup>16</sup>T. Takahashi *et al.*, *Phys. Rev. B* **42**, 381 (1990).

<sup>17</sup>See, for example, G. A. Thomas in *Proceedings of Scottish Universities Summer School on Physics of High- $T_c$  Superconductors*, edited by D. P. Tunstall (Hilger, Bristol, 1992), p. 169.

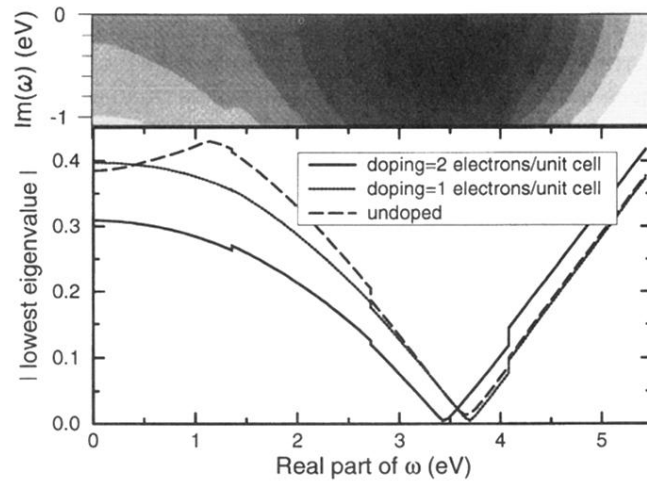


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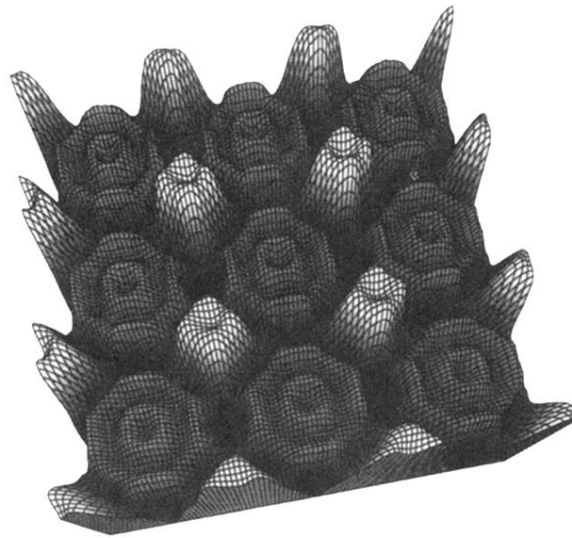


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